Supporting Information

Photophysics of Naphthalene Dimers Controlled by the Sulfur Bridge Oxidation

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Table S1. Vertical transition energies to the lowest excited bright singlet state for the *anti*-**D2** dimer computed with different functionals and conditions.

	TDDFT ωB97XD vacuum	TDA ωB97XD vacuum	TDDFT CAM-B3LYP vacuum	TDDFT ωB97XD DCM	experimental
bright S_n	S_1	S_3	S_1	S_1	-
eV	4.56	4.78	4.55	4.50	4.16
Δexp / eV	0.40	0.62	0.39	0.34	-
nm	272	259	273	276	298
f	0.20	0.20	0.19	0.26	-

All values correspond to the 6-31G(d) basis set for the ωB97X-D/6-31G(d) optimized geometry in vacuum.

Table S2. Vertical transition energies to the lowest excited bright singlet state for the *anti*-**D2** dimer computed at the TDDFT ωB97X-D level with different basis sets.

basis set	6-31G(d)	6-31+G(d)	experimental
bright S_n	S_1	S_1	-
eV	4.50	4.42	4.16
Δexp / eV	0.34	0.26	-
nm	276	281	298
f	0.26	0.27	-

Table S3. Vertical transition energies ΔE (in eV) and oscillator strengths (*f*) for the naphthalene-SO_n-Me molecules in DCM computed at the ωB97X-D/6-31+G(d) level.

SO_n	geometry	ΔE	*f*
S	S_0	4.53	0.18
	S_1	3.50	0.23
SO_1	S_0	4.52	0.19
	S_1	3.73	0.20
SO_2	S_0	4.52	0.18
	S_1	3.81	0.21

Table S4. Vertical transition energies ΔE (in eV), oscillator strength (*f*), electronic character (in %) LE (on naphthalene fragments), CT (between naphthalene moieties) and CT_B (from the SO_n bridge to the naphthalenes) and electronic couplings between the lowest LE, CT and CT_B diabatic states (in meV) for the lowest excited singlet of the different conformers of **D0**, **D1** and **D2** dimers in DCM computed at the ωB97X-D/6-31+G(d) level.

dimer	*conf.*	ΔE[a]	*f*	LE	CT	CT_B	LE/CT	LE/CT_B
D0	*syn*	4.24	0.335	37	14	49	102	509
	anti	4.31	0.326	59	5	36	65	244
	anti'	4.37	0.347	68	9	23	119	149
D1	*syn*	4.41	0.301	84	1	15	129	200
	syn'	4.35	0.280	78	4	18	98	221
	anti	4.43	0.312	91	1	8	126	195
	perp	4.33	0.329	44	11	45	128	153
D2	*syn*	4.38	0.273	94	6	0	121	0
	anti	4.42	0.272	96	4	0	162	0
	perp	4.47	0.341	100	0	0	41	0

[a]Experimental absorption maxima: 4.11 eV (**D0**), 4.19 eV (**D1**) and 4.16 eV (**D2**) [J. Am. Chem. Soc, *135* (**2013**) 8109].

Table S5. Estimated relative PL quantum yields (without considering non-radiative decay pathways) obtained as the numerical integration of the emission profiles of **Dn** dimers in DCM considering (i) ground state population (S_0) and (ii) excited state population (S_1) compared to the experimental yields from J. Amer. Chem. Soc, *135* (**2013**) 8109.

dimer	PL(S_0)	PL(S_1)	PL(exp)
D0	1.00	1.00	1.00
D1	0.22	0.32	2.92
D2	0.31	0.33	22.50

Table S6. S1/S0 energy gaps (in kcal/mol) at the inversion TS of **D1** (*syn* and *anti*) and **D2** (*anti*) dimers estimated as: $\Delta E(S_1/S_0) = \Delta E(S_0 \rightarrow S_1) - \lambda(S_1) + \Delta E(TS,S_1) - \Delta E(TS,S_0)$, where $\Delta E(S_0 \rightarrow S_1)$ is the vertical gap at the Franck-Condon geometry, $\lambda(S_1)$ is the reorganization energy of S_1, and $\Delta E(TS,S_0)$ and $\Delta E(TS,S_1)$ are the energy barriers at the S_0 transition state geometry on the S_0 and S_1 PES, respectively.

dimer	conformer	$\Delta E(S_1/S_0)$
D1	*syn*	32.4
	anti	49.5
D2	*anti*	29.1

FIGURES

Figure S1. Most stable conformers for the ground state of **D0** (top) and **D2** (bottom) dimers in DCM solution.

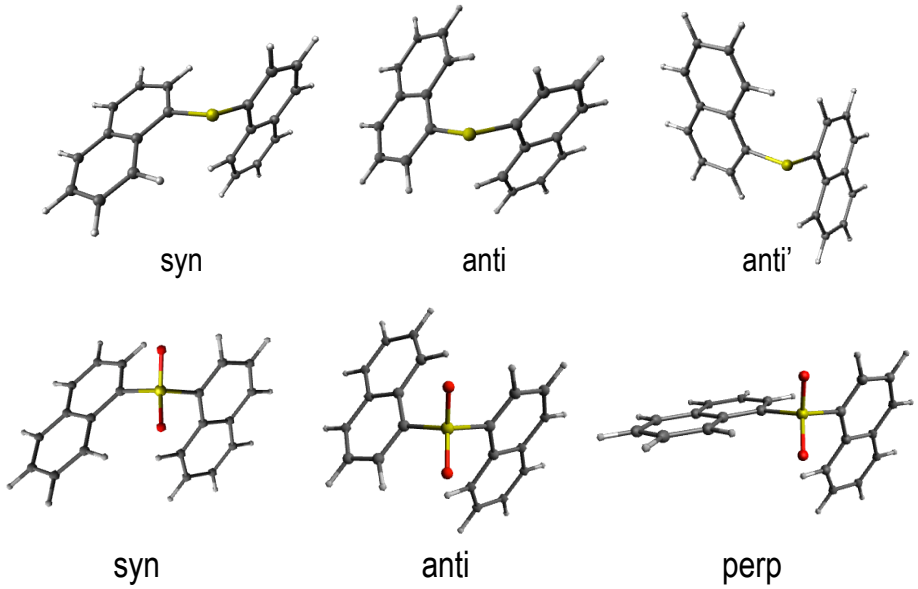


Figure S2. Ground and first excited state energy profiles for the interconversion between conformers of the **D0** dimer in DCM solution computed at the ωB97X-D/6-31+G(d) level. All structures have been relaxed on the ground state PES.

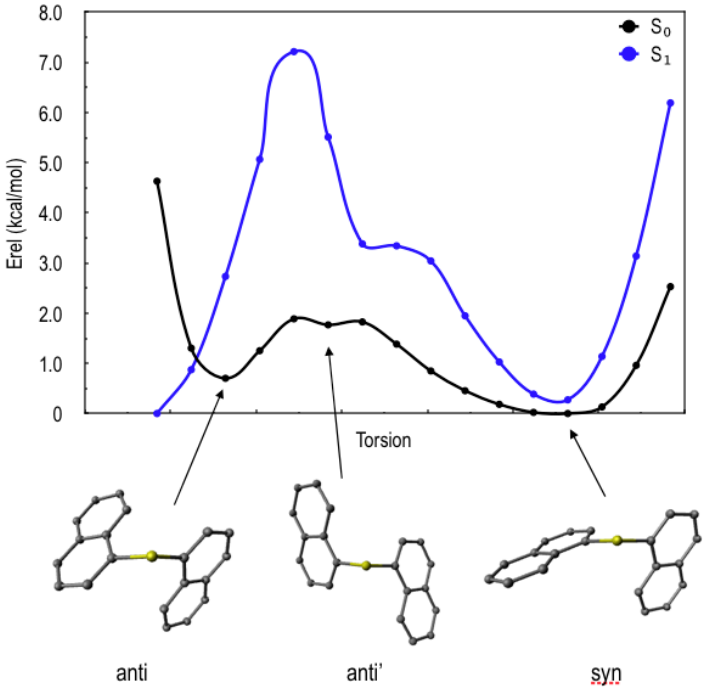


Figure S3. Ground and first excited state energy profiles for the interconversion between conformers of the **D1** dimer in DCM solution computed at the ωB97X-D/6-31+G(d) level. All structures have been relaxed on the ground state PES.

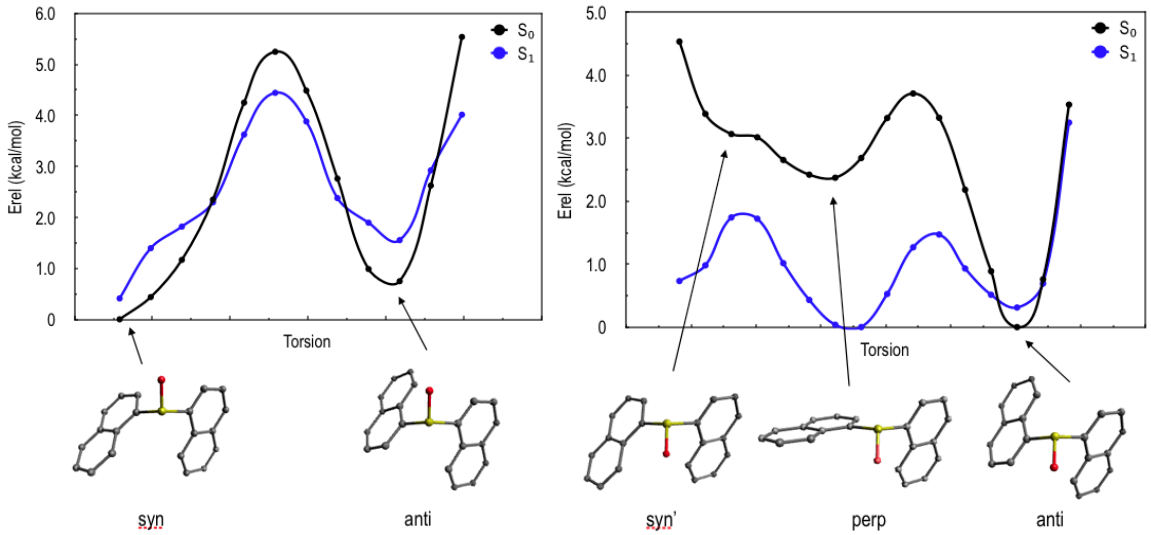


Figure S4. Ground and first excited state energy profiles for the interconversion between conformers of the **D2** dimer in DCM solution computed at the ωB97X-D/6-31+G(d) level. All structures have been relaxed on the ground state PES

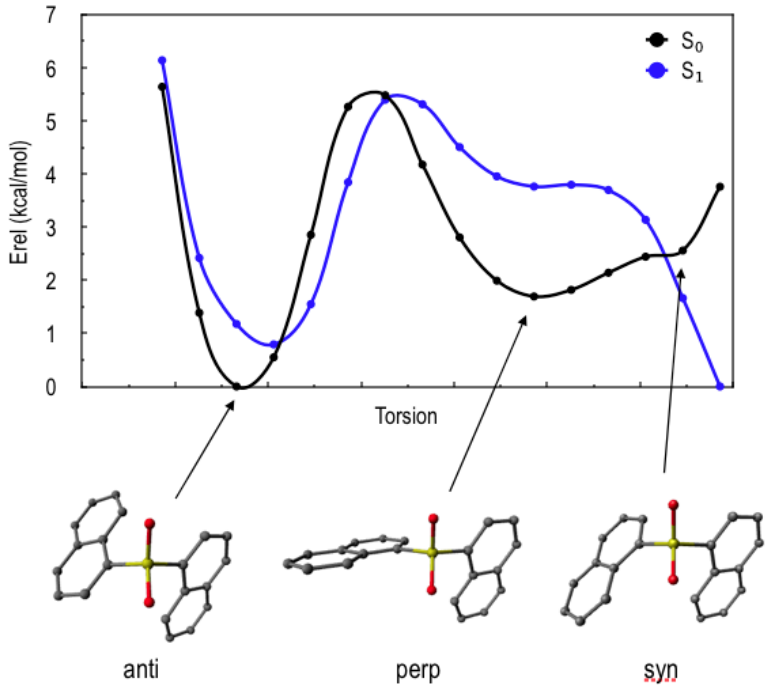


Figure S5. Molecular structure of excimeric states for **Dn** dimers optimized at the ωB97X-D/6-31+G(d) level in DCM solution.

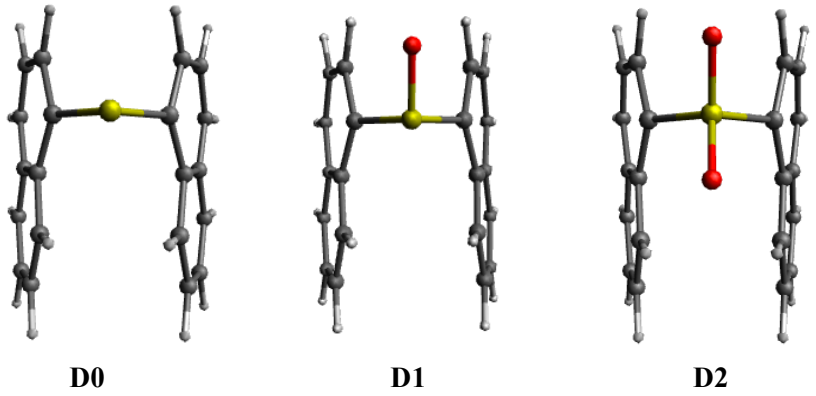


Figure S6. HOMO and LUMO orbitals accounting for the main electronic excitation contribution of **Dn** excimers computed at the ωB97X-D/6-31+G(d) level in DCM solution.

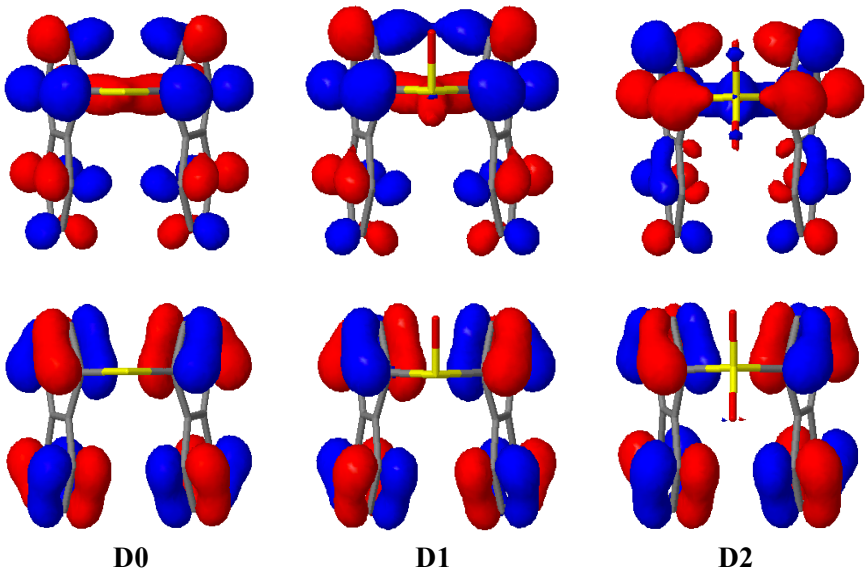
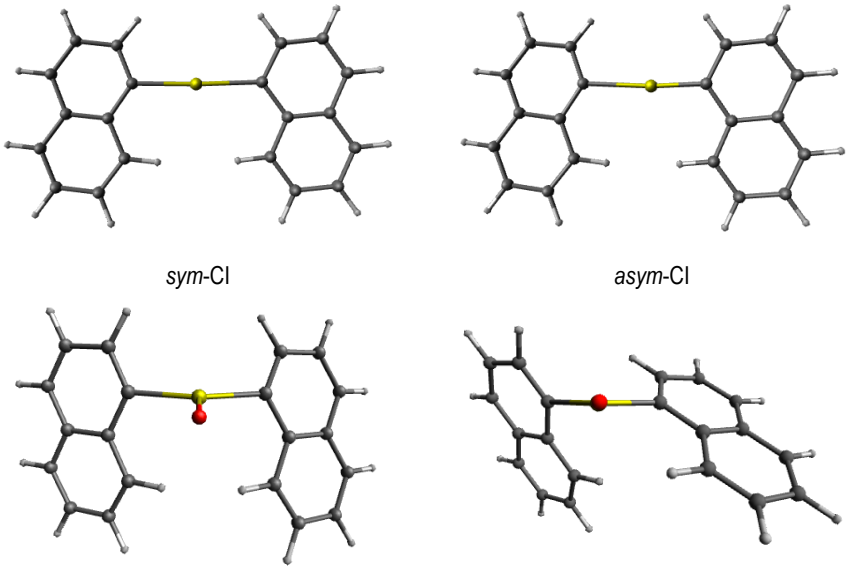


Figure S7. Molecular structures of **D0** (top) and **D1** (bottom) dimers at the *sym*-CI and *asym*-CI for the **Dn** dimers.



COMPUTATIONAL DETAILS

Transition states for the structural inversion

The transition states for the structural inversion of **D1** and **D2** were characterized as first order saddle points while those of **D0** were second order saddle points on the ground state PES. This second order saddle point which corresponds to a linear structure of **D0** is a transition state connecting two transition states (first order saddle points). These latter transition states connect the two enantiomers of *syn* and *anti* ground state conformers respectively.

CI relative energies

The values of ΔE(rel) for *inv*-TS and *sym*-CI (Table 4 of the main text) were calculated within the TDDFT. The values of ΔE(rel) for *asym*-CI were calculated by the following expression, since TDDFT cannot properly describe the situation of bond fragmentation.

ΔE(rel) = Δ*sym* + Δ*asym*
Δ*sym* = ΔE(rel) for *sym*-CI
Δa*sym* = relative energy of *asym*-CI with respect to *sym*-CI calculated by SF-DFT

Derivative couplings

Derivative couplings (atomic units) for the **D0** and **D1** dimers.

sym-CI	**D0**	71.3
	D1	169.8
asym-CI	**D0**	5550.8
	D1	2644.5

Note. The derivative coupling vectors correspond to the same nuclear motion as the imaginary frequencies of the transition states of **D1** and **D0**. Therefore, the nuclear motion that lowers the energy from the transition states to the ground state minima is equivalent to the motion that opens the gap of the S_0/S_1 crossing.

OPTIMIZED GEOMETRIES

Ground state optimized coordinates for the Dn dimers (in Angstroms).

syn-**D0** coordinates

6	-4.380813	0.053742	-0.139065
6	-3.102629	-0.349201	-0.613288
6	-2.656491	0.010328	-1.912501
6	-2.255339	-1.118771	0.239365
6	-1.419179	-0.382123	-2.353735
6	-0.578337	-1.160650	-1.526894
6	-0.974816	-1.521097	-0.259709
6	4.328485	-1.290494	-0.433799
6	3.975599	1.005679	0.417735
6	3.498800	-0.311664	0.179157
6	3.177877	1.944966	1.021386
6	2.171749	-0.654604	0.571714
6	3.864098	-2.559237	-0.660346
6	1.709533	-1.984332	0.299775
6	1.374302	0.338101	1.202094
6	2.539461	-2.903708	-0.299466
6	1.864544	1.602517	1.420506
1	1.238885	2.346342	1.905175
1	4.499615	-3.304499	-1.128759
1	0.365932	0.090673	1.517318
1	2.170602	-3.903737	-0.506555
16	0.080159	-2.522327	0.787337
1	-1.076033	-0.106695	-3.346574
6	-2.721913	-1.440386	1.544383
6	-4.805301	-0.281254	1.121812
1	-4.296428	-1.288373	2.974361
6	-3.961837	-1.033918	1.972894
1	-2.086149	-2.009517	2.215223
1	0.393170	-1.469882	-1.900947
1	5.340189	-1.014084	-0.719707
1	4.988556	1.256299	0.112667
1	3.551780	2.949146	1.198018
1	-3.309819	0.601820	-2.548600
1	-5.018715	0.637732	-0.797937
1	-5.784110	0.033296	1.471783

anti-**D0** coordinates

6	-3.605101	-0.734785	-0.065864
6	-2.938248	0.507646	-0.244064
6	-3.265721	1.359270	-1.333103
6	-1.945786	0.910149	0.699896
6	-2.635975	2.566223	-1.488163
6	-1.623512	2.956526	-0.582033
6	-1.269676	2.153803	0.479486
6	2.907644	0.022612	0.590775
6	3.567318	-0.481284	-0.562975
6	3.239441	-0.457408	1.886191
6	2.616123	0.046800	2.997305
6	1.918031	1.040786	0.441754
6	1.606222	1.026110	2.857849
6	1.248714	1.509087	1.618747
16	-0.007796	2.786476	1.583620
6	-1.692892	0.061876	1.811997
6	-3.321329	-1.540630	1.007539
1	-2.153000	-1.758301	2.821420
6	-2.361073	-1.128780	1.961110
1	2.874907	-0.314237	3.988053

6	3.279330	0.009150	-1.811424
6	1.661062	1.541874	-0.863356
6	2.322218	1.040369	-1.957739
1	1.090075	1.387737	3.742852
1	-2.891492	3.220832	-2.315850
1	-1.102055	3.896546	-0.739638
1	-0.967901	0.363783	2.557776
1	0.938257	2.337387	-0.995755
1	2.110977	1.442031	-2.944532
1	4.001292	-1.226922	1.980895
1	3.790410	-0.382873	-2.685803
1	4.312741	-1.262428	-0.435930
1	-3.838025	-2.487410	1.134127
1	-4.352742	-1.032755	-0.796743
1	-4.029569	1.039271	-2.037188

syn-**D1** coordinates

6	3.774638	0.207290	0.385030
6	3.911179	-0.800359	-1.874257
6	3.211269	-0.042437	-0.894805
6	3.364513	-1.031039	-3.109573
6	1.921368	0.481927	-1.199355
6	3.094520	0.943696	1.322651
6	1.244383	1.245208	-0.210128
6	1.384439	0.197741	-2.490146
6	1.817480	1.469703	1.017775
6	2.081869	-0.520830	-3.423738
1	1.637049	-0.695754	-4.399099
1	3.906893	-1.605306	-3.854133
1	1.285720	2.056969	1.760388
1	0.265572	1.666660	-0.416962
6	-2.848496	-1.926222	-0.393552
6	-4.034346	0.020563	0.567966
6	-3.046069	-0.524275	-0.296855
6	-4.225736	1.375658	0.652125
6	-2.244608	0.356966	-1.083536
6	-1.895702	-2.451215	-1.230967
6	-1.252061	-0.229237	-1.923682
6	-2.472669	1.758155	-0.976906
6	-1.086328	-1.590257	-2.001729
6	-3.436151	2.250395	-0.132597
1	-3.596040	3.322492	-0.066901
1	-1.752964	-3.524898	-1.300177
1	-1.883383	2.448803	-1.571866
1	-0.326358	-2.009430	-2.655479
16	-0.236872	0.839224	-2.981064
8	-0.449885	0.388245	-4.414458
1	3.534368	1.127842	2.298136
1	4.758614	-0.196562	0.609398
1	4.894391	-1.191563	-1.626180
1	-3.469074	-2.583103	0.210334
1	-4.982665	1.782044	1.316042
1	-4.637866	-0.660220	1.162829

anti-**D1** coordinates

6	3.599130	-0.727714	0.430856
6	2.708226	-1.858474	-1.578387
6	2.757526	-0.730825	-0.713464
6	1.916416	-1.857406	-2.696254
6	1.964265	0.419383	-1.000755
6	3.667361	0.371037	1.249810
6	2.077877	1.550550	-0.149206
6	1.111499	0.361488	-2.147045

6	2.904606	1.522810	0.947429
6	1.111513	-0.730810	-2.981554
1	0.475833	-0.740501	-3.863551
1	1.895013	-2.713987	-3.362157
6	-2.683489	2.082037	1.098111
6	-3.613027	-0.189430	0.790881
6	-2.750780	0.860278	0.374716
6	-3.702685	-1.355215	0.073040
6	-1.956578	0.686832	-0.798032
6	-1.873938	3.104107	0.676718
6	-1.088112	1.758096	-1.168217
6	-2.087137	-0.525319	-1.528878
6	-1.069498	2.939136	-0.474459
6	-2.937083	-1.517210	-1.104921
1	-1.837967	4.041605	1.222727
1	-0.420579	3.741948	-0.812268
16	-0.034915	1.664474	-2.650428
8	0.702834	2.988870	-2.715093
1	-4.207859	-0.048813	1.689760
1	-4.366261	-2.150287	0.399381
1	-3.297661	2.196668	1.987486
1	-3.024513	-2.432998	-1.681928
1	-1.522819	-0.673373	-2.442181
1	4.193527	-1.612648	0.643175
1	3.322327	-2.723449	-1.341492
1	4.314100	0.364790	2.122019
1	2.979897	2.399029	1.584618
1	1.528720	2.452964	-0.383159

syn-**D2** coordinates

6	-3.951095	-1.107175	0.250677
6	-3.037357	-0.116837	-0.202130
6	-3.009143	0.250600	-1.572030
6	-2.151901	0.507882	0.732166
6	-2.141298	1.207147	-2.030695
6	-1.255287	1.828666	-1.129399
6	-1.252140	1.489130	0.204793
6	3.914456	1.533694	-1.003253
6	3.775561	-0.878509	-0.490916
6	3.243141	0.435067	-0.400301
6	3.128384	-1.941069	0.086899
6	2.021219	0.648601	0.304007
6	3.404095	2.802978	-0.930780
6	1.521991	1.988545	0.342743
6	1.381608	-0.470966	0.902369
6	2.184027	3.031229	-0.255475
6	1.920683	-1.729358	0.790316
1	1.414199	-2.570346	1.254351
1	3.921664	3.636527	-1.393937
1	0.467193	-0.341708	1.468167
1	1.763067	4.030016	-0.211195
16	-0.019736	2.388880	1.164789
1	-2.124516	1.488888	-3.078168
6	-2.235141	0.111044	2.097960
6	-3.998707	-1.471777	1.570595
1	-3.172557	-1.134477	3.544904
6	-3.130522	-0.850432	2.497477
1	-1.586546	0.574805	2.828158
1	-0.564618	2.578965	-1.503088
8	-0.270287	3.819909	0.961786
8	0.046889	1.893962	2.543685
1	4.846861	1.347065	-1.529592
1	3.541301	-2.942266	0.010718

1	4.707772	-1.026015	-1.029793
1	-3.694138	-0.242182	-2.256835
1	-4.614637	-1.569612	-0.475361
1	-4.699923	-2.229249	1.907212

anti-**D2** coordinates

6	-3.641774	-0.863254	0.260802
6	-2.806288	0.130195	2.359144
6	-2.808382	0.065333	0.939673
6	-2.013195	1.026213	3.026077
6	-1.976624	0.945563	0.184275
6	-3.663385	-0.918564	-1.109293
6	-2.040049	0.878040	-1.234212
6	-1.138957	1.838835	0.925009
6	-2.857012	-0.032148	-1.859055
6	-1.161085	1.883926	2.297187
1	-0.511862	2.576961	2.821769
1	-2.021378	1.076866	4.109793
1	-1.456567	1.561428	-1.836868
6	2.804250	0.316977	-2.362095
6	3.631038	-0.862314	-0.358569
6	2.805646	0.128879	-0.953641
6	3.652870	-1.035794	1.001630
6	1.981363	0.947212	-0.124066
6	2.018280	1.273748	-2.948203
6	1.149898	1.907180	-0.783934
6	2.045440	0.757347	1.283206
6	1.172289	2.070955	-2.147063
6	2.855103	-0.210125	1.826166
1	2.887823	-0.335653	2.904256
1	2.027053	1.418375	-4.023416
1	1.468639	1.391378	1.943492
1	0.527465	2.811197	-2.608891
16	0.008133	2.955926	0.117484
8	0.750806	3.664997	1.166085
8	-0.731467	3.755551	-0.866057
1	3.446171	-0.314040	-2.971048
1	4.249003	-1.480399	-1.004510
1	4.286264	-1.796133	1.448120
1	-3.453172	-0.546626	2.911081
1	-2.888917	-0.064351	-2.943970
1	-4.302939	-1.631873	-1.619990
1	-4.266310	-1.528790	0.850803

Transition state structures for the inversion of Dn dimers (in Angstroms).

Saddle point for the inversion of *syn*-**D0**

6	-4.834903	-1.904762	2.258995
6	-3.928285	-2.123741	1.185933
6	-4.384386	-2.200049	-0.157011
6	-2.538023	-2.268200	1.482107
6	-3.499575	-2.414266	-1.181717
6	-2.116324	-2.558917	-0.923584
6	-1.667731	-2.481504	0.370765
6	4.605981	-3.202335	1.320169
6	4.650106	-1.279935	2.879115
6	3.942738	-2.148613	2.003680
6	4.010092	-0.260093	3.536442
6	2.540934	-1.942794	1.819348
6	3.912035	-4.030467	0.476697
6	1.874573	-2.843258	0.934400
6	1.907563	-0.877162	2.507969
6	2.523075	-3.855848	0.273657

6	2.622818	-0.057270	3.345145
1	2.120518	0.754389	3.862984
1	4.417605	-4.835461	-0.047858
1	0.844936	-0.718434	2.355480
1	1.979136	-4.515248	-0.391379
16	0.100568	-2.646706	0.680782
1	-3.846554	-2.474395	-2.208739
6	-2.113399	-2.196612	2.833232
6	-4.394980	-1.834920	3.556414
1	-2.673699	-1.934701	4.873035
6	-3.017721	-1.985183	3.844269
1	-1.057740	-2.318146	3.053496
1	-1.421142	-2.724558	-1.737362
1	5.672296	-3.340124	1.476124
1	5.716152	-1.441283	3.017076
1	4.565015	0.394681	4.201680
1	-5.446085	-2.087070	-0.358012
1	-5.891320	-1.793755	2.028316
1	-5.100555	-1.667210	4.364647

TS inversion for *syn*-**D1**

6	1.474437	0.083210	-2.504752
6	2.258714	-0.313616	-3.564971
6	3.642390	-0.523303	-3.381661
6	4.199180	-0.380179	-2.136257
6	3.410769	0.018143	-1.023554
6	3.991318	0.177542	0.263827
6	3.238730	0.604454	1.328151
6	1.868481	0.905297	1.146578
6	1.274175	0.754897	-0.082095
6	2.021921	0.294605	-1.198135
1	1.811690	-0.470033	-4.541346
1	4.250710	-0.824508	-4.228352
1	5.258872	-0.566851	-1.984093
1	5.048623	-0.041677	0.387815
1	3.692447	0.723078	2.307391
1	1.280666	1.263671	1.986296
1	0.224377	1.000061	-0.199648
6	-3.003324	-1.851131	-0.001558
6	-1.991078	-2.506836	-0.654685
6	-1.172832	-1.813985	-1.574835
6	-1.361625	-0.465621	-1.777206
6	-2.391257	0.262897	-1.103687
6	-2.598461	1.657906	-1.264376
6	-3.602948	2.295702	-0.577884
6	-4.450840	1.574320	0.295356
6	-4.267507	0.225895	0.473198
6	-3.232415	-0.464325	-0.212634
1	-3.645681	-2.386625	0.692303
1	-1.822802	-3.566195	-0.489898
1	-0.395148	-2.344661	-2.114653
1	-1.965220	2.217967	-1.946097
1	-3.749899	3.363579	-0.708596
1	-5.243890	2.092505	0.825950
1	-4.909645	-0.334561	1.147697
16	-0.233776	0.378469	-2.833561
8	-0.698161	1.316783	-3.975499

TS inversion for **D2**

6	-4.683281	1.324949	1.640483
6	-3.956242	3.500046	2.564416
6	-3.729938	2.376568	1.724986
6	-3.020439	4.495095	2.670996

6	-2.530072	2.292874	0.955287
6	-4.462497	0.233661	0.840466
6	-2.333438	1.146765	0.136187
6	-1.587239	3.353175	1.101682
6	-3.270458	0.146016	0.082614
6	-1.809201	4.411758	1.945142
1	-1.065468	5.193105	2.061525
1	-3.193476	5.350467	3.316623
1	-1.436442	1.058236	-0.467318
6	3.979188	3.687067	-2.272767
6	4.691098	1.435659	-1.539119
6	3.743988	2.496202	-1.534800
6	4.460615	0.279589	-0.839035
6	2.540936	2.352650	-0.779143
6	3.048905	4.692715	-2.295529
6	1.605344	3.427712	-0.834009
6	2.333825	1.139972	-0.065103
6	1.835194	4.553986	-1.582176
6	3.264611	0.132480	-0.096706
1	3.082841	-0.784733	0.455387
1	3.228454	5.599757	-2.864320
1	1.432625	1.003533	0.523482
1	1.096033	5.346734	-1.631574
16	0.009105	3.358689	0.132515
8	0.798553	3.301192	1.422103
8	-0.779780	3.402512	-1.157964
1	4.908875	3.783223	-2.827227
1	5.604343	1.558830	-2.115710
1	5.190435	-0.524282	-0.852148
1	-4.883873	3.552909	3.128075
1	-3.096725	-0.719487	-0.549716
1	-5.197120	-0.564063	0.785827
1	-5.593506	1.401873	2.229773