Supporting information for
Dynamical Correlation Effects on Photoisomerization: Ab Initio Multiple Spawning Dynamics with MS-CASPT2 for a Model *trans*-Pronated Schiff Base

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This document contains geometries in Cartesian coordinates and energies (in Angstrom and Hartree, respectively), optimized using state-averaged complete active space self-consistent-field theory[1-2] (SA-CASSCF) and multi-reference complete active space self-consistent-field second order perturbation theory[3] (MS-CASPT2). State averaging is performed over the lowest three singlet states with equal weighting, the active space contains six electrons in six orbitals, and the 6-31 and 6-31G* basis sets[4-5] have been used. All of the calculations are performed using Molpro2006.2,[6] including local modifications to calculate analytic nonadiabatic coupling vectors for MSPT2 wavefunctions. The package HDF_free (which is based on Molpro2006.2 and FMS90) is used for the dynamic simulation. Finally, we give a brief summary of seam space nudged elastic band method (SS-NEB).[7]

Summary of Contents:

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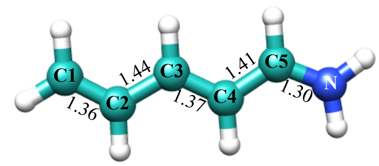
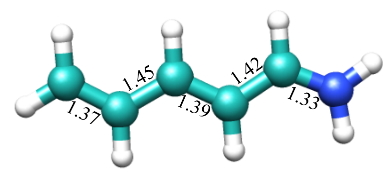
Table S1. *trans*-PSB3 S_0 state, SA3-CASSCF(6,6)/6-31G
$E(S_0)$= -248.16906212; $E(S_1)$= -247.98872740; $E(S_2)$= -247.96080158



C	-6.0192702	-0.7185904	-0.0592481
C	-4.6640071	-0.7396361	0.0078880
H	-6.5730076	0.2006016	-0.0945302
H	-6.5892532	-1.6249176	-0.0800091
H	-4.1437760	-1.6787369	0.0415145
C	-3.8766723	0.4637196	0.0366550
C	-2.5085577	0.4890888	0.1041349
H	-4.4128900	1.3972191	0.0022517
H	-1.9471799	-0.4260184	0.1396261
C	-1.8152353	1.7206859	0.1280460
H	-2.3706433	2.6387237	0.0928148
N	-0.5231805	1.8349417	0.1910250
H	-0.0734009	2.7271963	0.2057473
H	0.0789281	1.0364048	0.2275579

Table S2. *trans*-PSB3 S_0 state, SA3-MS-CASPT2(6,6)/6-31G
$E(S_0)$= -248.659212029; $E(S_1)$= -248.505173325; $E(S_2)$= -248.461213538



C	-6.0483538	-0.7287346	-0.0607687
C	-4.6768375	-0.7604095	0.0073764
H	-6.6013608	0.2110914	-0.0959540
H	-6.6407138	-1.6406081	-0.0824934
H	-4.1501190	-1.7161053	0.0413955
C	-3.8880122	0.4564575	0.0362771
C	-2.4969358	0.4847292	0.1048613
H	-4.4338968	1.4063407	0.0013577
H	-1.9244671	-0.4455431	0.1410750
C	-1.8117133	1.7294880	0.1281360
H	-2.3758782	2.6632237	0.0922391
N	-0.4852844	1.8541456	0.1926488
H	-0.0334313	2.7676254	0.2071861
H	0.1288584	1.0389814	0.2301368

Table S3. *trans*-PSB3 S_0 state, SA3-MS-CASPT2(6,6)/6-31G*
$E(S_0)$= -248.982323697; $E(S_1)$= -248.825737690; $E(S_2)$= -248.783168790

C	-6.0198267	-0.7048615	-0.0595385
C	-4.6586598	-0.7570852	0.0082853
H	-6.5525669	0.2418611	-0.0938575
H	-6.6227442	-1.6063074	-0.0818053
H	-4.1420690	-1.7137199	0.0418953
C	-3.8768935	0.4467655	0.0368417
C	-2.4949466	0.4714456	0.1050268
H	-4.4173308	1.3940486	0.0021107
H	-1.9191899	-0.4518432	0.1412697
C	-1.8315843	1.7097193	0.1273575
H	-2.3980256	2.6381704	0.0914643
N	-0.5218776	1.8477007	0.1909060
H	-0.0813215	2.7667388	0.2049976
H	0.0988889	1.0380496	0.2285203

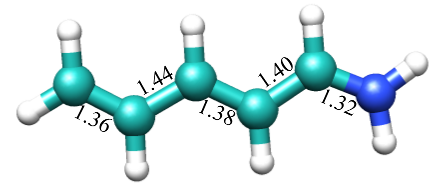


Table S4. *cis*-PSB3 S_0 state, SA3-CASSCF(6,6)/6-31G
$E(S_0)$= -248.16433461; $E(S_1)$= -247.98895661; $E(S_2)$= -247.95564471

C	-6.1682167	0.4316199	1.0013900
C	-4.8300110	0.4575223	1.2240710
H	-6.5770779	0.4147964	0.0091602
H	-6.8683912	0.4261405	1.8116627
H	-4.4771205	0.4731887	2.2377686
C	-3.8848267	0.4643892	0.1335775
C	-2.5132622	0.4897199	0.1899502
H	-4.3137719	0.4474700	-0.8515460
H	-1.9600519	0.4911726	-0.7303931
C	-1.7765244	0.5143264	1.3983976
H	-2.2794970	0.5139269	2.3443082
N	-0.4792096	0.5384294	1.4475835
H	0.0153155	0.5554829	2.3160784
H	0.0827915	0.5410102	0.6190916

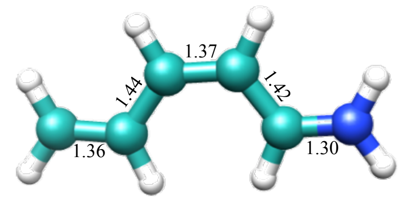


Table S5. *cis*-PSB3 S_0 state, SA3-MS-CASPT2(6,6)/6-31G
$E(S_0)$= -248.648214403; $E(S_1)$= -248.501656501; $E(S_2)$= -248.444383957

C	-6.1892827	0.4309869	1.0044910
C	-4.8405782	0.4573800	1.2323606
H	-6.6006987	0.4141857	-0.0050795
H	-6.9075135	0.4256286	1.8207048
H	-4.4766677	0.4734802	2.2609528
C	-3.8949384	0.4641574	0.1225517
C	-2.5078641	0.4897384	0.1751276
H	-4.3401542	0.4468485	-0.8754075
H	-1.9430858	0.4912891	-0.7591798
C	-1.7697133	0.5145330	1.4015067
H	-2.2827287	0.5141902	2.3630264
N	-0.4492948	0.5389933	1.4558437
H	0.0497498	0.5562861	2.3423824
H	0.1229163	0.5414978	0.6118196

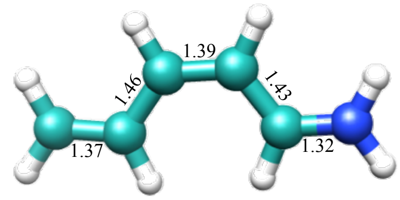


Table S6. *cis*-PSB3 S_0 state, SA3-MS-CASPT2(6,6)/6-31G*
$E(S_0)$= -248.977519226; $E(S_1)$= -248.827447712; $E(S_2)$= -248.777577666

C	-6.1650511	0.4313949	0.9983582
C	-4.8228633	0.4578858	1.2409080
H	-6.5585865	0.4146849	-0.0142779
H	-6.8892437	0.4255951	1.8058958
H	-4.4679357	0.4738487	2.2684156
C	-3.8962101	0.4644028	0.1405366
C	-2.5086293	0.4898431	0.1838931
H	-4.3426798	0.4471353	-0.8527732
H	-1.9497866	0.4912436	-0.7499649
C	-1.7887310	0.5141097	1.3915500
H	-2.2903159	0.5140986	2.3550735
N	-0.4724740	0.5384284	1.4474840
H	0.0260136	0.5557491	2.3366903
H	0.0966394	0.5407755	0.5993112

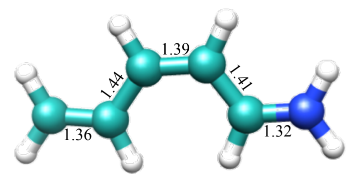


Table S7. PSB3 S_1 minima, S_{1min_CenL}, SA3-MS-CASPT2(6,6)/6-31G
$E(S_0)$= -248.584107398; $E(S_1)$= -248.519711531; $E(S_2)$= -248.407421010

C	-5.7953118	-0.8975788	-0.6881912
C	-4.7775764	-0.7324751	0.3478370
H	-5.5449356	-0.7261650	-1.7395249
H	-6.8401915	-1.0999763	-0.4332757
H	-4.6823802	-1.4545927	1.1687308
C	-4.0012381	0.5522565	0.3301200
C	-2.5974924	0.5829203	0.1039052
H	-4.5786028	1.4804557	0.4176624
H	-2.0616836	-0.3772406	0.0638187
C	-1.8368607	1.7750539	-0.0808974
H	-2.3263582	2.7504886	-0.0758246
N	-0.4833142	1.7708711	-0.2140599
H	0.0343107	2.6411376	-0.3007828
H	0.0615652	0.9114271	-0.2352388

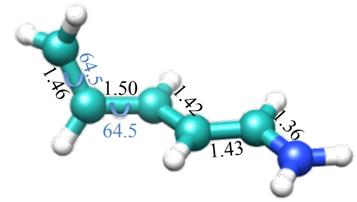


Table S8. PSB3 S_1 minima, S_{1min_CenL}, SA3-MS-CASPT2(6,6)/6-31G*
$E(S_0)$= -248.900991047; $E(S_1)$= -248.846742028; $E(S_2)$= -248.724991910

C	-5.7082028	-0.8791328	-0.6929537
C	-4.7736516	-0.7075832	0.3989937
H	-5.3876024	-0.6914809	-1.7177422
H	-6.7695850	-1.0487327	-0.5051512
H	-4.7029368	-1.4411523	1.2080763
C	-4.0205794	0.5433499	0.3605115
C	-2.6245047	0.5848623	0.1099269
H	-4.5823206	1.4788433	0.4316992
H	-2.0980609	-0.3728414	0.0370337
C	-1.8681103	1.7608428	-0.0577283
H	-2.3388217	2.7415149	-0.0114289
N	-0.5377840	1.7378183	-0.2516741
H	-0.0078350	2.6002723	-0.3395668
H	-0.0100763	0.8700019	-0.3057173

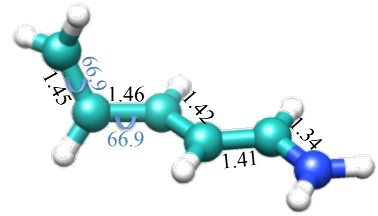


Table S9. PSB3 S_1 minima, S_{1min_Cen}, SA3-CASSCF(6,6)/6-31G
$E(S_0)$= -248.07466091; $E(S_1)$= -248.05548533; $E(S_2)$= -247.94967633

C	-5.9683172	-0.8170926	0.1587440
C	-4.6206511	-0.7989651	0.4175494
H	-6.5065419	0.0771922	-0.0919678
H	-6.5335654	-1.7266919	0.1993194
H	-4.0961545	-1.6996155	0.6648920
C	-3.9175804	0.4117208	0.3737761
C	-2.4973737	0.5425187	0.6098950
H	-4.4900096	1.2891157	0.1071402
H	-1.8820182	0.4446500	-0.2704262
C	-1.9511824	0.8043168	1.8219394
H	-2.5824684	0.9144472	2.6826157
N	-0.6338300	0.9472079	2.0815276
H	-0.3146481	1.1397811	2.9980481
H	0.0549975	0.8786039	1.3719293

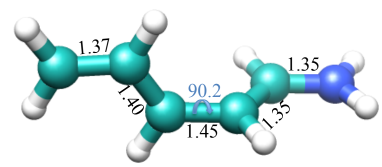


Table S10. PSB3 S_1 minima, S_{1min_CN}, SA3-CASSCF(6,6)/6-31G
$E(S_0)$= -248.05702406; $E(S_1)$= -248.04530311; $E(S_2)$= -247.94422315

C	-6.0428051	-0.8524165	-0.1053429
C	-4.6811225	-0.7452428	0.0435135
H	-6.6596385	0.0071667	-0.2855657
H	-6.5347886	-1.8014804	-0.0463563
H	-4.1125685	-1.6414732	0.2217976
C	-3.9747240	0.4803695	-0.0248182
C	-2.5672867	0.5621904	0.1321967
H	-4.5258332	1.3858961	-0.2026619
H	-2.0289352	-0.3526330	0.3100649
C	-1.8751319	1.7381431	0.0686079
H	-2.2925668	2.7116125	-0.1019328
N	-0.4477625	1.7561541	0.2361073
H	-0.0222180	1.8877572	1.1411691
H	0.1789576	1.6777673	-0.5504102

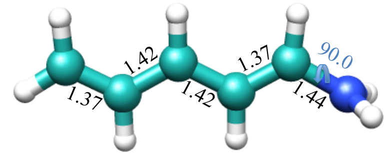


Table S11. PSB3 S_1 minima, S_{1min_Ter}, SA3-CASSCF(6,6)/6-31G
$E(S_0)$= -248.06994659; $E(S_1)$= -248.00329540; $E(S_2)$= -247.96251308

C	-6.0783807	-0.7508888	-0.0669780
C	-4.6740550	-0.6473391	0.0829874
H	-6.6208752	-0.1818002	-0.8065891
H	-6.6653202	-1.4623695	0.4938144
H	-4.1816747	-1.3505029	-0.5926574
C	-3.9515680	0.1552977	0.8981738
C	-2.5167458	0.1757815	0.9674425
H	-4.4762055	0.8336654	1.5483216
H	-1.9618776	-0.4887468	0.3320328
C	-1.8644863	1.0138306	1.8151650
H	-2.4294249	1.6740795	2.4460657
N	-0.5243608	1.1149636	1.9606630
H	-0.1270610	1.7529233	2.6027997
H	0.1034495	0.5586760	1.4344663

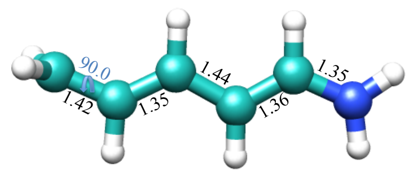
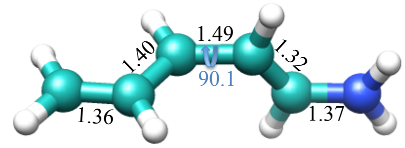
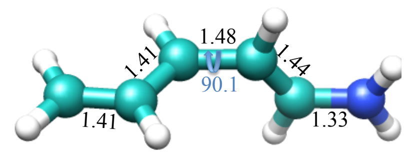


Table S12. PSB3 MECI(S_1/S_0), MECI$_{Cen}$, SA3-CASSCF(6,6)/6-31G
E(S_0)= -248.06368383; E(S_1)= -248.06368042 ; E(S_2)= -247.93594718



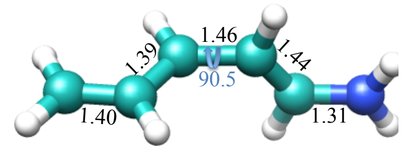
C	-5.9308358	-0.7534527	-0.2256255
C	-4.5797885	-0.5728905	-0.2809921
H	-6.5475958	-0.2579574	0.5002206
H	-6.4333116	-1.4024588	-0.9160321
H	-3.9754358	-1.0719608	-1.0081494
C	-3.9663501	0.3040226	0.6270435
C	-2.5045770	0.5601850	0.6806167
H	-4.6184607	0.7734804	1.3519217
H	-1.9974260	-0.1255279	1.3372023
C	-1.8915222	1.5369478	0.0354533
H	-2.4491126	2.2080226	-0.5915074
N	-0.5534665	1.8191849	0.0613070
H	-0.1836469	2.5740732	-0.4556856
H	0.0754099	1.2877775	0.6088739

Table S13. PSB3 MECI(S_1/S_0), MECI$_{Cen}$, SA3-MS-CASPT2(6,6)/6-31G
E(S_0)= -248.568534227; E(S_1)= -248.568519529; E(S_2)= -248.443990302



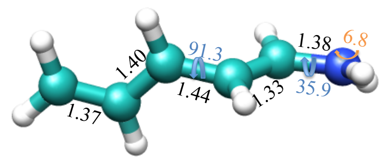
C	-6.2017318	1.3030090	0.7044865
C	-4.7990738	1.2677862	0.8065648
H	-6.7375750	0.6614653	0.0076054
H	-6.7918382	1.9778734	1.3159934
H	-4.3331735	1.9510542	1.5234105
C	-3.9601737	0.4199990	0.0594525
C	-2.4861023	0.4525999	0.1583692
H	-4.3652206	-0.2453684	-0.7105010
H	-1.8859341	1.1317047	-0.4632746
C	-1.7601999	-0.4123705	1.0527726
H	-2.2927394	-1.1085124	1.6996609
N	-0.4360803	-0.3873279	1.1232681
H	0.0812187	-0.9967794	1.7602697
H	0.1240926	0.2439689	0.5436891

Table S14. PSB3 MECI(S_1/S_0), $MECI_{Cen}$, SA3-MS-CASPT2(6,6)/6-31G*
E(S_0)= -248.886166854; E(S_1)= -248.886162595; E(S_2)= -248.762916078



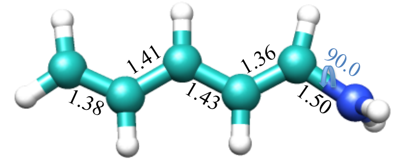
C	-6.1740640	1.3194131	0.6940317
C	-4.7840222	1.2440841	0.8037816
H	-6.7185281	0.6974427	-0.0072733
H	-6.7428956	2.0003056	1.3123605
H	-4.3097311	1.9095379	1.5265665
C	-3.9687421	0.3760170	0.0852248
C	-2.5106692	0.4338684	0.1700952
H	-4.3523158	-0.2524634	-0.7212988
H	-1.9038195	1.1155284	-0.4365974
C	-1.7700471	-0.4244107	1.0560275
H	-2.2801878	-1.1381995	1.6967220
N	-0.4679749	-0.3597006	1.1172563
H	0.0734225	-0.9581200	1.7469314
H	0.0650436	0.2957988	0.5379394

Table S15. PSB3 MECI(S_1/S_0), $MECI_{BP}$, SA3-CASSCF(6,6)/6-31G
E(S_0)= -248.04499946; E(S_1)= -248.04496487; E(S_2)= -247.92928735



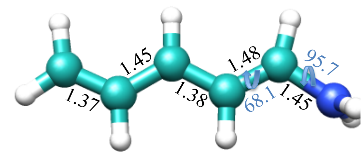
C	-5.9374459	-0.7865377	-0.1627175
C	-4.6160739	-0.5090833	-0.3739797
H	-6.4879212	-0.3560892	0.6525023
H	-6.4769047	-1.4545324	-0.8053310
H	-4.0780353	-0.9308228	-1.1961115
C	-3.9414856	0.2956889	0.5546342
C	-2.5260936	0.5452026	0.5316316
H	-4.5381705	0.6705212	1.3744069
H	-1.9956360	-0.1691280	1.1464587
C	-1.8926004	1.5974295	0.0123731
H	-2.4506118	2.3375985	-0.5355591
N	-0.5591643	1.9076070	0.1818501
H	-0.0244224	2.1827073	-0.5998392
H	-0.0515597	1.5412592	0.9442978

Table S16. PSB3 MECI(S_1/S_0), $MECI_{CN}$, SA3-CASSCF(6,6)/6-31G
E(S_0)= -248.04293341; E(S_1)= -248.04292951; E(S_2)= -247.94135899



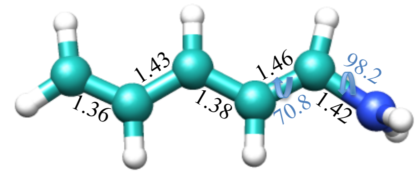
C	-6.0501979	-0.8957287	-0.1034359
C	-4.6882344	-0.7266700	0.0381160
H	-6.7042026	-0.0642446	-0.2835391
H	-6.4983765	-1.8655578	-0.0376984
H	-4.0904511	-1.6054797	0.2173617
C	-4.0145920	0.5149350	-0.0341563
C	-2.5964555	0.6176405	0.1223579
H	-4.5781142	1.4115687	-0.2115743
H	-2.0627468	-0.3026150	0.2991462
C	-1.9015115	1.7822897	0.0620924
H	-2.2180944	2.7901676	-0.0995824
N	-0.4164562	1.7266523	0.2458441
H	0.0153379	1.8198051	1.1599323
H	0.2176749	1.6110475	-0.5384950

Table S17. PSB3 MECI(S_1/S_0), $MECI_{CN}$, SA3-MS-CASPT2(6,6)/6-31G
E(S_0)= -248.521729381; E(S_1)= -248.521723580; E(S_2)= -248.465958313



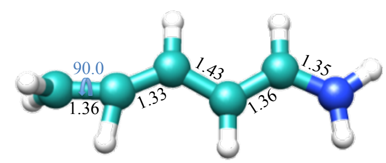
C	-5.8565787	-0.8909517	-0.4530764
C	-4.6332557	-0.7558471	0.1504180
H	-6.2978709	-0.0905607	-1.0480960
H	-6.4370024	-1.8063664	-0.3651591
H	-4.2251825	-1.5715878	0.7513605
C	-3.8402252	0.4572561	0.0284562
C	-2.6457518	0.6476640	0.7002589
H	-4.2400328	1.2629935	-0.5956185
H	-2.2226374	-0.1596152	1.3103535
C	-1.8664716	1.9032362	0.6098424
H	-2.1548900	2.9027380	0.9322602
N	-0.6687539	1.7274018	-0.1902620
H	0.1915819	1.3425438	0.2162527
H	-0.6893546	1.8449069	-1.2106212

Table S18. PSB3 MECI(S_1/S_0), $MECI_{CN}$, SA3-MS-CASPT2(6,6)/6-31G*
E(S_0)= -248.842452213; E(S_1)= -248.842428925; E(S_2)= -248.781827882



C	-5.7816282	-0.8735991	-0.4766806
C	-4.5745161	-0.7319605	0.1444457
H	-6.2188437	-0.0689377	-1.0613607
H	-6.3459209	-1.7975611	-0.4105786
H	-4.1630135	-1.5463251	0.7378622
C	-3.8267412	0.4858736	0.0476167
C	-2.6495669	0.6899018	0.7426217
H	-4.2302524	1.2905457	-0.5673102
H	-2.2356256	-0.1210764	1.3498401
C	-1.8728293	1.9208860	0.6329111
H	-2.1485941	2.9185481	0.9688253
N	-0.7395164	1.7295289	-0.1965309
H	0.0485595	1.1688337	0.1406895
H	-0.8479367	1.7491535	-1.2159821

Table S19. PSB3 MECI(S_1/S_0), $MECI_{Ter}$, SA3-CASSCF(6,6)/6-31G
E(S_0)= -247.99555591; E(S_1)= -247.99552900; E(S_2)= -247.885170030



C	-6.0414254	-0.8434804	-0.1566651
C	-4.8223362	-0.4366207	0.2857368
H	-6.4860946	-0.4199958	-1.0435055
H	-6.5299462	-1.7089433	0.2626976
H	-4.5067949	-1.2522495	-0.5086122
C	-3.9812652	0.2855024	1.0264975
C	-2.5480765	0.2308412	1.0205360
H	-4.4583112	0.9807139	1.6965015
H	-2.0554596	-0.4563124	0.3593642
C	-1.8197519	1.0359404	1.8388286
H	-2.3259337	1.7186086	2.4951015
N	-0.4756059	1.0759145	1.9231188
H	-0.0209364	1.6937472	2.5475789
H	0.1033516	0.4939042	1.3685292

Table S20. PSB3 MECI(S_1/S_0), MECI$_{Ter}$, SA3-MS-CASPT2(6,6)/6-31G
E(S_0)= -248.523119656; E(S_1)= -248.523113625; E(S_2)= -248.419930148

C	-6.1062362	-0.8369169	-0.1573931
C	-4.8166891	-0.4655673	0.2417741
H	-6.5781817	-0.4022794	-1.0491394
H	-6.6114819	-1.7105494	0.2766190
H	-4.4604597	-1.2772078	-0.5394009
C	-3.9662131	0.2710590	1.0109074
C	-2.5325330	0.2215771	1.0105311
H	-4.4570673	0.9707561	1.6948927
H	-2.0168189	-0.4709942	0.3407180
C	-1.8071572	1.0482788	1.8547568
H	-2.3308734	1.7387115	2.5189411
N	-0.4465126	1.0916457	1.9463505
H	0.0158872	1.7223658	2.5884879
H	0.1457489	0.4966914	1.3776632

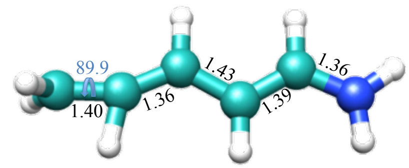


Table S21. PSB3 MECI(S_1/S_0), MECI$_{Ter}$, SA3-MS-CASPT2(6,6)/6-31G*
E(S_0)= -248.851051190; E(S_1)= -248.850489075; E(S_2)= -248.747610470

C	-6.0741616	-0.8328939	-0.1501115
C	-4.7921734	-0.4203467	0.1947553
H	-6.5742026	-0.4621276	-1.0541529
H	-6.5450630	-1.6934932	0.3467278
H	-4.4192834	-1.2798499	-0.4878973
C	-3.9589639	0.3026561	0.9834956
C	-2.5438128	0.2313091	0.9970494
H	-4.4489646	1.0174548	1.6420223
H	-2.0322336	-0.4625198	0.3352372
C	-1.8257733	1.0412326	1.8495128
H	-2.3457200	1.7322508	2.5076967
N	-0.4873621	1.0669793	1.9554709
H	-0.0244646	1.6842326	2.6096703
H	0.1035927	0.4726861	1.3862312

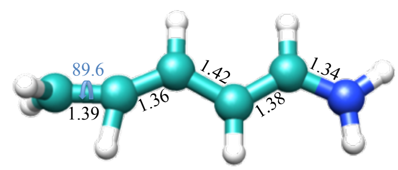
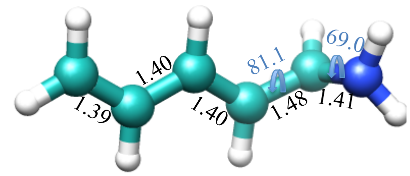


Table S22. PSB3 MECI(S_1/S_0), $MECI_{CenR}$, SA3-CASSCF(6,6)/6-31G
E(S_0)= -248.01073766; E(S_1)= -248.01072922; E(S_2)= -247.91423427



C	-5.8660014	-0.7202977	0.5423698
C	-4.6130607	-0.6185937	-0.0485497
H	-6.2618762	0.0664177	1.1546463
H	-6.4735318	-1.5915063	0.4050046
H	-4.2566064	-1.4306441	-0.6550406
C	-3.8014966	0.5054177	0.1207133
C	-2.5485963	0.6082310	-0.4972044
H	-4.1460547	1.3182091	0.7330672
H	-2.2186365	-0.2275911	-1.0936354
C	-1.6207198	1.7447037	-0.3162129
H	-1.8621002	2.7065206	-0.7263358
N	-0.8116489	1.5892769	0.8309859
H	-0.8965375	2.2523503	1.5669505
H	0.1093008	1.2336921	0.7042954

Table S23. Energies (kcal/mol) of equilibrium geometries of PSB3 using SA3-CASSCF(6,6)/6-31G and SA3-MS-CASPT2(6,6)/6-31G with varying numbers of uncorrelated (core) occupied orbitals. The zero of energy is defined by the S_0 *trans* minimum.

Core Orbitals	$\boldsymbol{MECI_{Cen}}$	$\boldsymbol{MECI_{Ter}}$	$\boldsymbol{MECI_{CN}}$	$\boldsymbol{S_0}$***-trans***
6 (default)	56.9	85.4	86.3	0.0/96.7[a]/124.2[b]
13	57.3	91.4	95.2	0.0/101.2[a]/127.2[b]
14	55.7	93.3	93.7	0.0/102.1[a]/127.9[b]
15	57.8	92.1	93.1	0.0/103.7[a]/128.6[b]
CASSCF	**66.1**	**108.9**	**79.1**	0.0/113.2[a]/130.7[b]

[a]Vertical excitation energy of 1st excited state relative to $\boldsymbol{S_0}$***-trans***.
[b]Vertical excitation energy of 2nd excited state relative to $\boldsymbol{S_0}$***-trans***.

Table S24. Intersection topography characterization for CI seam beads connecting **MECI$_{\mathbf{Cen}}$** and **MECI$_{\mathbf{CN}}$** at the SA3-CASSCF(6,6)/6-31G level.

Bead	C=C$_{cen}$ twist (degrees)	C=N twist (degrees)	Energy (kcal/mol)	s^x	s^y	Δ_{gh}	d_{gh}	s_x	s_y
1	90.1	0.4	66.1	-0.43	-1.65	0.32	0.13	-0.04	-0.12
2	90.2	4.1	66.2	0.70	1.48	0.45	0.13	0.08	0.10
3	90.2	7.7	66.3	0.59	1.48	0.40	0.13	0.06	0.10
4	90.1	10.9	66.5	-0.01	-1.56	0.29	0.13	0.00	-0.12
5	90.0	12.7	66.6	-0.57	1.37	0.42	0.13	-0.06	0.10
6	89.9	15.1	66.9	0.71	0.72	0.75	0.15	0.10	0.04
7	89.9	18.7	67.3	-0.68	-0.59	0.69	0.14	-0.09	-0.03
8	90.1	22.5	68.0	-0.51	0.22	0.80	0.16	-0.08	0.01
9	90.3	26.4	69.6	-0.27	0.06	0.80	0.16	-0.04	0.00
10	90.9	29.2	77.1	-1.07	-0.07	0.66	0.11	-0.11	0.00
11	91.3	35.9	78.0	-0.57	-1.25	0.33	0.11	-0.05	-0.08
12	91.2	37.5	79.1	-0.01	-1.82	0.44	0.10	0.00	-0.10
14	91.0	40.1	79.0	-0.70	0.97	0.73	0.12	-0.08	0.04
15	91.1	41.8	80.0	0.77	-0.15	0.69	0.11	0.08	-0.01
16	91.3	44.6	81.1	0.61	-0.20	0.81	0.11	0.06	-0.01
17	91.6	47.6	83.0	-0.38	0.58	0.68	0.11	-0.04	0.03
18	91.9	51.3	85.9	-0.15	-0.47	0.56	0.11	-0.01	-0.02
19	92.2	55.7	90.5	0.27	0.24	0.41	0.10	0.02	0.01
20	92.0	60.5	96.9	-0.02	-1.18	0.74	0.12	0.00	-0.05
21	90.8	65.2	104.8	0.09	-2.11	0.75	0.12	0.01	-0.09
22	88.4	69.9	112.8	1.49	0.24	0.49	0.10	0.13	0.01
23	85.2	74.3	119.5	0.47	-3.21	0.59	0.10	0.04	-0.15
24	82.0	78.4	124.3	1.42	-2.43	0.61	0.10	0.13	-0.11
25	78.9	82.2	127.9	-1.54	-2.70	0.44	0.09	-0.12	-0.13
26	76.0	85.9	130.1	1.79	-2.61	0.45	0.10	0.14	-0.13
27	72.7	88.6	131.3	-2.04	-2.55	0.07	0.09	-0.14	-0.16
28	69.5	89.1	132.6	-2.00	-2.56	-0.25	0.09	-0.11	-0.19
29	66.3	89.2	133.9	-1.61	2.96	-0.16	0.09	-0.10	0.21
30	62.9	89.2	135.2	1.77	-1.11	0.90	0.14	0.24	-0.04
31	59.4	89.3	136.6	2.60	-2.22	0.52	0.10	0.23	-0.11
32	55.7	89.4	138.0	-1.78	-3.14	-0.35	0.10	-0.10	-0.26
33	51.7	89.6	139.4	-2.06	-1.82	0.89	0.14	-0.29	-0.06
34	47.7	90.0	141.3	-1.59	3.66	-0.38	0.10	-0.09	0.31
39	36.4	91.4	83.8	0.57	0.90	0.36	0.10	0.05	0.05
40	32.5	91.2	82.9	0.68	-0.39	0.78	0.13	0.08	-0.02
41	28.2	91.1	82.1	-0.71	-0.60	0.77	0.13	-0.08	-0.03
42	24.7	91.0	81.5	0.82	0.19	0.71	0.12	0.09	0.01
43	21.5	90.9	81.0	0.68	1.26	0.46	0.11	0.06	0.07
44	18.6	90.8	80.6	0.83	0.88	0.59	0.11	0.08	0.05
45	15.8	90.7	80.2	0.74	1.21	0.52	0.11	0.07	0.06
46	13.1	90.6	79.9	0.42	1.58	0.46	0.11	0.04	0.09
47	10.4	90.5	79.6	0.27	1.67	0.46	0.11	0.03	0.09
48	7.8	90.3	79.4	0.14	1.73	0.46	0.11	0.01	0.10
49	5.3	90.2	79.3	0.10	1.75	0.47	0.11	0.01	0.10
50	2.7	90.0	79.1	-0.06	-1.76	0.47	0.11	-0.01	-0.10
51	0.0	90.0	79.1	-0.85	-0.64	0.68	0.12	-0.09	-0.03

Table S25. Intersection topography characterization for CI seam beads connecting **$MECI_{Ter}$** and **$MECI_{Cen}$** at the SA3-MS-CASPT2(6,6)/6-31G level with 14 core orbitals.

Beads	$C{=}C_{Ter}$ twist (degrees)	$C{=}C_{Cen}$ twist (degrees)	Energy (kcal/mol)	s^x	s^y	Δ_{gh}	d_{gh}	s_x	s_y
1	0.3	90.1	55.7	0.01	0.01	0.41	0.12	0.00	0.00
2	2.6	89.3	56.6	0.04	0.04	0.54	0.13	0.00	0.00
3	14.3	89.2	60.3	0.06	0.27	0.63	0.13	0.01	0.02
4	33.1	88.7	71.2	0.22	0.39	0.45	0.12	0.02	0.02
5	55.6	84.9	93.4	-1.03	0.65	0.30	0.13	-0.10	0.05
6	77.6	70.2	110.0	-0.95	-1.26	-0.86	0.12	-0.03	-0.14
7	91.5	54.3	103.9	0.18	-1.00	0.69	0.26	0.04	-0.10
8	91.0	33.9	99.0	0.18	0.97	0.59	0.21	0.03	0.09
9	91.1	22.8	96.3	-0.03	1.07	0.61	0.21	-0.01	0.10
10	90.8	11.9	94.5	0.52	-0.25	0.59	0.21	0.10	-0.02
11	90.1	0.2	93.6	-0.53	-0.05	0.60	0.21	-0.10	0.00

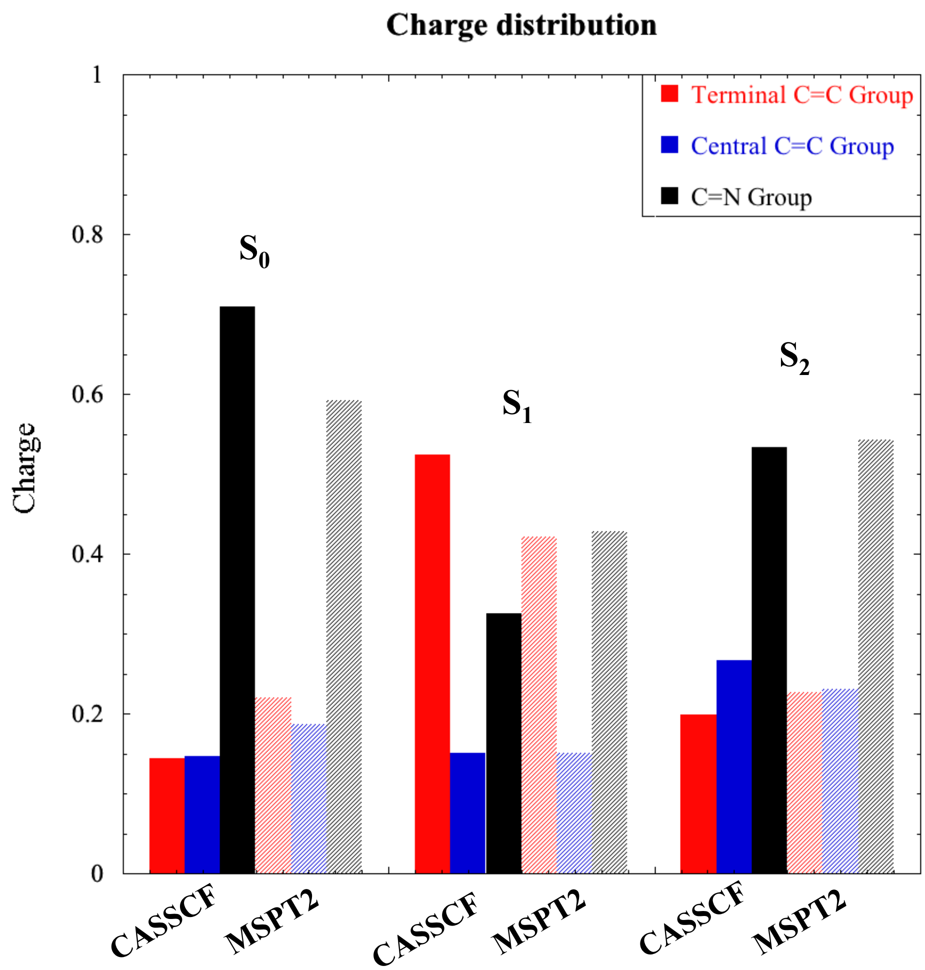
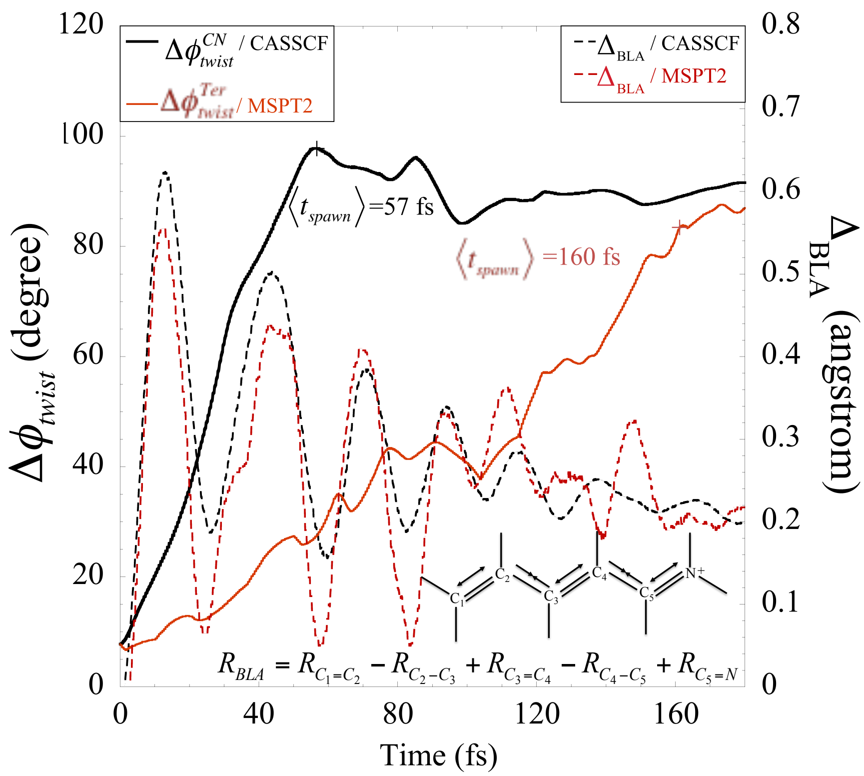


Figure S1. Charge distributions of *trans*-PSB3 (S_0 minimum) in different electronic states at the SA3-CAS(6,6)/6-31G and MS-SA3-CASPT2(6,6)/6-31G levels. Charges on hydrogens are summed into heavy atoms. Terminal C=C group consists of C1 and C2, central C=C group consists of C3 and C4, and C=N group consists of C5 and N (numbering follows Figure 1 in the main text).

Figure S2. Time evolution of twist angles and bond length alternation from AIMS-CASSCF and AIMS-MSPT2 dynamics. Averages are calculated over all TBFs which twist around the C=N or terminal C=C bond for AIMS-CASSCF and AIMS-MSPT2, respectively. Note that in both cases, these are the minor channels (23% and 9% of the initial conditions for CASSCF/MSPT2, respectively). For both CASSCF and MSPT2 dynamics, the dominant outcome is torsion about the central C=C bond.



Section S1. Brief summary of seam space nudged elastic band (SS-NEB) method

We first define the energy difference gradient vector **g** and the non-adiabatic derivative coupling vector **h** as

$$\mathbf{g}_{IJ} = \frac{\partial E_I}{\partial \mathbf{R}} - \frac{\partial E_J}{\partial \mathbf{R}}$$

$$\mathbf{h}_{IJ} = \left(E_J - E_I\right)\left\langle \psi_I \left| \frac{\partial}{\partial \mathbf{R}} \right| \psi_J \right\rangle$$

Here, I and J label the degenerate adiabatic electronic states. For the beads of the seam path, they should satisfy the two conditions

$$\mathbf{g}_{IJ} \cdot \delta\mathbf{R} = 0$$
$$\mathbf{h}_{IJ} \cdot \delta\mathbf{R} = 0$$

where $\delta\mathbf{R}$ is an infinitesimal geometry displacement away from the CI.

The total force that we minimize on the ith bead with the SS-NEB method is

$$\mathbf{f}_i\left(\mathbf{R}_i\right) = \mathbf{f}_{i,\|\tau}^{spring}\left(\mathbf{R}_i\right) + \mathbf{f}_{i,\perp g,h,\tau'}\left(\mathbf{R}_i\right) + \mathbf{f}_{i,\|g,h}^{Egap}\left(\mathbf{R}_i\right)$$

Here τ' is the tangent direction within the CI seam for the ith molecular configuration (bead):

$$\tau' = \hat{\mathbf{P}}_{\perp g,h}\tau$$

where τ represents the tangent direction of the path at the ith point and $\hat{\mathbf{P}}_{\perp g,h}$ is the projection operator:

$$\hat{\mathbf{P}}_{\perp g,h} \equiv \hat{I} - \mathbf{g}\mathbf{g}^T - \mathbf{h}\mathbf{h}^T$$

$\mathbf{f}_{i,\|\tau}^{spring}$ is the harmonic spring force within the CI seam and $\mathbf{f}_{i,\perp g,h,\tau'}$ is the component of the averaged potential energy surface gradient that is perpendicular to **g**, **h**, and τ':

$$\mathbf{f}_{i,\|\tau}^{spring} = \hat{\mathbf{P}}_{\perp g,h} \mathbf{F}_{i,\|\tau}^{spring}$$

$$\mathbf{f}_{i,\perp g,h,\tau'} = \frac{1}{2} \nabla_{\perp g,h,\tau'} \left(E_J + E_I \right)$$

and

$$\mathbf{f}_{i,\|g,h}^{Egap} = 2\left(E_J - E_I \right) \mathbf{g}$$

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