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Supporting Information

(Total of 13 pages)
for

Theoretical Study of the Dark Photochemistry of 1,3-Butadiene via the Chemiexcitation of Dewar Dioxetane

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Table S1. Cartesian coordinates (in Å) of the optimized Dewar dioxetane structures at the CASSCF/ANO-RCC-VDZP level of theory.

Reactant:

H	-0.10601967	-2.49925566	0.12950332
C	-0.10434255	1.44351792	0.00537897
C	1.20502232	0.77416577	0.22820401
C	1.23697894	-0.75668867	0.14037256
C	-0.09048461	-1.42532236	0.07338887
C	-1.20187852	-0.73289068	-0.06905159
C	-1.20529267	0.73441401	-0.13817978
H	-0.12216081	2.51758128	-0.03610816
H	2.01155072	1.25039747	-0.31147186
H	1.93217316	-1.16800074	-0.57946433
H	-2.14930221	-1.23701627	-0.13347696
H	-2.14828159	1.22399125	-0.30271245
O	1.85411933	-0.83837654	1.47874714
O	1.56892116	0.71349319	1.66232626

TS_{S0} :

H	-0.07937550	-2.48201790	0.30082462
C	-0.09824899	1.43417859	-0.02819354
C	1.18358633	0.78284286	0.38417202
C	1.25251950	-0.73748625	0.12042603
C	-0.07766082	-1.41620016	0.15747943
C	-1.19329834	-0.74308496	-0.02877777
C	-1.18620312	0.71400543	-0.21364168
H	-0.10726866	2.50318812	-0.13586208
H	2.04600349	1.26874111	-0.05119435
H	1.76123583	-0.95410507	-0.81520867
H	-2.14213719	-1.24799729	-0.04244322
H	-2.10918290	1.19070122	-0.49148377
O	2.14527879	-1.16955776	1.16260612
O	1.28575459	0.85680206	1.82875289

Min_{S1} :

H	-0.07908801	-2.49010474	0.31420129
C	-0.12525031	1.41840006	-0.01013810
C	1.13358683	0.78192408	0.50159753
C	1.22333821	-0.72134292	0.08372621
C	-0.09361950	-1.42850289	0.14648204

C	-1.21260020	-0.76353361	-0.05216965
C	-1.19842682	0.69101753	-0.25322102
H	-0.14122993	2.48889897	-0.10120308
H	2.01909464	1.28642189	0.13237468
H	1.58601125	-0.74088582	-0.94474300
H	-2.16182391	-1.26776671	-0.06004257
H	-2.10782870	1.16507132	-0.57711730
O	2.24655714	-1.37223939	0.80920804
O	1.17729007	0.95629710	1.91274415

Min_{T1} :

H	-0.07784424	-2.49011934	0.30709967
C	-0.12674920	1.41857568	-0.00654236
C	1.13589469	0.78325003	0.49913877
C	1.22451084	-0.72106554	0.08705271
C	-0.09314598	-1.42792045	0.14360530
C	-1.21248185	-0.76353367	-0.05358316
C	-1.19972477	0.69144903	-0.25010198
H	-0.14300395	2.48915793	-0.09603173
H	2.01570288	1.29098269	0.12041907
H	1.59417010	-0.74730925	-0.93908519
H	-2.16090918	-1.26917440	-0.06418966
H	-2.10956300	1.16600715	-0.57199006
O	2.23868982	-1.38214558	0.81683529
O	1.18046461	0.96550061	1.90907255

TS_{S1} :

H	-0.15053172	-2.54541652	0.41432172
C	-0.12961157	1.45658099	0.00759276
C	1.11748408	0.94170467	0.63203119
C	1.29799745	-0.98425229	-0.05261980
C	-0.07786071	-1.50817029	0.14092407
C	-1.17903031	-0.76888824	-0.02284651
C	-1.14890124	0.67412122	-0.28785555
H	-0.18524994	2.51788608	-0.16489957
H	2.04422171	1.35902287	0.26897848
H	1.52450312	-0.58973213	-1.03814793
H	-2.14775675	-1.22106866	0.09235904
H	-2.03392490	1.11365270	-0.71388054
O	2.25857530	-1.45767851	0.63313015
O	1.07609622	1.01589299	1.99261172

TS_{T1} :

H	-0.13119706	-2.45682873	0.54502297
C	-0.13598664	1.49473450	-0.04748257
C	1.12476827	1.06799778	0.65031673
C	1.24168741	-0.81019499	0.08500868
C	-0.09575233	-1.42334585	0.25070334
C	-1.18769732	-0.72307634	0.02686553
C	-1.15624179	0.70228058	-0.31227768
H	-0.19899367	2.54260651	-0.28950824
H	2.04521377	1.34932452	0.14650244
H	1.53032602	-0.64320861	-0.94825926
H	-2.15085914	-1.19378871	0.10832254
H	-2.03904949	1.11664821	-0.76654271
O	2.23181633	-1.46028293	0.71549653
O	1.15138571	1.05365509	1.90789265

Z,Z-2,4-Hexadienedial$_{S0}$ (p):

H	0.09456516	-2.62671783	0.90398521
C	0.10266517	1.90190288	0.11791848
C	-0.19130982	2.43574759	1.46062655
C	0.51033687	-2.30544908	-1.17477305
C	0.21646858	-1.83713370	0.18371747
C	0.09051107	-0.55877394	0.58631663
C	0.22461316	0.61560044	-0.26156560
H	0.22949991	2.66019496	-0.63557052
H	-0.24925478	3.52322170	1.51537209
H	0.64836664	-1.57076858	-1.96381192
H	-0.12733038	-0.38077471	1.61994397
H	0.44216320	0.45343030	-1.30092484
O	0.60267302	-3.47886731	-1.43883610
O	-0.36454775	1.78490832	2.45966259

Z,Z-2,4-Hexadienedial$_{S0}$ (t):

H	-0.3657560	-2.5512646	0.8370547
C	-0.0653022	1.6910302	-0.1352129
C	0.9352944	1.7867469	0.9466935
C	1.2433022	-1.6242598	-0.2576920
C	-0.1026301	-1.6396715	0.3304634
C	-0.9973253	-0.6485296	0.2505005
C	-0.8666550	0.6560130	-0.4242595
H	-0.1882004	2.5955695	-0.7068158

H	1.1738214	2.8034081	1.2620440
H	1.5394303	-0.7455158	-0.8223392
H	-1.9731277	-0.8218413	0.6757051
H	-1.5866480	0.8154444	-1.2119138
O	1.9977534	-2.5574302	-0.1480572
O	1.4854629	0.8568217	1.4758902

E,Z-2,4-Hexadienedial$_{S0}$:

H	-0.6249095	-2.7323779	-0.7409783
C	0.2731305	1.3425527	-0.0086558
C	0.6000130	2.6469245	0.6040388
C	1.2323954	-1.9002524	-0.0350879
C	-0.2078480	-1.8343860	-0.3204217
C	-1.0115100	-0.7975878	-0.0442510
C	-0.6280255	0.5053821	0.5181232
H	0.7814011	1.1026979	-0.9267513
H	1.2189199	3.3162994	0.0066321
H	1.6862927	-1.0647968	0.4907927
H	-2.0664612	-0.9201828	-0.2291715
H	-1.1554540	0.8161954	1.4045313
O	1.9021936	-2.8541670	-0.3430886
O	0.2292830	2.9902198	1.6963491

E,Z-2,4-Hexadienedial$_{T1}$ $^3(\pi\pi^*)$:

H	-0.409675	-2.756115	0.147366
C	0.153060	1.460559	-0.208842
C	0.892748	2.054414	0.864128
C	1.315183	-1.548503	-0.161595
C	-0.107616	-1.730202	0.038744
C	-1.106048	-0.750108	0.102809
C	-1.034047	0.622680	0.003566
H	0.443547	1.712425	-1.214721
H	1.719496	2.706351	0.592120
H	1.706967	-0.544559	-0.281526
H	-2.098953	-1.136549	0.257266
H	-1.963824	1.159418	0.093827
O	2.077007	-2.490192	-0.203015
O	0.641576	1.856902	2.041934

Z,Z-2,4-Hexadienedial$_{S1}$ $^{1}(n\pi^{*})$:

H	-0.291169	-2.611278	0.671193
C	-0.094513	1.637376	-0.045346
C	0.913608	1.678492	0.940541
C	1.277176	-1.545814	-0.348084
C	-0.069134	-1.659287	0.222310
C	-1.015126	-0.708968	0.188340
C	-0.926498	0.646000	-0.374835
H	-0.195654	2.565311	-0.580926
H	1.534892	2.532099	1.122421
H	1.530677	-0.636781	-0.883748
H	-1.986417	-0.969252	0.579013
H	-1.674652	0.873768	-1.115825
O	2.100874	-2.448962	-0.254424
O	1.161944	0.650951	1.781067

Z,Z-2,4-Hexadienedial$_{T1}$ $^{3}(n\pi^{*})$:

H	-0.28648188	-2.61110363	0.68367320
C	-0.09002660	1.63974487	-0.04552067
C	0.89720287	1.68784604	0.96100197
C	1.27131779	-1.56086283	-0.36821722
C	-0.06522602	-1.66270147	0.22682450
C	-1.00515011	-0.70628318	0.19967088
C	-0.91394627	0.64189175	-0.38072063
H	-0.18197874	2.56358342	-0.58931295
H	1.51123912	2.54767108	1.14418312
H	1.52767506	-0.64886686	-0.89776253
H	-1.97262635	-0.95741732	0.60598365
H	-1.64980374	0.85823623	-1.13718922
O	2.08399791	-2.47749469	-0.30312804
O	1.13981496	0.68941160	1.80221092

Table S2. Energies (in kcal/mol) of the low-lying singlet and triplet states at the optimized geometries of Dewar dioxetane relative to the ground-state energy of the reactant (Reac).

	Reac	TS_{S0}	Min_{S1}	Min_{T1}	TS_{S1}	TS_{T1}	Z,Z-$Hexa_{S0}$ (p)	Z,Z-$Hexa_{S0}$ (t)	E,Z-$Hexa_{S0}$	E,Z-$Hexa_{T1}$	Z,Z-$Hexa_{S1}$	Z,Z-$Hexa_{T1}$
					CASSCF/ANO-RCC-VDZP							
S_0	0.00	13.89	11.19	11.22	3.74	3.97	-47.89	-65.64	-68.65	-21.88	-45.95	-51.07
S_1	79.55	19.04	14.33	14.40	33.32	32.26	31.92	26.64	23.11	19.95	4.82	-0.63
S_2	130.02	21.54	15.16	15.19	49.83	47.04	90.82	29.00	23.70	30.50	42.67	72.60
S_3	156.02	25.14	17.13	17.22	54.90	51.68	91.46	93.20	82.59	49.91	74.99	92.05
T_1	61.68	16.63	11.20	11.20	30.39	29.58	11.06	16.23	10.86	-22.21	2.62	-5.91
T_2	116.29	19.06	14.67	14.71	42.27	41.19	16.46	17.79	17.69	19.54	12.51	15.80
T_3	123.23	21.64	14.79	14.85	48.16	45.47	47.50	25.95	18.55	31.58	35.82	31.95
T_4	175.98	26.25	17.92	18.02	53.75	50.45	76.41	66.20	23.66	49.13	37.07	75.59
					CASPT2/ANO-RCC-VTZP//CASSCF/ANO-RCC-VDZP							
S_0	0.00	25.21	21.46	21.51	-4.28	-4.53	-70.47	-62.34	-64.43	-16.04	-46.37	-49.74
S_1	71.65	28.32	22.74	22.78	32.09	30.52	6.87	19.80	16.78	16.56	7.28	8.06
S_2	124.31	31.26	23.72	23.78	48.08	45.03	56.50	28.82	18.15	26.19	33.18	77.49
S_3	154.17	36.16	28.30	28.42	59.64	55.77	49.37	78.22	70.55	54.07	69.48	100.15
T_1	50.71	25.68	21.82	21.84	30.15	29.01	-1.34	15.63	11.62	-15.16	3.31	5.01
T_2	113.90	29.92	25.96	26.08	47.88	46.42	1.83	20.08	11.34	17.19	18.06	32.28
T_3	116.59	31.83	25.88	25.89	47.87	45.27	33.14	30.43	12.29	28.84	28.10	36.00

Table S3. Zero-point vibrational energies (in kcal/mol) of the low-lying singlet and triplet states at the optimized geometries of Dewar dioxetane relative to the ground-state energy of the reactant (Reac).

	Reac	TS_{S0}	Min_{S1}	Min_{T1}	TS_{S1}	TS_{T1}	Z,Z-$Hexa_{S0}$ (p)	Z,Z-$Hexa_{S0}$ (t)	E,Z-$Hexa_{S0}$	E,Z-$Hexa_{T1}$	Z,Z-$Hexa_{S1}$	Z,Z-$Hexa_{T1}$
						CASSCF/ANO-RCC-VDZP						
S_0	0.00	12.55	9.66	10.00	-0.46	-0.08	-49.98	-68.54	-71.65	-26.67	-49.34	-55.37
S_1	79.55	17.70	12.80	13.18	29.13	28.20	29.82	23.74	20.11	15.15	1.42	-4.93
S_2	130.02	20.19	13.64	13.97	45.63	42.98	88.72	26.10	20.70	25.71	39.27	68.30
S_3	156.02	23.80	15.60	16.00	50.70	47.62	89.36	90.30	79.59	45.12	71.59	87.75
T_1	61.68	15.29	9.67	9.98	26.19	25.52	8.96	13.33	7.86	-27.01	-0.78	-10.21
T_2	116.29	17.71	13.14	13.49	38.07	37.13	14.36	14.90	14.69	14.74	9.11	11.50
T_3	123.23	20.30	13.27	13.63	43.96	41.42	45.40	23.05	15.55	26.79	32.42	27.65
T_4	175.98	24.90	16.39	16.80	49.56	46.39	74.31	63.30	20.66	44.34	33.68	71.29

Table S4. Gibbs free energies (in kcal/mol) of the low-lying singlet and triplet states at the optimized geometries of Dewar dioxetane relative to the ground-state energy of the reactant (Reac).

	Reac	TS_{S0}	Min_{S1}	Min_{T1}	TS_{S1}	TS_{T1}	Z,Z-$Hexa_{S0}$ (p)	Z,Z-$Hexa_{S0}$ (t)	E,Z-$Hexa_{S0}$	E,Z-$Hexa_{T1}$	Z,Z-$Hexa_{S1}$	Z,Z-$Hexa_{T1}$
						CASSCF/ANO-RCC-VDZP						
S_0	0.00	12.81	9.56	9.80	-0.89	-0.43	-52.22	-70.27	-73.78	-28.71	-50.48	-57.00
S_1	79.55	17.96	12.70	12.98	28.69	27.86	27.59	22.01	17.98	13.12	0.29	-6.56
S_2	130.02	20.46	13.53	13.76	45.20	42.63	86.49	24.37	18.57	23.67	38.14	66.67
S_3	156.02	24.06	15.50	15.79	50.27	47.27	87.13	88.57	77.46	43.08	70.46	86.12
T_1	61.68	15.55	9.57	9.78	25.76	25.17	6.73	11.60	5.73	-29.04	-1.91	-11.84
T_2	116.29	17.97	13.04	13.29	37.64	36.78	12.13	13.16	12.56	12.71	7.98	9.87
T_3	123.23	20.56	13.16	13.42	43.53	41.07	43.17	21.32	13.42	24.75	31.29	26.02
T_4	175.98	25.16	16.29	16.59	49.12	46.04	72.08	61.57	18.53	42.30	32.54	69.66

Table S5. Relative electronic, zero-point vibrational and Gibbs free energies (kcal/mol) of the main stationary structures of the thermal decomposition of the Dewar dioxetane.

	ZPVE	Gibbs
REACT	72.2	53.0
TS_{S0}	70.8	51.9
Min_{S1}	70.9	51.6
Min_{T1}	70.6	51.4
TS_{S1}	68.0	48.4
TS_{T1}	68.1	48.6
Z,Z-2,4-Hexadienedial$_{S0}$(p)	70.1	48.7
Z,Z-2,4-Hexadienedial$_{S0}$(t)	69.3	48.4
E,Z-2,4-Hexadienedial$_{S0}$	69.2	47.9
E,Z-2,4-Hexadienedial$_{T1}$	67.4	46.2
Z,Z-2,4-Hexadienedial$_{S1}$	68.8	48.5
Z,Z-2,4-Hexadienedial$_{T1}$	67.9	47.1

Table S6. Spin-orbit interactions (cm^{-1}) of the main transition states.

State 1	State 2	$\lvert\langle\Psi_1\rvert H_{SO}\rvert\Psi_2\rangle\rvert$ (cm^{-1})		
		TS_{S0}	TS_{S1}	TS_{T1}
$T_1(M_S=-1)$	$S_0(M_S=0)$	17.142	2.600	40.538
$T_1(M_S=0)$	$S_0(M_S=0)$	12.754	66.113	30.505
$T_1(M_S=1)$	$S_0(M_S=0)$	17.142	2.600	40.538
$T_2(M_S=-1)$	$S_0(M_S=0)$	13.891	30.781	5.024
$T_2(M_S=0)$	$S_0(M_S=0)$	2.55	26.360	60.114
$T_2(M_S=1)$	$S_0(M_S=0)$	13.891	30.781	5.024
$T_1(M_S=-1)$	$S_1(M_S=0)$	9.083	>1.000	4.193
$T_1(M_S=0)$	$S_1(M_S=0)$	45.312	3.506	3.492
$T_1(M_S=1)$	$S_1(M_S=0)$	9.083	>1.000	4.193
$T_2(M_S=-1)$	$S_1(M_S=0)$	20.775	3.448	4.173
$T_2(M_S=0)$	$S_1(M_S=0)$	80.219	38.850	6.451
$T_2(M_S=1)$	$S_1(M_S=0)$	20.775	3.448	4.173
$T_1(M_S=-1)$	$S_2(M_S=0)$	11.874	4.263	>1.000
$T_1(M_S=0)$	$S_2(M_S=0)$	3.613	3.228	9.620
$T_1(M_S=1)$	$S_2(M_S=0)$	11.874	4.263	>1.000
$T_2(M_S=-1)$	$S_2(M_S=0)$	21.333	18.886	1.006
$T_2(M_S=0)$	$S_2(M_S=0)$	6.716	20.754	30.840
$T_2(M_S=1)$	$S_2(M_S=0)$	21.333	18.886	1.006
$T_2(M_S=-1)$	$T_1(M_S=-1)$	71.9	42.347	12.731
$T_2(M_S=0)$	$T_1(M_S=-1)$	21.552	1.896	4.548
$T_2(M_S=1)$	$T_1(M_S=0)$	21.552	1.896	4.548
$T_2(M_S=-1)$	$T_1(M_S=0)$	21.552	1.896	4.458
$T_2(M_S=0)$	$T_1(M_S=1)$	21.552	1.896	4.458
$T_2(M_S=1)$	$T_1(M_S=1)$	71.9	42.347	12.731

Figure S1. CASPT2/ANO-RCC-VTZP//CASSCF/ANO-RCC-VDZP MEP computed on the S_0 state from a geometry after the Min_{S1}/Min_{T1} (TS_{T1}).