Excited-state Wolff rearrangement reaction of 5-diazo Meldrum's acid: An ab initio on-the-fly nonadiabatic dynamic simulation

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Supporting Information

Table S1 Vertical excitation/de-excitation energies for all optimized geometries at 3SA-CASSCF(12,11)/6-31G* level, but at 3SA-CASSCF(10,8)/6-31G* level for Carbene I and Ketene I plus MS-CASPT2 and MRCI energy correction (all energy in eV units).

Structure	State	CASSCF	MS-CASPT2	MRCI
DMA-S_0	S_0	0.00	0.00	0.00
	S_1	3.71	3.45	3.50
	S_2	6.24	5.73	5.80
DMA-S_1	S_0	1.44	1.40	1.39
	S_1	2.31	2.34	2.32
	S_2	6.23	6.12	6.10
$(S_2/S_1)_X$	S_0	1.34	1.23	1.25
	S_1	4.02	3.60	3.65
	S_2	4.02	3.73	3.77
$(S_1/S_0)_X$	S_0	2.52	2.29	2.36
	S_1	2.52	2.49	2.42
	S_2	5.80	5.39	5.42
Diazirine-S_0	S_0	1.18	1.73	1.66
	S_1	6.66	6.99	6.93
	S_2	7.42	7.68	7.63
Carbene1-boat	S_0	0.00	0.00	0.00
	S_1	1.80	1.81	1.88
	S_2	2.72	2.82	2.96
Carbene1-chair	S_0	0.18	-0.42	-0.48
	S_1	2.18	1.54	1.53
	S_2	3.21	2.59	2.66
Ketene I	S_0	-1.67	-2.06	-2.12
	S_1	0.91	0.99	1.05
	S_2	3.99	3.56	3.62

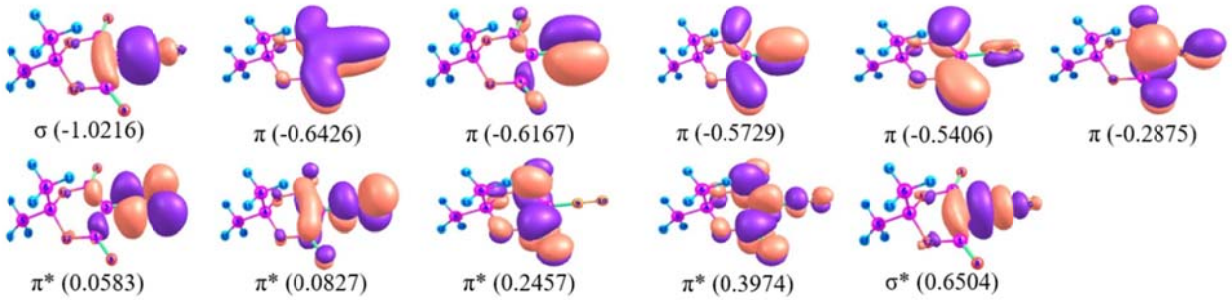

Fig. S1 Active space of 12 electrons in 11 orbitals calculated at S_0 minimum of DMA for optimizing of minima and conical intersections, as well as on-the-fly potential energies and its gradients in full-dimensional trajectory surface hopping dynamics.

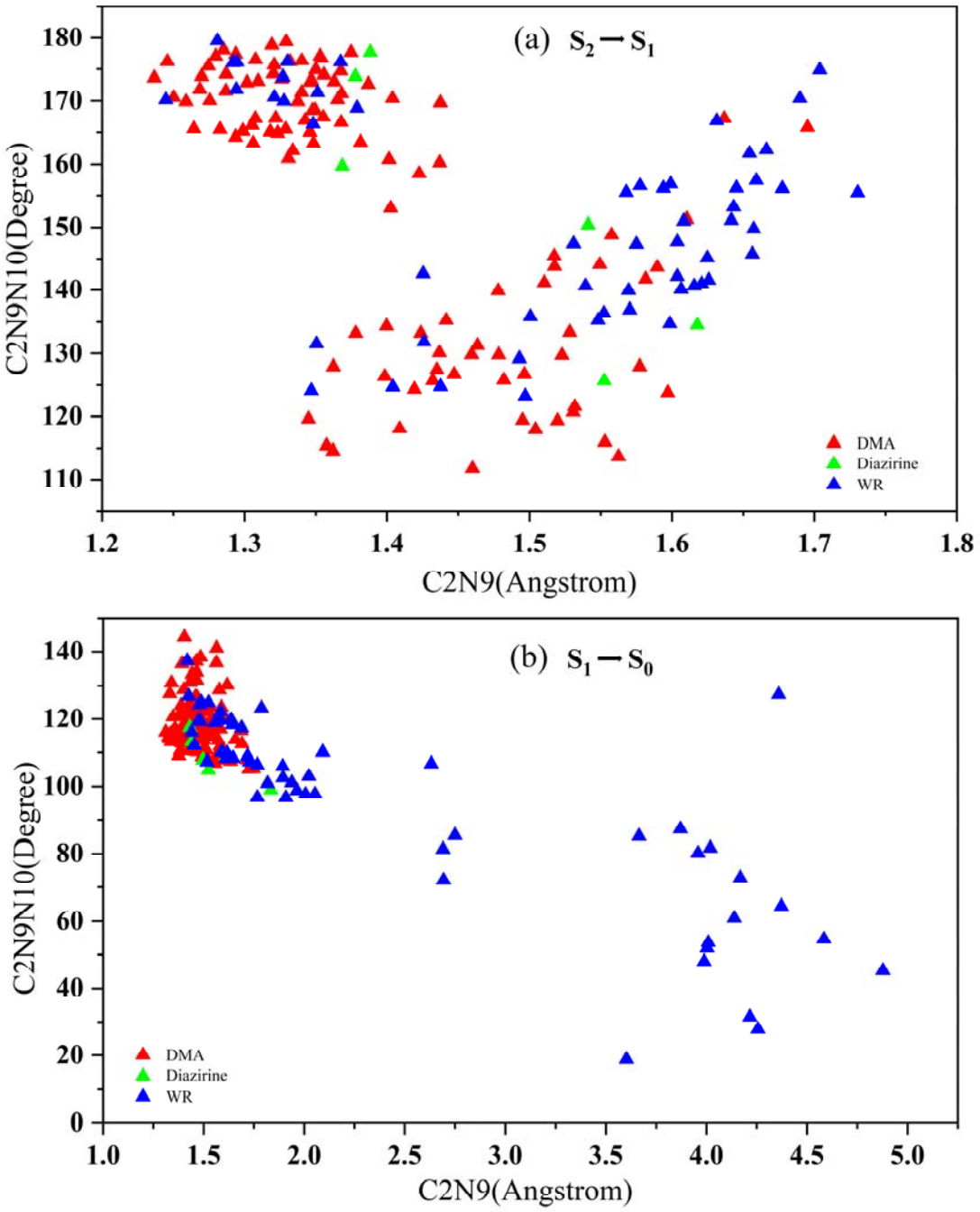

Fig. S2 The hopping distribution points in terms of dissociation bond C_2N_9 and bond angle $C_2N_9N_{10}$. Red triangle stands for trajectory going back to DMA ground state, green for isomerization to diazirine and blue for the WR to ketene I. (a) $S_2 \rightarrow S_1$ and (b) $S_1 \rightarrow S_0$.

Table S2 Cartesian coordinates (in angstrom) of optimized geometries at the 3SA-CASSCF(12,11)/6-31G* level for DMA-S_0, DMA-S_1, $(S_2/S_1)_X$, $(S_1/S_0)_X$, and Diazirine-S_0, and at 3SA-CASSCF(10,8)/6-31G*level for Carbene I and Ketene I.

Table S2.1: DMA-S_0

	X	Y	Z
C	0.3927155331	-1.2849152413	-0.1947791176
C	1.0627727564	0.0000834295	-0.0491897620
C	0.3925131660	1.2850053964	-0.1944752009
C	-1.6060386279	-0.0001218473	0.0661102113
C	-2.9406011842	-0.0001956850	-0.6446028543
C	-1.7413695768	-0.0001773626	1.5822405441
O	0.9352045260	2.3452772058	-0.2010590641
O	0.9356210958	-2.3450757633	-0.2018168906
N	2.3913859313	0.0001618753	0.1118063328
N	3.5077916342	0.0002179324	0.2567565677
O	-0.9318093241	1.1663652008	-0.3651057421
O	-0.9316482835	-1.1664991066	-0.3651773031
H	-0.7736332185	-0.0001275627	2.0704785234
H	-2.2823260073	0.8825393289	1.8989181103
H	-2.2822089945	-0.8829828610	1.8988690223
H	-2.7781081308	-0.0001333965	-1.7141290671
H	-3.5027359849	-0.8837582195	-0.3710027746
H	-3.5028813100	0.8832486766	-0.3709195353

Table S2.2: DMA-S_1

	X	Y	Z
C	0.7225687699	-0.0935669970	-1.5322465335
C	1.1223360067	-0.1603809201	-0.1277284612
C	0.1129870189	-0.0602933613	0.9314884440
O	-1.1580019635	-0.0316754875	0.5103433924
C	-1.4869300000	-0.5451275838	-0.7654731605
O	-0.6044098001	-0.0273912782	-1.7371545693
C	-1.4393060329	-2.0666835244	-0.7518673257
C	-2.8563280887	-0.0011660807	-1.1018789067
O	0.3849370345	0.0360751549	2.0930220050
O	1.4951560284	-0.0480953296	-2.4484404100
N	2.4819545711	-0.2818091502	0.3144906308
N	3.4228984989	-0.3621917982	-0.4054772389
H	-0.4509789143	-2.4411496918	-0.5072787869
H	-2.1341653417	-2.4460762712	-0.0136765841
H	-1.7117296847	-2.4474925923	-1.7278657154
H	-2.8246743439	1.0800510447	-1.0949773721
H	-3.1552729450	-0.3415467937	-2.0848148328
H	-3.5770158138	-0.3403123395	-0.3690765751

Table S2.3: $(S_2/S_1)_X$

	X	Y	Z
C	0.3783796845	-1.2749322108	-0.2955042725
C	1.0739105640	-0.0005234514	-0.2380596709
C	0.3788794360	1.2741177226	-0.2964599972
C	-1.6075919938	0.0000711534	0.0521679396
C	-2.9784821112	0.0001681756	-0.5844243557
C	-1.6571527043	0.0004562141	1.5734256863
O	0.9251884347	2.3385610117	-0.2939485653
O	0.9242513934	-2.3395963451	-0.2923536600
N	2.5156474086	-0.0007140191	-0.0642749164
N	3.2440346446	-0.0006151451	0.8583139722
O	-0.9531539168	1.1629011665	-0.4175719100
O	-0.9535822679	-1.1632089375	-0.4170198471
H	-0.6641383211	0.0004263061	2.0094579849
H	-2.1784913549	0.8835135562	1.9201180009
H	-2.1787447665	-0.8822803492	1.9205558166
H	-2.8748683420	-0.0000661146	-1.6612019538
H	-3.5248596651	-0.8830963310	-0.2799696129
H	-3.5245771223	0.8837305977	-0.2803286386

Table S2.4: $(S_1/S_0)_X$

	X	Y	Z
C	0.3673430743	-1.3684230099	0.0321709279
C	0.9786421438	-0.1370937142	-0.4665017894
C	0.5233587730	1.1729082624	0.0224250424
C	-1.4866987588	0.0075368363	0.6117795356
C	-2.2264299213	0.0551323624	-0.7179701770
C	-2.4137166552	0.0671828672	1.8043835245
O	1.0649343952	2.2161322850	-0.1776271296
O	0.8389692832	-2.4540404945	-0.1360603102
N	2.1817959643	-0.3439346009	-1.3239082695
N	3.0424846098	0.4257852887	-1.0454627774
O	-0.6150180750	1.1123912678	0.7329347070
O	-0.7630579923	-1.1995871611	0.7312477838
H	-1.8306524033	0.0309134292	2.7147660050
H	-2.9817192535	0.9881719119	1.7825613851
H	-3.0930323469	-0.7751619232	1.7837711621
H	-1.5467964185	0.0094363491	-1.5620191760
H	-2.9055811886	-0.7850377686	-0.7860501146
H	-2.7901772301	0.9765988123	-0.7875183298

Table S2.5: Diazirine-S_0

	X	Y	Z
C	0.4619998086	-1.3008940490	-0.1946174579
C	1.1932866341	-0.0066535154	-0.0225856286
C	0.4652248876	1.2798984971	-0.2160672329
C	-1.5284906179	0.0003960489	0.0422973553
C	-2.8714479120	0.0071865116	-0.6513263712
C	-1.6401416142	0.0042214675	1.5603360620
O	1.0257510767	2.3486135787	-0.2467186605
O	0.9982572007	-2.3621533072	-0.1999968888
O	-0.8506868605	1.1618764211	-0.3997678800
O	-0.8592704059	-1.1615404486	-0.3993584321
H	-0.6646154001	0.0018408503	2.0355134792
H	-2.1718013366	0.8893501687	1.8854174578
H	-2.1777235572	-0.8762700268	1.8883036563
H	-2.7223114921	0.0048055187	-1.7227636708
H	-3.4343445651	-0.8730953557	-0.3692515426
H	-3.4254635834	0.8938851294	-0.3717087334
N	2.3536001371	0.0009457212	0.8495138357
N	2.6100706002	-0.0116382106	-0.3306393475

Table S2.6 : Carbene I-boat

	X	Y	Z
C	-0.9868630818	1.1936003238	-0.0819105937
C	-1.4998597031	-0.0054801772	0.6201085289
C	-0.9681548254	-1.1680597802	-0.0635269457
C	1.0792465774	-0.0110472029	0.0515276002
C	2.3210308760	-0.0069588543	-0.8093861930
C	1.3852181934	-0.0114121806	1.5426872161
O	-1.7119139843	-2.0264363575	-0.4538292521
O	-1.6520974682	2.1128633193	-0.4436405453
O	0.3472420237	-1.1768967108	-0.3015743296
O	0.3422829051	1.1488527788	-0.3012050276
H	0.4806250632	-0.0107553715	2.1417550793
H	1.9577815905	-0.8942447115	1.7967199450
H	1.9585629502	0.8711568677	1.7956669380
H	2.0359016410	-0.0073128135	-1.8526725622
H	2.9077381483	0.8783641588	-0.6011443597
H	2.9142090940	-0.8882722882	-0.6018854985

Table S2.7 : Carbene I-chair

	X	Y	Z
C	-1.0131614918	1.1419413074	-0.0264995577
C	-1.6188761568	-0.0550457142	-0.6259863256
C	-0.9634826441	-1.2511744134	-0.0318861728
C	1.0723611730	-0.0032682385	-0.0101904828
C	2.2866225162	-0.0140127106	-0.9067520376
C	1.3949636109	0.0984650753	1.4706941458
O	-1.5370711972	-2.1464585103	0.4929155862
O	-1.5224212930	1.9974848573	0.5979411451
O	0.3652303657	-1.2126000303	-0.2544310087
O	0.2865658634	1.1236461329	-0.4002871779
H	0.4893885780	0.0963257538	2.0677210598
H	2.0035206349	-0.7448742851	1.7704241618
H	1.9295757561	1.0185928572	1.6672914259
H	1.9737803782	-0.0812419181	-1.9402454099
H	2.8543843860	0.8964318622	-0.7651592573
H	2.9095885206	-0.8662720253	-0.6678600939

Table S2.8 : Ketene I

	X	Y	Z
C	0.8837228207	-0.2836109976	-0.1619127148
C	0.4863554272	1.1348422527	-0.0934484443
C	-1.3496284901	-0.2244352526	0.0151261862
C	-2.4252944314	-0.4313467261	-1.0261628597
C	-1.8010843885	-0.5012477047	1.4364840936
O	1.1405033071	2.1223798879	-0.0550379822
O	-0.8633199877	1.1017430715	-0.0729333172
O	-0.2414489405	-1.0506594302	-0.3115441379
H	-0.9769052719	-0.3562516125	2.1253436569
H	-2.6031987671	0.1731979924	1.7104969206
H	-2.1500180455	-1.5231778475	1.5221116541
H	-2.0316406373	-0.1991554443	-2.0071207230
H	-2.7564730987	-1.4626102144	-1.0129882903
H	-3.2705069701	0.2142357609	-0.8213417282
C	2.0987959986	-0.7183020288	-0.0518787672
O	3.1919674753	-1.0399157065	0.0265684536