Supporting Information for

Disulfide Bond Photochemistry: The Effects of Higher Excited States and Different Molecular Geometries on Disulfide Bond Cleavage

Jun Cao,*[,1,2,3] and Dong-Chu Chen[1]

[1]*School of Materials Science and Energy Engineering, Foshan University, Foshan, Guangdong, 528000, P. R. China*

[2]*Guizhou Provincial Key Laboratory of Computational Nano-material Science, Guizhou Education University, Guiyang, Guizhou, 550018, P. R. China*

[3]*Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China*

Contents:

Table S1. The MS-CASPT2(6,4)/6-31G* calculated vertical excitation energies (kcal/mol) of the singlet and triplet states at the optimized S_0 minima.

state / species	S_1	S_2	S_3	T_1	T_2	T_3	T_4
DTL	93.3	128.7	184.5	76.6	116.5	141.7	199.4
DTA	103.6	126.9	198.2	85.8	112.1	143.5	204.5
DTP	110.9	122.7	205.2	92.1	106.8	143.6	206.3
DMDS	118.0	121.1	211.7	99.1	104.5	145.6	210.5

Table S2. Relative energies (kcal/mol) of the optimized structures.

species	S_0 min.	S_1 min.	T_1 min.	S_1/S_2 CI	S_1/S_0 CI	S_1/T_2 STC	T_1/S_0 STC
DTL	0.0	45.1	42.6		51.7 (53.5)[a]	52.4	51.0
DTA	0.0	52.3	45.7	60.9	60.4	59.0	57.9
DTP	0.0		51.8		53.1		
DMDS	0.0		49.0		56.7		

[a]relative energy of DTL_S_1S_0a optimized starting from DTL_S_1.

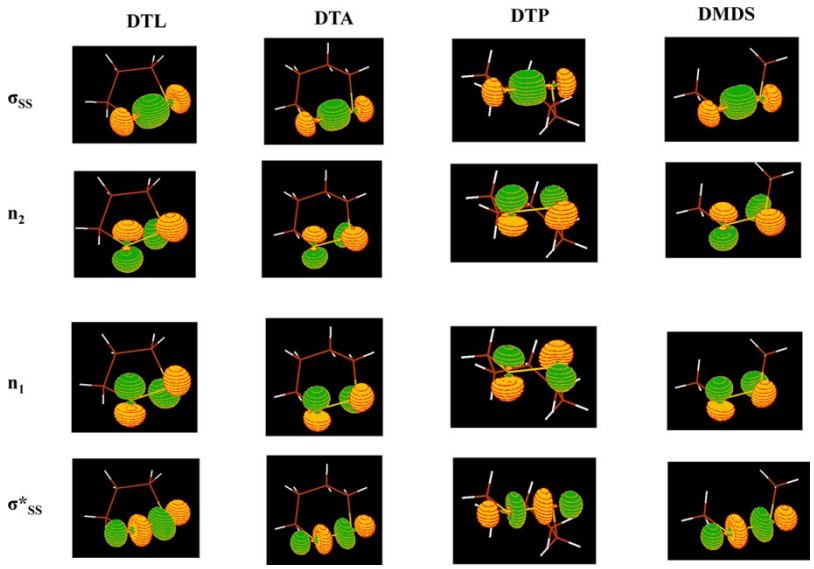

Figure S1. State-averaged CASSCF molecular orbitals in the active space CAS(6,4) of the four compounds, obtained with the 6-31G* basis set at the MS-CASPT2 optimized ground state minimum geometries.

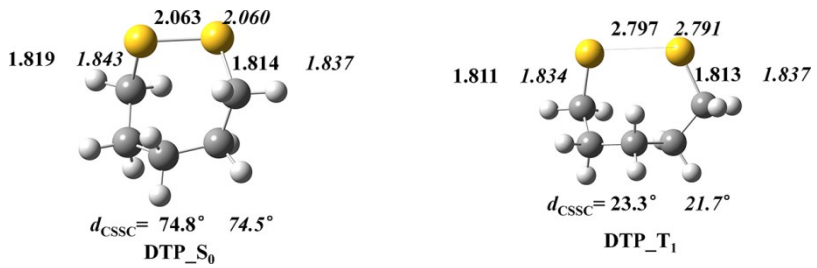

Figure S2. Optimized S_0 and T_1 structures for DTP with different basis sets: the italic

ones are from the mixed basis set 6-31G*(S)/3-21G(C, H), and others from 6-31G*.

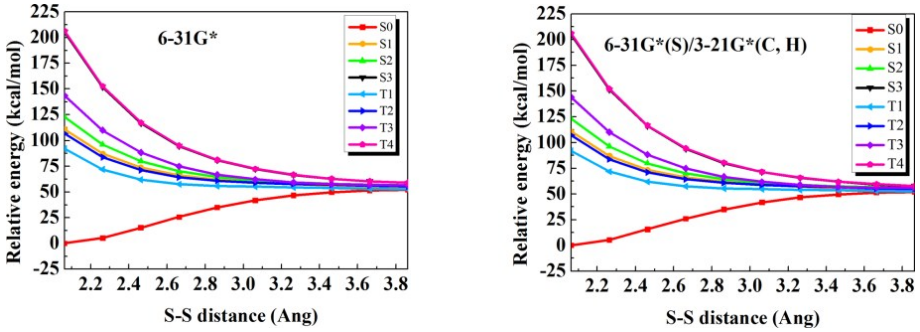

Figure S3. The MS-CASPT2(6,4) potential energy curves of DTP along the S-S distance for the mixed basis set 6-31G*(S)/3-21G(C, H) against 6-31G*.

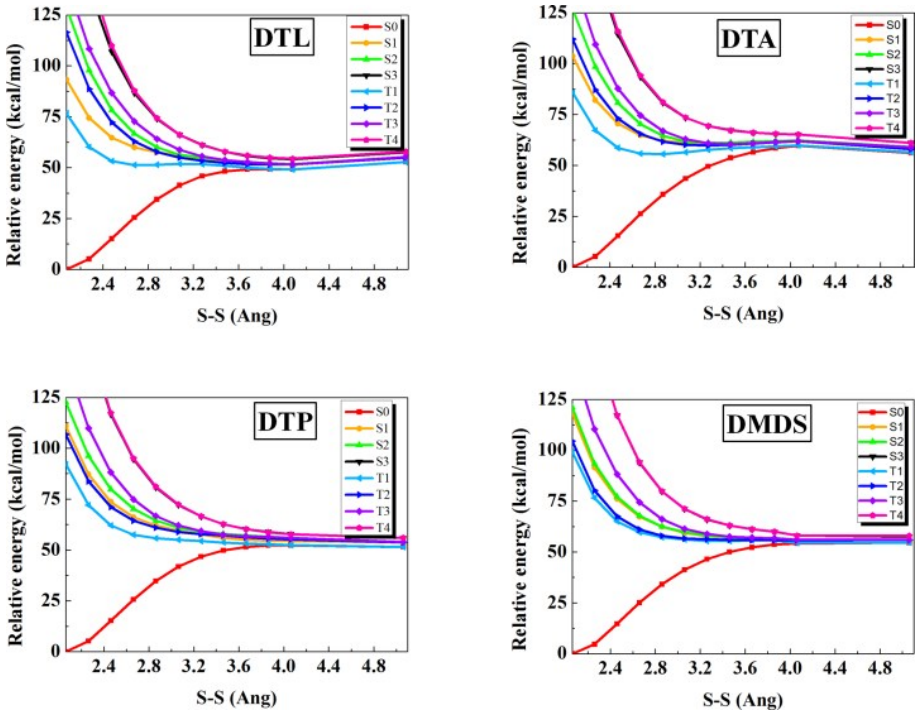

Figure S4. The potential energy curves with respect to the S–S distance reaction coordinate for all compounds.

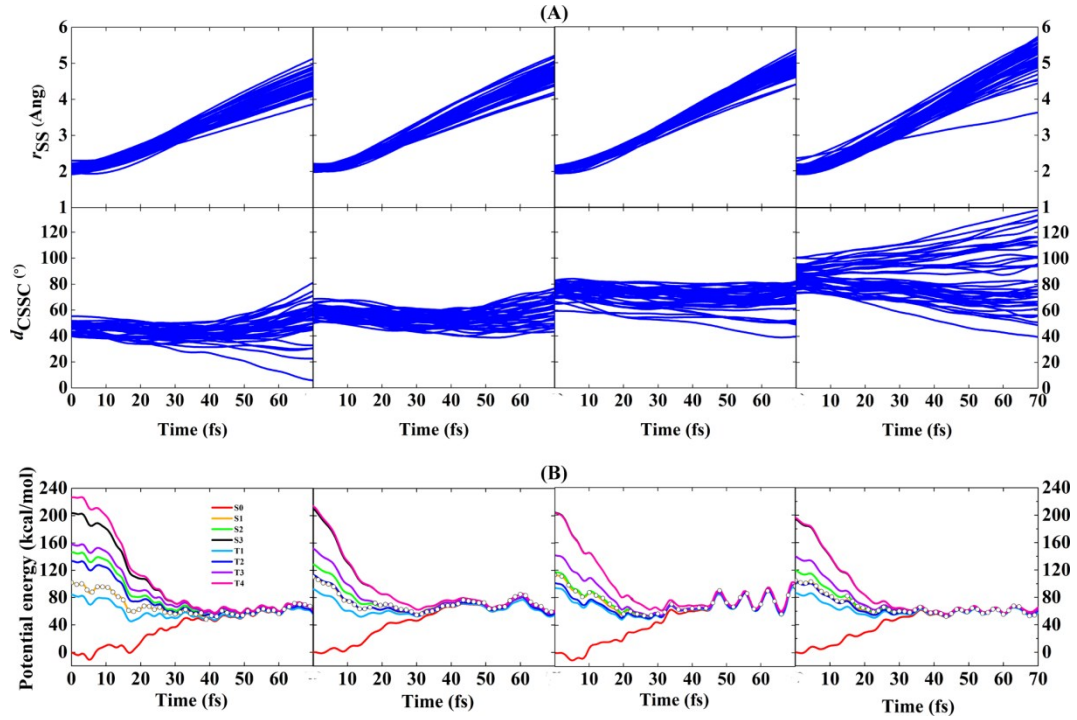

Figure S5. Time evolution of (A) the S–S distance (r_{SS}) and the CSSC dihedral angle (d_{CSSC}), and (B) potential energies of illustrative trajectories. All trajectories were started in the S_1 state, and the states are indicated in color while the populated state is indicated in while cyclic. The energies are plotted relative to the first geometry of the trajectory.

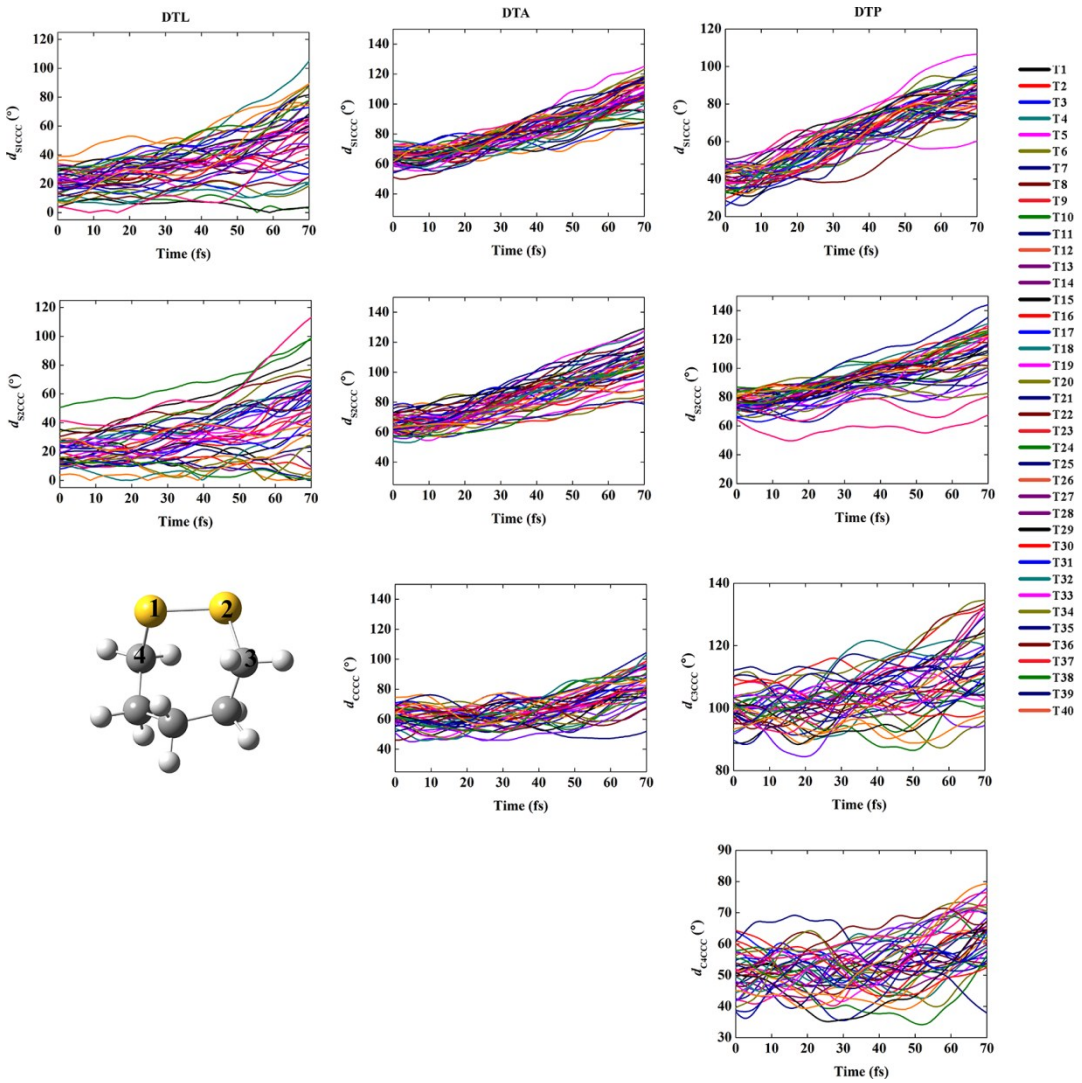

Figure S6. Time evolution of other geometrical parameters associated with the bridge linkage in the cyclic molecules. The atom numbering scheme is given in the structure of DTP, and the different colors indicate the different trajectories.

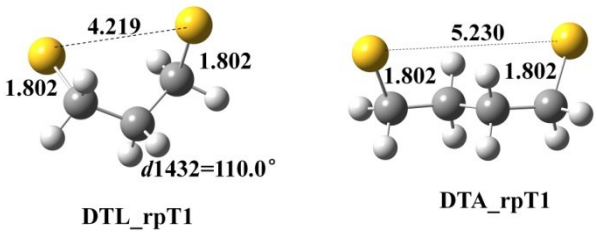

Figure S7. The optimized ring-opening T_1 minimum for DTL (DTL_rpT1) and DTA (DTA_rpT1), respectively.

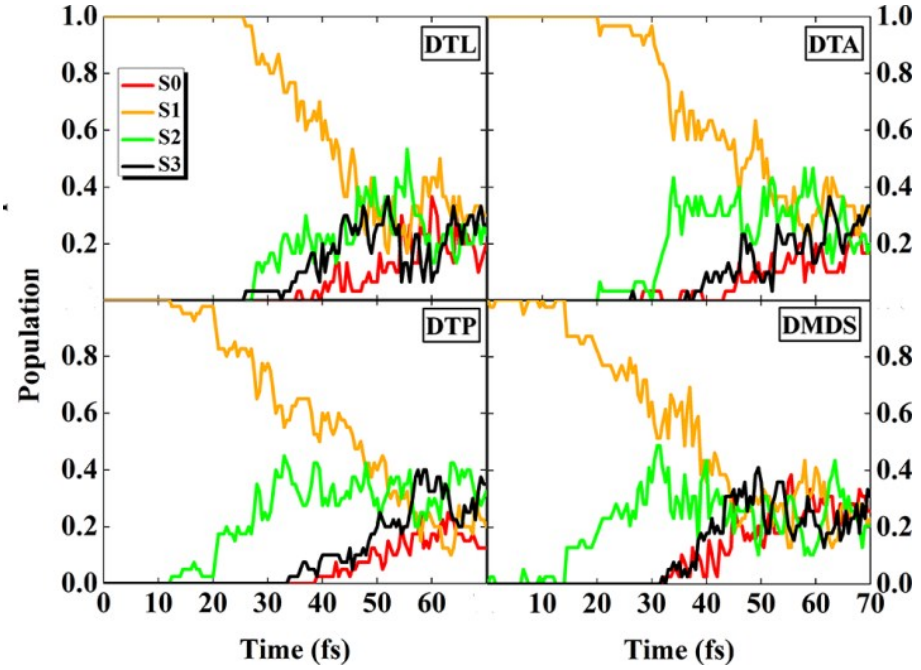

Figure S8. Populations for the singlet-only dynamics. The singlet-only dynamics considers the first four singlet states and uses the same initial conditions as the singlet-triplet dynamics.

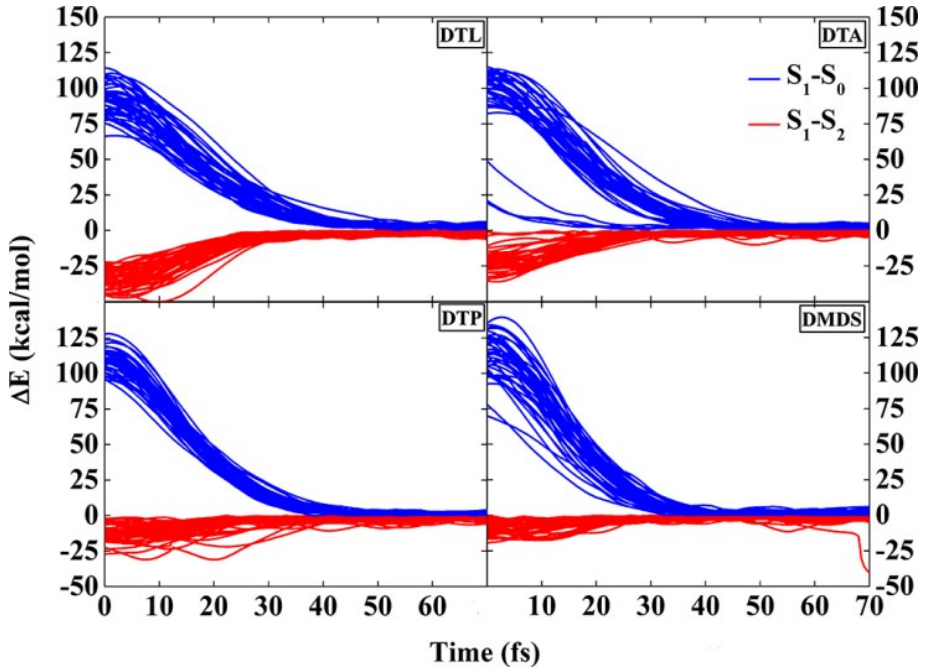

Figure S9. Time evolution of the energy gaps (ΔE) between S_1 and S_2, and S_1 and S_0.

S1. Coordiantes and absolute energies (hartree) of the optimized structures.

DTL_S_0: -912.748320358012

S	-0.868423553	0.451249732	0.593557431
S	1.068710576	-0.077742181	1.129482022
C	1.666358186	0.418611282	-0.513273625

C	0.696526580	-0.114037138	-1.590275940
C	-0.684350380	-0.438447928	-0.980045155
H	0.595154762	0.638805182	-2.377164168
H	1.101377992	-1.020709991	-2.048817741
H	-0.771268503	-1.509148361	-0.784063276
H	-1.504070297	-0.134808649	-1.637871929
H	1.712746499	1.508927772	-0.549159399
H	2.677307438	0.020264805	-0.639892154

DTL_T_1: -912.680486682783

S	-0.948960795	-0.677177843	0.742716735
S	1.495972331	0.242021713	1.169518154
C	1.614531671	0.575140351	-0.606908682
C	0.750092262	-0.378441060	-1.424055051
C	-0.716020256	-0.299967075	-1.013949502
H	0.840774269	-0.125185632	-2.488608843
H	1.112296240	-1.403851724	-1.293112563
H	-1.318037733	-1.002444408	-1.598544154
H	-1.105513625	0.708726785	-1.200596600
H	1.299843154	1.611829159	-0.781566969
H	2.665091783	0.492314259	-0.902416462

DTL_S_1: -912.676377368414

S	-1.098025038	-0.740094976	0.692842980
S	1.675059108	0.261284865	1.169363190
C	1.631800489	0.574821509	-0.608517473
C	0.743171698	-0.399467329	-1.377932833
C	-0.735132056	-0.280115687	-1.015453501
H	0.852478734	-0.191714615	-2.450265802
H	1.084253897	-1.425543393	-1.206294649
H	-1.330144839	-0.924979561	-1.670600945
H	-1.074548287	0.750674816	-1.175447232
H	1.282833472	1.602183055	-0.770040680
H	2.658322122	0.515915839	-0.985176991

DTL_S_1S_0a: -912.6628452/-912.66315775

S	-1.361192801	-0.760034660	0.597382688
S	2.028630928	0.313801760	1.154823234
C	1.635937897	0.598900381	-0.582520118
C	0.733441597	-0.401110507	-1.296994833
C	-0.782266442	-0.350238598	-1.045923247
H	0.851492184	-0.234209122	-2.376409769
H	1.091177195	-1.421513946	-1.113394407
H	-1.302844495	-0.883268183	-1.834899290
H	-1.106359199	0.713445312	-1.091701453
H	1.276080836	1.620387252	-0.745234284
H	2.625971685	0.546804860	-1.062653409

DTL_S_1S_0: -912.66534798/ -912.66630974

S	-1.142940761	1.860096467	-0.438192168
S	1.427716546	0.059519367	1.383209966
C	1.734366189	0.435187967	-0.353952846
C	0.625528149	-0.202830283	-1.215837186
C	-0.809132030	0.125490110	-0.795024231
H	0.795437140	0.147163222	-2.239596484
H	0.734668636	-1.293969902	-1.234908728
H	-1.111825323	-0.493025518	0.059098593
H	-1.500723414	-0.136045329	-1.610794972
H	1.687134843	1.517202077	-0.536838505
H	2.688980323	0.014725036	-0.683198534

DTL_S_1T_2: -912.664715928846/-912.664758900077

S	-1.290640100	-0.854872500	0.601926600
S	1.913790900	0.301683000	1.152342300
C	1.639916800	0.592179700	-0.605977600
C	0.738163000	-0.410979000	-1.325230600
C	-0.752861300	-0.272372900	-1.017609700
H	0.867145300	-0.254272700	-2.404820000
H	1.068042600	-1.429884500	-1.101907300
H	-1.327010400	-0.871095700	-1.737666000
H	-1.081415500	0.764591800	-1.154269300
H	1.272780700	1.615187500	-0.749649200
H	2.642157400	0.562799900	-1.054663200

DTL_T_1S_0: -912.666911229137/-912.666880124413

S	-1.321231070	-0.588038620	0.616982040
S	2.077328950	0.159548160	1.117069360
C	1.607266480	0.599634530	-0.569773660
C	0.760473710	-0.428635870	-1.324344790
C	-0.737266310	-0.341899590	-1.056259970
H	0.905376910	-0.265073510	-2.401154030
H	1.125884700	-1.437084990	-1.105074800
H	-1.316166650	-0.953787230	-1.755109100
H	-1.090719460	0.692228490	-1.238717580
H	1.116548910	1.580208100	-0.585056770
H	2.562573060	0.725864900	-1.096084710

DTA_S_0: -951.92072214

S	-0.990639832	0.300862724	1.007526141
S	0.990651421	-0.300862460	1.007515132
C	1.489034832	0.473442712	-0.557539312
C	-0.756628963	0.118279810	-1.759939821
C	0.756609712	-0.118279892	-1.759948226
C	-1.489040663	-0.473442657	-0.557522665

H	-1.179328358	-0.321945872	-2.671683620
H	-0.958170428	1.195166128	-1.800852149
H	1.179298949	0.321945676	-2.671696785
H	0.958150727	-1.195166215	-1.800862663
H	-1.322248682	-1.552779748	-0.487516139
H	-2.567190563	-0.299013391	-0.645160344
H	1.322243641	1.552779810	-0.487531036
H	2.567183748	0.299013409	-0.645188974

DTA_T_1: -951.847887118505

S	-1.218506451	-0.535963123	1.079537462
S	1.218518922	0.535963309	1.079523781
C	1.638381580	0.601520385	-0.680134045
C	-0.735911802	0.216386417	-1.600824125
C	0.735894319	-0.216386478	-1.600832337
C	-1.638388791	-0.601520340	-0.680115668
H	-1.143116536	0.112121191	-2.613509728
H	-0.813878122	1.278646476	-1.340914860
H	1.143087711	-0.112121342	-2.613522511
H	0.813863553	-1.278646506	-1.340923822
H	-1.621233057	-1.653758545	-0.986191306
H	-2.673159266	-0.254794122	-0.773126915
H	1.621222457	1.653758554	-0.986209614
H	2.673151024	0.254794157	-0.773156771

DTA_S_1: -951.837359764943

S	-1.468057595	0.546923053	0.978612153
S	1.475526897	-1.019420062	0.885956169
C	1.579252926	0.155132930	-0.478847659
C	-0.737662050	0.226344808	-1.665283118
C	0.736654976	-0.174325632	-1.712523489
C	-1.585468255	-0.413092086	-0.546223609
H	-1.190415951	-0.067974976	-2.619143637
H	-0.826010778	1.318368120	-1.613838763
H	1.182321538	0.344319413	-2.571310462
H	0.818142604	-1.247075748	-1.919467826
H	-1.244819750	-1.436402925	-0.364409253
H	-2.631786141	-0.437407887	-0.860139472
H	1.352641160	1.158190275	-0.099004968
H	2.640692119	0.168997068	-0.758965673

DTA_S_1S_2: -951.82367608/-951.82345251

S	-1.455036799	0.492168683	1.013165652
S	1.455653086	-0.485199674	1.011107219
C	1.587031239	0.414070909	-0.560943973
C	-0.755408856	0.147352043	-1.717321351
C	0.754502037	-0.146568203	-1.720629793

C	-1.586473313	-0.412196721	-0.556680154
H	-1.166189462	-0.276339420	-2.646850144
H	-0.919974874	1.232257859	-1.782932317
H	1.164814271	0.278967647	-2.648539457
H	0.918164609	-1.228740790	-1.786378602
H	-1.332135168	-1.458992345	-0.365217650
H	-2.641980910	-0.398325014	-0.838413744
H	1.339239178	1.456863675	-0.363859454
H	2.644287450	0.396423036	-0.845156697

DTA_S_1S_0: -951.824368849498/ -951.824588777474

S	-1.540201099	0.649831590	0.897629526
S	1.584377707	-1.082733899	0.853083098
C	1.576455861	0.144515462	-0.467895079
C	-0.741100257	0.233081397	-1.641536333
C	0.732178074	-0.179216147	-1.701360342
C	-1.597459086	-0.437826306	-0.530707707
H	-1.199504422	-0.063535789	-2.589746058
H	-0.828548236	1.324223566	-1.593790315
H	1.171940892	0.346587548	-2.561723796
H	0.814091728	-1.249632063	-1.914145536
H	-1.228669821	-1.454454654	-0.363205417
H	-2.627671431	-0.441825427	-0.887393999
H	1.350552750	1.148315509	-0.083234411
H	2.634569029	0.185245541	-0.760563570

DTA_S_1T_2: -951.826639015346/-951.826652674555

S	-1.576848000	0.672902100	0.928125100
S	1.464859200	-0.609767400	0.948929600
C	1.519953100	0.451549300	-0.511059700
C	-0.766437500	0.133173300	-1.721050700
C	0.736274700	-0.148285100	-1.693031700
C	-1.585745500	-0.385626400	-0.533890500
H	-1.165713100	-0.329664000	-2.632903000
H	-0.934584600	1.211468400	-1.822264300
H	1.166987000	0.270601700	-2.610093800
H	0.914116800	-1.229575500	-1.739447400
H	-1.260473700	-1.389963900	-0.238629400
H	-2.637879000	-0.475527900	-0.828495100
H	1.112116600	1.435332500	-0.257482300
H	2.567533200	0.574414200	-0.800003600

DTA_T_1S_0: -951.828516922769/-951.828479491714

S	-1.479251310	-1.085532210	0.901102840
S	1.475327240	1.088663600	0.900189800
C	1.751267620	0.682410640	-0.837222460
C	-0.712884070	0.285510290	-1.403169080

C	0.712920860	-0.285249910	-1.404395390
C	-1.751409630	-0.683300730	-0.837954840
H	-1.013442790	0.554808610	-2.422797420
H	-0.748180900	1.206465760	-0.811776570
H	1.012849810	-0.551206190	-2.425134660
H	0.748924530	-1.207863780	-0.815643000
H	-1.728969600	-1.631113010	-1.391845910
H	-2.761981690	-0.276004320	-0.946974350
H	1.733115490	1.629182160	-1.393116070
H	2.761639700	0.273229620	-0.941662810

DTP_S_0: -991.078704203391

S	-4.614827266	0.185041706	-3.385185530
S	-5.347271277	-1.583417150	-2.615666989
C	-4.556325963	-1.675297658	-0.985976018
C	-5.592141677	1.369761052	-2.409871770
C	-4.880484602	-0.539621641	-0.011859602
C	-4.926130811	1.838818574	-1.112679878
C	-4.157341651	0.786326120	-0.307027585
H	-3.472967189	-1.764096880	-1.113269502
H	-5.966213251	-0.392886495	0.039986674
H	-6.553579871	0.889051399	-2.211084224
H	-5.712131888	2.276835999	-0.483327856
H	-4.919919606	-2.628427013	-0.581328005
H	-5.786854433	2.230712813	-3.059223498
H	-4.570270517	-0.888130042	0.981311970
H	-4.228336740	2.652986503	-1.341855683
H	-3.881419176	1.257297699	0.643935685
H	-3.213916219	0.566197828	-0.817739743

DTP_T_1: -990.996194743622

S	-4.841110531	0.712141976	-3.684432210
S	-4.438124192	-1.819651383	-2.565720826
C	-4.483705345	-1.825238496	-0.753543684
C	-5.728940922	1.518133636	-2.327157226
C	-4.975690149	-0.518914312	-0.130233487
C	-4.876174214	1.865854638	-1.104003622
C	-4.101135818	0.690508409	-0.507848815
H	-3.464644529	-2.046026270	-0.414025072
H	-6.016547220	-0.360998530	-0.430293521
H	-6.567006121	0.873538744	-2.048263824
H	-5.548998298	2.289672553	-0.346344623
H	-5.114326790	-2.667130959	-0.444861515
H	-6.166289969	2.435543886	-2.736729396
H	-4.993154475	-0.652253364	0.958114305

H	-4.167876533	2.656988529	-1.375586385
H	-3.555264281	1.046638753	0.372819656
H	-3.341142749	0.382345002	-1.232751310

DTP_S_1S_0: -990.993740315876/ -990.994238463052

S	-4.906702855	1.254100577	-3.800579163
S	-4.190467946	-2.367791426	-2.232725424
C	-4.401306629	-1.957959661	-0.482691423
C	-5.753223997	1.770771075	-2.293178766
C	-5.059407849	-0.579866538	-0.330949270
C	-4.852374551	1.872702439	-1.061570810
C	-4.127374736	0.568067338	-0.729787265
H	-3.413657978	-1.963358289	-0.009169648
H	-5.973836402	-0.567509270	-0.932879294
H	-6.606069086	1.108289098	-2.120487841
H	-5.468787750	2.191147406	-0.209510112
H	-5.011469915	-2.728480982	0.005375442
H	-6.182702223	2.754576824	-2.527563000
H	-5.375184540	-0.453362135	0.710733187
H	-4.110634241	2.661339789	-1.232601299
H	-3.410426863	0.744195276	0.081708797
H	-3.536504570	0.274291292	-1.604985682

DMDS_S_0: -874.75523132

S	-1.182727078	-0.249196421	1.415483272
S	0.807352224	-0.759615059	1.571891707
C	1.629554626	0.823017806	1.247063282
C	-1.471180949	-0.396814418	-0.368089361
H	-1.252847463	-1.407466618	-0.714560918
H	-2.530964134	-0.181899899	-0.531829636
H	-0.875980206	0.324095771	-0.931135409
H	2.703169787	0.645326830	1.356348702
H	1.316234791	1.578718323	1.968104148
H	1.433739403	1.175442687	0.232911214

DMDS_T_1: -874.67707763

S	-1.231098873	0.380734894	0.437781184
S	1.345332103	-0.073310564	0.615425140
C	1.648954893	1.327007478	1.709525445
C	-1.533618155	-1.016520134	-0.660527033
H	-0.604447477	-1.551566843	-0.870966811
H	-2.242632991	-1.702809837	-0.192918720
H	-1.959413193	-0.657866105	-1.599923483
H	2.076330108	0.971304288	2.649326011
H	0.719920194	1.862453623	1.919683854
H	2.357024390	2.012182200	1.238781414

DMDS_S_1S_0: -874.66436696/-874.66530069

S	-1.999671932	-0.180196898	1.286051043
S	1.678548061	-0.886075994	1.774539336
C	1.834488973	0.815772341	1.217219657
C	-1.770374230	-0.281952102	-0.488460984
H	-1.427639149	-1.286478053	-0.747369293
H	-2.633361750	0.015945103	-1.076908781
H	-0.908813297	0.352903476	-0.724551156
H	2.889456670	0.937468972	0.951373008
H	1.592786321	1.548979740	1.989351697
H	1.247829368	1.014799633	0.317701384