Electronic Supplementary Information for "Nonadiabatic Dynamics of a Truncated Indigo Model"

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1 Vertical Excitation Energies

Vertical excitation energies were calculated by using TDDFT with the hybrid B3LYP functional [1, 2] and the range-separated CAM-B3LYP functional [3] as well as DFT/MRCI [4] with the hybrid BHLYP functional. [5] The 6-31+G* [6] and TZVP [7] basis sets were employed. The calculations were carried out with the following programs: TDDFT, GAUSSIAN09; [8] DFT/MRCI, TURBOMOLE5.7. [9] Table 1 lists the calculated vertical excitation energies.

Table 1: Vertical Excitation Energy (eV) to the $S_1(^1\pi\pi^*)$ State of **2**.

	OM2/MRCI	B3LYP[a]	CAM-B3LYP[a]	DFT/MRCI[b]	RI-CC2[c]	Exp.[d]
S_1	2.76	2.62	2.82	2.63	2.68	2.57

[a] 6-311++G** basis set, B3LYP/6-31+G* optimized structure; [b] BHLYP functional and TZVP basis set; [c] See Reference [10]; [d] From gas-phase absorption spectrum of tetramethylated **2**. [11]

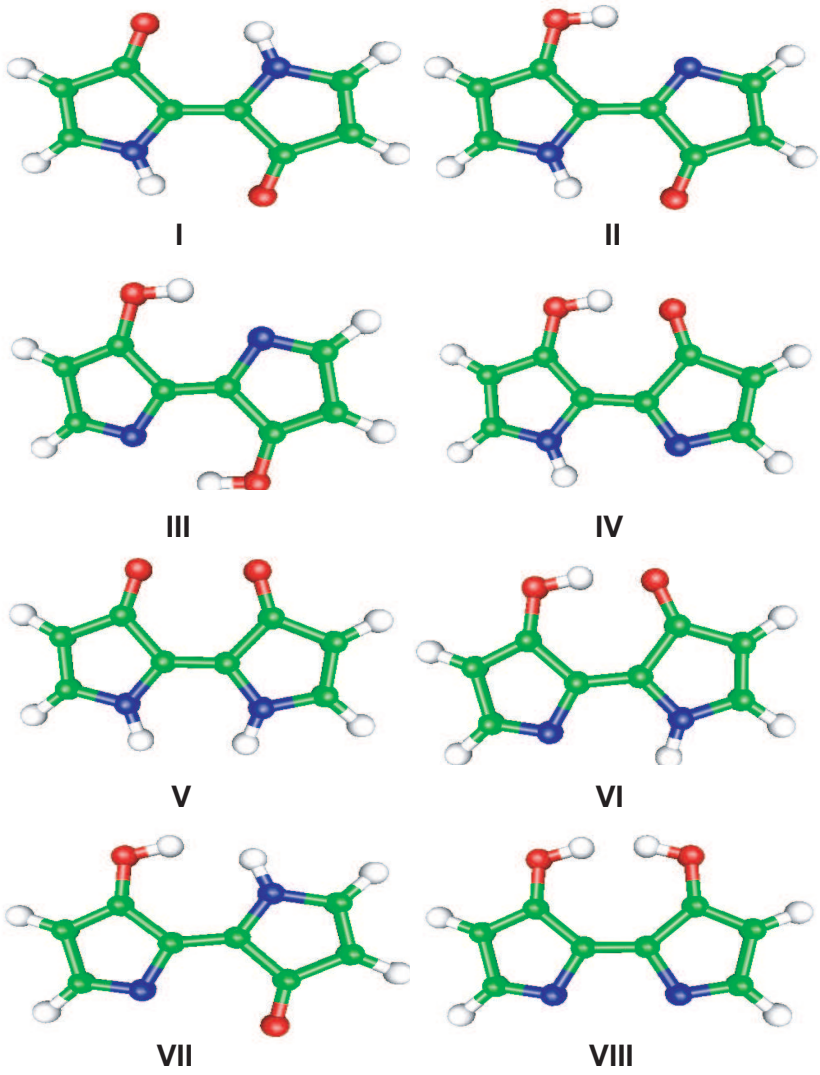

Figure 1: OM2/MRCI optimized ground-state isomers of **2**. Structures I and II correspond to S0-MIN and S0-SPT, respectively.

Table 2: OM2/MRCI Computed Relative Energies (kcal/mol) of Different Isomers of **2**

isomer	I	II	III	IV	V	VI	VII	VIII
relative energy	0.0	12.6	29.3	13.8	13.3	14.1	26.5	48.4

2 Ground-State Isomers

Eight minimum-energy structures of **2** on the S_0 surface were located at the OM2/MRCI level. These isomers can be interconverted either through hydrogen transfers (tautomers) or double-bond isomerizations. Their structures are shown in Fig. 1, and their relative energies are given in Table 2.

3 Optimized Structures

The appendix (see below) contains the Cartesian coordinates of all structures optimized at the OM2/MRCI, B3LYP, MP2, and RI-CC2 levels.

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Structures

Isomer I, S0-MIN: OM2/MRCI

N	1.1563292174	-1.4642950682	-0.0000068742
C	0.8005715876	-2.8015599880	-0.0000018455
C	-0.5733539076	-2.9602835735	-0.0000052597
C	-1.1710453364	-1.6269558182	-0.0000041978
C	0.0076879688	-0.6882200419	-0.0000065374
C	-0.0077724196	0.6881027209	-0.0000045124
O	-2.3403116849	-1.2316475134	-0.0000038389
H	-1.1243384010	-3.8807243473	0.0000019940
H	1.5474016698	-3.5968775570	-0.0000051859
N	-1.1564139501	1.4641772700	-0.0000119045
C	-0.8006555156	2.8014417236	0.0000063304
C	0.5732701802	2.9601642813	0.0000090889
C	1.1709620626	1.6268365199	0.0000049778
O	2.3402286861	1.2315288142	0.0000080332
H	1.1242549746	3.8806048683	0.0000240805
H	-1.5474850215	3.5967598013	0.0000063296
H	-2.0978219168	1.0950849124	-0.0000132503
H	2.0977370699	-1.0952024839	0.0000026624

Isomer II, S0-SPT: OM2/MRCI

N	1.1111693775	-1.5609433674	-0.0037699159
C	0.6600591218	-2.8991372432	-0.0313773067
C	-0.7071862885	-3.0363392160	-0.0571447781
C	-1.2371481246	-1.6563519533	-0.0459495996
C	0.0400493542	-0.7940151959	-0.0110302475
C	0.0181724952	0.6180479010	0.0094700758
O	-2.3833293832	-1.2257133785	-0.0594813342
H	-1.3011844480	-3.9285010929	-0.0806407301
H	1.3894869740	-3.7115899929	-0.0307173464
N	-1.1329721022	1.4007434990	0.0010404987
C	-0.7806544124	2.7225653739	0.0267096918
C	0.6227886593	2.8420981056	0.0528302067
C	1.1322630944	1.5166365282	0.0420913840
O	2.4318509678	1.1963262743	0.0599210927
H	1.1968337350	3.7481714480	0.0762085992
H	-1.4987717233	3.5368126896	0.0262759262
H	-2.0750341938	1.0296969958	-0.0207778758
H	2.5119597968	0.2001796217	0.0465843532

Isomer III: OM2/MRCI

N	1.4214072641	-1.2386506045	-0.0200031609
C	1.2465713487	-2.5427092701	-0.0200031609
C	-0.1635470964	-2.9568587458	-0.0200031609
C	-0.8797181661	-1.7841863029	-0.0200031609
C	0.1369724100	-0.6756805667	-0.0200031609
C	-0.1350880466	0.6618437143	-0.0200031609
O	-2.2000760477	-1.6197734651	-0.0200031609
H	-0.5240424414	-3.9646009376	-0.0200031609
H	2.0637923836	-3.2699873534	-0.0200031609
N	-1.4195244384	1.2248156420	-0.0200031609
C	-1.2446970803	2.5288756185	-0.0200031609
C	0.1654189694	2.9430234813	-0.0200031609
C	0.8815989375	1.7703564203	-0.0200031609
O	2.2019603628	1.6059608130	-0.0200031609
H	0.5259000524	3.9507696773	-0.0200031609
H	-2.0619152327	3.2561561809	-0.0200031609
H	-2.4036672748	-0.6374480624	-0.0200031609
H	2.4055624213	0.6236383734	-0.0200031609

Isomer IV: OM2/MRCI

N	1.5567362284	-1.4740886177	0.0025347413
C	1.1692036478	-2.8260262562	0.0024010104
C	-0.1926119382	-3.0275645233	0.0004973201
C	-0.7798028790	-1.6767570733	-0.0007871867
C	0.4514127866	-0.7503499916	0.0007001877
C	0.3726306578	0.6592538607	0.0001171932
O	-1.9519525311	-1.3113678201	-0.0025983419
H	-0.7459878536	-3.9451022655	-0.0000180702
H	1.9330341728	-3.6070704692	0.0037617841
N	1.5258659113	1.4490780672	0.0015386883
C	1.1832634218	2.7711412551	0.0005794439
C	-0.2186114962	2.8907581520	-0.0014803679
C	-0.7403519062	1.5676679331	-0.0017918900
O	-2.0485194968	1.3165962807	-0.0035865361
H	-0.7932318915	3.7967051593	-0.0026511933
H	1.9043070486	3.5831441887	0.0013525371
H	2.4641538514	1.0707099538	0.0029968007
H	-2.2222978610	0.3267273219	-0.0035542049

Isomer V: OM2/MRCI

N	1.4869433292	-1.4900706559	-0.0000027043
C	1.1228505053	-2.8296978691	-0.0000027043
C	-0.2467949243	-2.9675961317	-0.0000027043
C	-0.8400421476	-1.6226190127	-0.0000027043
C	0.3441946659	-0.6857198196	-0.0000027043
C	0.3433007864	0.6917962705	-0.0000027043
O	-2.0207454879	-1.2852699212	-0.0000027043
H	-0.8131408360	-3.8796415542	-0.0000027043
H	1.8659195727	-3.6283369488	-0.0000027043
N	1.4850131299	1.4976200307	-0.0000027043
C	1.1191713215	2.8367699485	-0.0000027043
C	-0.2506532914	2.9728924001	-0.0000027043
C	-0.8421603128	1.6271496778	-0.0000027043
O	-2.0224242572	1.2882637915	-0.0000027043
H	-0.8181704899	3.8842099346	-0.0000027043
H	1.8612033463	3.6363731897	-0.0000027043
H	2.4384579216	1.1764122726	-0.0000027043
H	2.4399660111	-1.1676246149	-0.0000027043

Isomer VI: OM2/MRCI

N	1.5192965808	-1.4592580047	-0.0200016804
C	1.1605958050	-2.7927181091	-0.0200016804
C	-0.2151980064	-2.9421467358	-0.0200016804
C	-0.7970904688	-1.6039828639	-0.0200016804
C	0.3824541864	-0.6621300390	-0.0200016804
C	0.4076452727	0.7139096040	-0.0200016804
O	-1.9718650412	-1.2215712692	-0.0200016804
H	-0.7756617664	-3.8562481985	-0.0200016804
H	1.9007672510	-3.5938338605	-0.0200016804
N	1.6024733474	1.4425650972	-0.0200016804
C	1.2550987836	2.7126025991	-0.0200016804
C	-0.1957943131	2.9303075493	-0.0200016804
C	-0.7550087822	1.6784997118	-0.0200016804
O	-2.0536365960	1.3916018684	-0.0200016804
H	-0.6905232805	3.8783686622	-0.0200016804
H	1.9698830939	3.5419673169	-0.0200016804
H	2.4636986490	-1.0980779530	-0.0200016804
H	-2.2032570544	0.3941887473	-0.0200016804

Isomer VII: OM2/MRCI

N	0.5193973693	-1.5018590534	-1.0803164816
C	0.4489153645	-2.8289885593	-0.6567865332
C	0.2930449591	-2.9036130376	0.7060276559
C	0.2566306109	-1.5280013448	1.2319287105
C	0.4111768126	-0.6415510508	0.0017240108
C	0.4363694294	0.7332935475	-0.0155252535
O	0.1320535168	-1.1420019588	2.3875319832
H	0.2095377741	-3.7866154769	1.3105841705
H	0.5148815274	-3.6577677914	-1.3617165193
N	0.3148396511	1.4882776102	1.1679934150
C	0.3746947917	2.7492197463	0.8283276570
C	0.5429194180	2.9541820367	-0.6237500310
C	0.5819300875	1.6909233605	-1.1557607396
O	0.7275414074	1.4460951853	-2.4755491945
H	0.6161957540	3.8968968756	-1.1292649627
H	0.3093659487	3.5837110904	1.5284043137
H	0.6335155752	-1.2382577599	-2.0469614289
H	0.7287648332	0.4628160883	-2.6328013868

Isomer VIII: OM2/MRCI

N	0.2190642659	-1.3875690262	-1.1818763397
C	0.3038138139	-2.6726498457	-0.9698131718
C	0.3105652114	-3.0210981090	0.4610899552
C	0.2213958391	-1.8232554390	1.1243817276
C	0.1601629611	-0.7391554484	0.0769865263
C	0.0668099993	0.6314839459	0.1014092001
O	0.2022415306	-1.7749251597	2.4676901705
H	0.3725989000	-4.0070439709	0.8766858497
H	0.3644664483	-3.4294419275	-1.7541264682
N	0.0342365776	1.3261264607	-1.1335225184
C	-0.0554724509	2.6024988965	-0.8758180976
C	-0.0925583325	2.8976835489	0.5665537629
C	-0.0169389633	1.6760484778	1.1867339635
O	-0.0261208635	1.5779629252	2.5274335224
H	-0.1637354612	3.8675751633	1.0169998187
H	-0.0998546084	3.3878602009	-1.6326523938
H	0.1344715448	-0.8317112283	2.7831011837
H	0.0353463923	0.6236818370	2.8090336584

S0-MIN: RI-CC2

N	1.3642576	-1.2493296	0.0000000
C	1.2058065	-2.6195104	0.0000000
C	-0.1145561	-2.9810028	0.0000000
C	-0.8969412	-1.7616081	0.0000000
C	0.1211230	-0.6678212	0.0000000
C	-0.1212119	0.6678038	0.0000000
O	-2.1305528	-1.5621134	0.0000000
H	-0.5038100	-3.9846830	0.0000000
H	2.0799548	-3.2531452	0.0000000
N	-1.3643066	1.2493818	0.0000000
C	-1.2057747	2.6195590	0.0000000
C	0.1146117	2.9809690	0.0000000
C	0.8969276	1.7615381	0.0000000
O	2.1305220	1.5619590	0.0000000
H	0.5039216	3.9846280	0.0000000
H	-2.0798795	3.2532525	0.0000000
H	-2.2231448	0.7116193	0.0000000
H	2.2230531	-0.7114969	0.0000000

S0-SPT: RI-CC2

N	1.1192148	-1.4478496	0.0000000
C	0.7083229	-2.8050158	0.0000000
C	-0.6395482	-3.0069639	0.0000000
C	-1.2381416	-1.6810791	0.0000000
C	-0.0139508	-0.7542338	0.0000000
C	-0.0433813	0.6325530	0.0000000
O	-2.4147615	-1.2984228	0.0000000
H	-1.1700843	-3.9441049	0.0000000
H	1.4792183	-3.5634627	0.0000000
N	-1.1526699	1.4558333	0.0000000
C	-0.7349401	2.7524150	0.0000000
C	0.6571047	2.8021505	0.0000000
C	1.1002896	1.4711326	0.0000000
O	2.3556551	1.0091483	0.0000000
H	1.2634688	3.6917347	0.0000000
H	-1.4480716	3.5607951	0.0000000
H	-2.1031537	1.1093110	0.0000000
H	2.2754288	0.0160591	0.0000000

S0-SPT: B3LYP/6-31+G*

N	-1.15680	1.39107	-0.00015
C	-2.56027	1.25399	-0.00007
C	-3.02517	-0.03089	0.00012
C	-1.84135	-0.87601	-0.00019
C	-0.68788	0.15334	-0.00005
C	0.67142	-0.14786	-0.00002
O	-1.68414	-2.09386	0.00017
H	-4.05042	-0.37236	0.00036
H	-3.15678	2.16041	-0.00001
N	1.25371	-1.40928	-0.00008
C	2.60396	-1.27077	-0.00002
C	2.94682	0.08238	0.00001
C	1.73443	0.79542	0.00004
O	1.55741	2.11916	0.00013
H	3.94645	0.49228	0.00003
H	3.25048	-2.13781	-0.00003
H	0.71449	-2.26647	-0.00015
H	0.57956	2.29143	0.00017

S0-SPT: MP2/6-31++G**

N	-1.16650	1.39480	-0.00003
C	-2.59312	1.24791	0.00000
C	-3.03684	-0.03463	0.00003
C	-1.82788	-0.86549	-0.00005
C	-0.69199	0.16556	-0.00001
C	0.67877	-0.13767	-0.00003
O	-1.67849	-2.09164	0.00002
H	-4.05266	-0.39262	0.00010
H	-3.18848	2.14979	0.00003
N	1.23556	-1.39993	-0.00001
C	2.59615	-1.28960	0.00001
C	2.94825	0.06123	0.00002
C	1.74707	0.78799	0.00000
O	1.59673	2.13064	0.00001
H	3.94912	0.45946	0.00004
H	3.22298	-2.16627	0.00002
H	0.68711	-2.24942	-0.00004
H	0.63006	2.31124	0.00000

S0-MIN: B3LYP/6-31+G*

N	1.64763	-0.87599	0.00000
C	1.85934	-2.24352	0.00000
C	0.66507	-2.94106	0.00000
C	-0.41811	-1.96032	0.00000
C	0.28384	-0.62698	0.00000
C	-0.28384	0.62698	0.00000
O	-1.64763	-2.06863	0.00000
H	0.53034	-4.00531	0.00000
H	2.86272	-2.67158	0.00000
N	-1.64763	0.87599	0.00000
C	-1.85934	2.24352	0.00000
C	-0.66507	2.94106	0.00000
C	0.41811	1.96032	0.00000
O	1.64763	2.06864	0.00000
H	-0.53034	4.00531	0.00000
H	-2.86272	2.67158	0.00000
H	-2.36139	0.15970	0.00000
H	2.36139	-0.15970	0.00000

S0-MIN: MP2/6-31++G**

N	1.10251	-1.49314	0.00000
C	0.68299	-2.80960	0.00000
C	-0.68299	-2.91228	0.00000
C	-1.21493	-1.55977	0.00000
C	-0.00765	-0.68144	0.00000
C	0.00764	0.68145	0.00000
O	-2.38680	-1.12708	0.00000
H	-1.25836	-3.82244	0.00000
H	1.41980	-3.59885	0.00000
N	-1.10251	1.49315	0.00000
C	-0.68299	2.80960	0.00000
C	0.68299	2.91228	0.00000
C	1.21493	1.55977	0.00000
O	2.38680	1.12708	0.00000
H	1.25837	3.82244	0.00000
H	-1.41980	3.59885	0.00000
H	-2.04811	1.13349	0.00000
H	2.04811	-1.13348	0.00000

S1-MIN: OM2/MRCI

N	1.2131526591	-1.6605602483	0.0290318931
C	0.7260459633	-2.8710302873	0.0550973304
C	-0.7531529988	-2.9194387695	0.0613578275
C	-1.2142799846	-1.5661739378	0.0358139291
C	0.0506900416	-0.8115134135	0.0161274875
C	0.0756465959	0.5683943382	-0.0116946359
O	-2.3264773417	-0.9779085068	0.0279681569
H	-1.3461908310	-3.8171904259	0.0815217625
H	1.3328293657	-3.7816115210	0.0712236772
N	-1.1217165064	1.2931222438	-0.0219833068
C	-0.8436144957	2.6150608488	-0.0495572743
C	0.5650040092	2.8266196813	-0.0588393251
C	1.1538554359	1.5508143200	-0.0352921476
O	2.4580443808	1.2911584492	-0.0347294192
H	1.0688059428	3.7720235875	-0.0796389555
H	-1.5992654048	3.3985210512	-0.0626099440
H	-2.0292357773	0.7896312361	-0.0086169518
H	2.5892357215	0.2989656150	-0.0152503603

S1S0-MIN: OM2/MRCI

N	1.0876122492	-1.2673744460	-0.0053611719
C	0.8333893414	-2.5910106890	0.0047234087
C	-0.5743510709	-2.8486408305	0.0502375048
C	-1.1924832769	-1.5690585747	0.0011560520
C	-0.1101052561	-0.5606329943	-0.0001978719
C	-0.0342269104	0.8167396553	-0.0084303875
O	-2.5012772378	-1.3285063758	0.0424417798
H	-1.0596602045	-3.7945399822	-0.1028384880
H	1.6119188410	-3.3574861323	0.0460702976
N	-1.2053206437	1.7431791045	0.0033747829
C	-0.7066847881	2.8980424121	0.0044273756
C	0.7945748529	2.8832966106	0.0024959552
C	1.2208834404	1.5096960820	-0.0163815922
O	2.3466172594	0.9218139097	-0.0291870671
H	1.4080020941	3.7755676136	0.0044749210
H	-1.2648377104	3.8467439488	0.0227911818
H	-2.6487882809	-0.3407499128	0.0130772959
H	1.9939656651	-0.7380817768	-0.0325649591