Supplementary Materials

CASSCF and CASMP2 Study on the Photoisomerization Mechanisms of [Tris(trialkylsilyl)silyl]cyclotetrasilene and Related Cyclobutene Molecules

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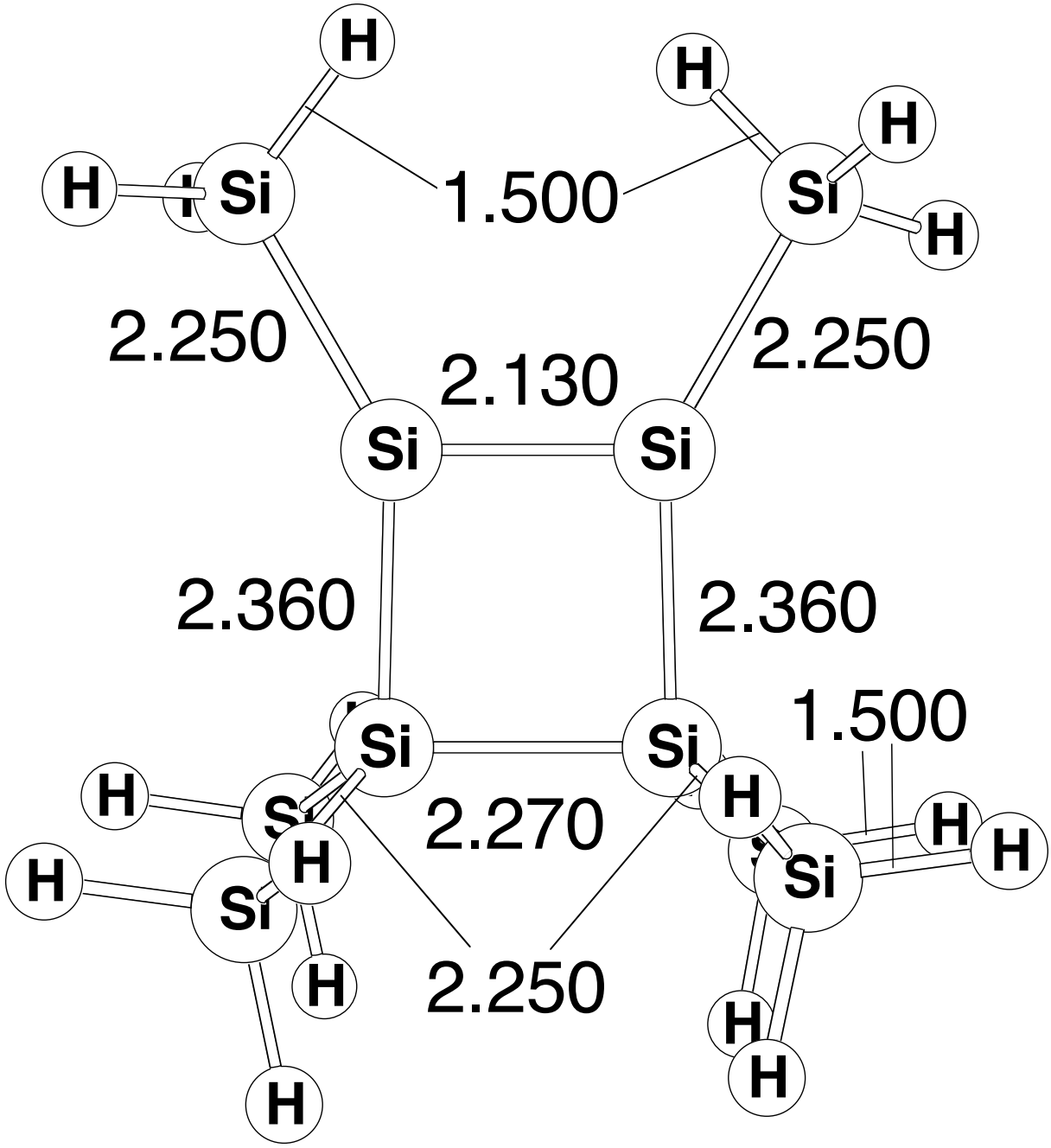
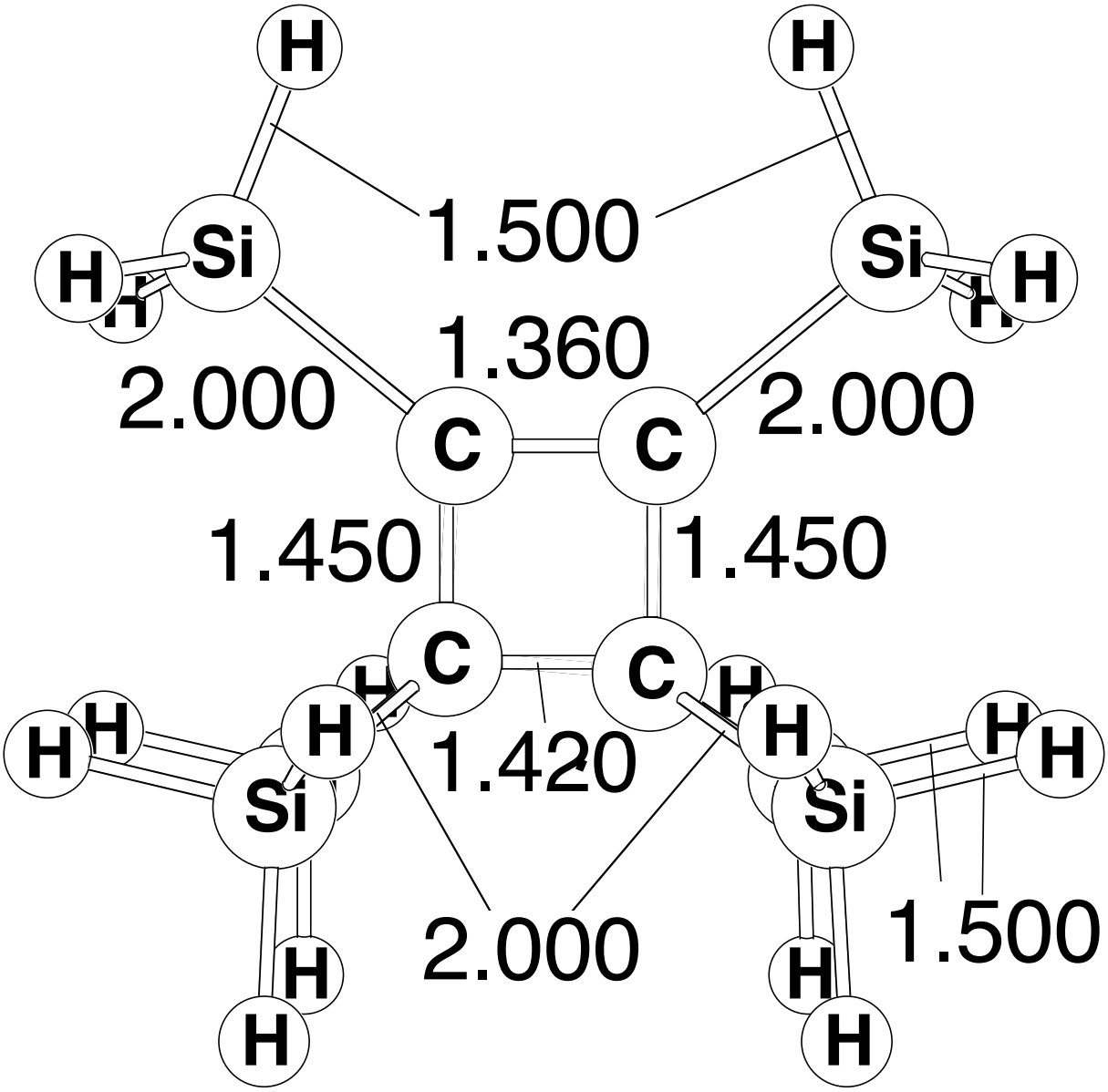
The fixed geometrical parameters (Å) are shown below:



(Also see Figure 1 (a))



(Also see Figure 1 (b))

(All were calculated at the CAS(6,6)/6-311G(d) (geometry) and MP2-CAS-(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) (energy) levels of theory)

(1) Si-Rea-S_0

Atomic Number	Coordinates (Angstroms) X	Y	Z
14	0.040703	-0.009189	1.159277
14	0.042236	-0.028796	3.542755
14	2.391057	0.032518	1.258478
14	2.392456	0.073266	3.437477
14	4.315495	0.452953	4.717402
1	4.029648	1.339739	5.859785
1	4.883601	-0.818837	5.204275
1	5.294747	1.099219	3.819710
14	4.309050	0.431148	-0.018941
1	5.450723	0.241304	0.900072
1	4.430990	-0.503970	-1.152101
1	4.314645	1.818738	-0.519191
14	-1.216884	1.707782	4.498749
1	-1.022834	1.742569	5.962654
1	-2.646383	1.452525	4.214459
1	-0.848189	3.016559	3.923979
14	-0.991622	1.895209	0.253724
1	-0.811192	1.916612	-1.213033
1	-2.439956	1.861851	0.553859
1	-0.412908	3.124425	0.831111
14	-0.886675	-1.936798	0.196918
1	-0.253586	-3.142691	0.767226
1	-0.677993	-1.923753	-1.266227
1	-2.339377	-1.985566	0.471750
14	-0.632806	-2.080969	4.457013
1	-0.435911	-2.054755	5.922528
1	0.187881	-3.165327	3.882262
1	-2.058187	-2.350811	4.170170

MP2-CAS-(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -2902.740922

(2) Si-FC-S_1

MP2-CAS-(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -2902.632916

(3) Si-FC-T_1

MP2-CAS-(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -2902.591714

(4) Si-CI

Atomic Number	Coordinates (Angstroms) X	Y	Z
24	0.575231	-0.033525	0.002860
6	-0.406978	-0.082807	-1.833763
6	0.519844	1.974396	-0.004758
6	-0.423785	-0.077702	1.831560
6	0.702708	-2.037471	0.000414
6	-3.779831	-0.051266	-0.002867
6	2.507590	0.055580	0.017715
8	-0.891018	-0.107733	-2.863346
8	0.567144	3.117259	-0.013103
8	-0.922620	-0.101344	2.854265
8	0.848831	-3.172060	-0.001342
8	-4.914314	-0.072711	-0.027971
16	4.103643	0.125021	0.021513

Derivative Coupling

-1	-0.0067980577	0.0001693235	-0.0000706855
-2	0.0017620749	0.0263058949	0.0006378557
-3	-0.0038688297	-0.0000692355	-0.0061869520
-4	0.0133004496	-0.0277476744	0.0016260719
-5	-0.0058369392	0.0022356192	0.0031227138
-6	0.0001835898	0.0001770716	0.0001429826
-7	-0.0002201559	-0.0000767213	-0.0005161607
-8	0.0006796116	-0.0007332530	0.0006086703
-9	-0.0022762436	0.0028709295	0.0018600919
-10	-0.0001804930	0.0002659982	-0.0000131691
-11	0.0001247713	0.0000488652	0.0000383438
-12	0.0002091603	0.0008580808	0.0003746944
-13	-0.0007040608	-0.0007327715	-0.0012001565
-14	-0.0002235903	0.0000923130	-0.0001637765
-15	0.0003730551	0.0005820590	0.0005129830

-16	-0.0000431435	-0.0000971645	0.0000003453
-17	0.0004849931	-0.0001047223	-0.0002767678
-18	-0.0000842805	0.0000825024	0.0000374686
-19	-0.0001302853	0.0000744285	-0.0000131397
-20	0.0000337809	0.0000383834	0.0000034798
-21	-0.0005393711	0.0005123585	-0.0002671638
-22	0.0001632219	-0.0003075093	0.0000102425
-23	0.0000922614	-0.0001146499	-0.0000643368
-24	0.0000915794	-0.0001127792	-0.0000463791
-25	0.0033822997	-0.0036687246	-0.0002417575
-26	0.0004306072	-0.0003751349	0.0009209972
-27	0.0000041413	-0.0010851935	-0.0005685520
-28	-0.0004101471	0.0009117063	-0.0002679434

Gradient Difference

-1	-0.0041401494	-0.0028176748	-0.0075852709
-2	-0.0151503436	0.0284502492	-0.0184223107
-3	-0.0072988773	0.0099771420	0.0376203450
-4	0.0143491608	-0.0450793346	-0.0065231825
-5	0.0047701310	0.0142292578	-0.0041711252
-6	-0.0002086777	0.0002840413	-0.0016854443
-7	-0.0006879763	-0.0000375278	-0.0008332803
-8	0.0013388839	-0.0036565787	0.0028818509
-9	-0.0002007231	0.0045603659	-0.0041483986
-10	0.0008118827	0.0004775736	-0.0003099995
-11	0.0010710794	0.0010226102	0.0013589492
-12	-0.0006398014	0.0002531751	0.0007461371
-13	0.0004253153	0.0024970470	0.0003013638
-14	0.0001450179	0.0000169782	0.0011079067
-15	-0.0001029097	0.0000088602	0.0002757415
-16	-0.0002058244	0.0005914680	0.0002616620
-17	0.0006670358	0.0000112250	-0.0002604958
-18	-0.0001242061	0.0003447618	-0.0002341681
-19	-0.0007579515	-0.0002732541	0.0001646605
-20	-0.0001354992	0.0004249105	-0.0000954627
-21	-0.0016179473	0.0006859027	-0.0027679393
-22	0.0009957608	-0.0004843238	0.0003796812
-23	0.0001943162	-0.0011577096	0.0007423303
-24	-0.0004314750	-0.0004036704	0.0001912390
-25	0.0046450283	-0.0077277524	0.0011634081
-26	0.0007544762	-0.0007157023	0.0023558613

-27	0.0002759913	-0.0010518101	-0.0024137099
-28	0.0012582825	-0.0004302298	-0.0001003489

MP2-CAS-(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -2902.673647

(5) Si-Pro-S_0

Atomic Number	Coordinates (Angstroms) X	Y	Z
14	0.000000	0.000000	0.000000
14	0.000000	0.000000	2.370453
14	1.677414	0.000000	-1.649281
1	2.086396	-1.391718	-1.922650
1	2.846980	0.776814	-1.196492
1	1.163058	0.598799	-2.896422
14	1.720667	-0.003299	3.970676
1	1.154183	-0.083496	5.331857
1	2.512656	1.236291	3.853245
1	2.598626	-1.170191	3.755706
14	-0.945876	1.785533	1.150430
14	-0.952872	-1.767590	1.182441
14	0.460434	3.684563	1.155101
1	1.875595	3.268074	1.229658
1	0.159665	4.554156	2.312605
1	0.261467	4.478800	-0.075809
14	-3.239620	2.348554	1.071728
1	-4.050344	1.205451	0.612189
1	-3.426685	3.471671	0.127378
1	-3.719131	2.775481	2.402608
14	0.442891	-3.673949	1.168013
1	0.312269	-4.421967	2.436298
1	1.853926	-3.267521	1.001600
1	0.075224	-4.582805	0.061241
14	-3.248307	-2.328264	1.257038
1	-3.406122	-3.584032	2.023728
1	-3.782366	-2.541507	-0.104168
1	-4.033696	-1.272372	1.923313

MP2-CAS-(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -2902.706975

(6) Si-TS-S_0

	Atomic Number	Coordinates (Angstroms) X	Y	Z
	14	0.217248	-0.246158	1.107968
	14	0.340645	-0.592228	3.457707
	14	2.562423	0.192107	1.259313
	14	2.689664	-0.973767	3.226271
	14	3.902588	-0.567154	5.194738
	1	3.081543	-1.167880	6.269017
	1	5.262559	-1.132106	5.253461
	1	3.949062	0.894351	5.405336
	14	3.114280	2.424363	1.701660
	1	4.519242	2.517302	2.134608
	1	2.865705	3.287654	0.533204
	1	2.245494	2.887430	2.805934
	14	-0.434720	1.257029	4.732517
	1	0.056275	1.213512	6.124242
	1	-1.910344	1.136643	4.748440
	1	-0.091234	2.566105	4.143783
	14	-1.153603	1.478748	0.244278
	1	-0.943692	1.588907	-1.215284
	1	-2.579938	1.161706	0.477955
	1	-0.846640	2.778027	0.872476
	14	-0.256142	-2.242569	-0.077170
	1	0.760430	-3.276657	0.197908
	1	-0.257171	-1.951053	-1.527184
	1	-1.587274	-2.783198	0.279662
	14	-0.445484	-2.676209	4.146118
	1	0.271498	-3.093864	5.369156
	1	-0.054873	-3.590044	3.049420
	1	-1.902228	-2.756885	4.356376

-1	-0.16	-0.15	-0.14
-2	-0.01	-0.05	0.03
-3	-0.29	-0.45	-0.24
-4	-0.04	-0.07	-0.14
-5	0.01	-0.05	0.00
-6	-0.01	-0.12	-0.04

-7	-0.05	-0.18	-0.18
-8	-0.05	-0.06	-0.09
-9	0.07	0.01	-0.11
-10	-0.01	0.03	0.01
-11	-0.06	0.02	-0.08
-12	0.02	0.03	0.10
-13	-0.00	-0.01	-0.01
-14	-0.11	-0.11	-0.01
-15	-0.02	-0.08	-0.15
-16	-0.01	0.14	0.01
-17	-0.02	-0.03	0.01
-18	-0.11	-0.20	-0.04
-19	-0.04	-0.15	-0.11
-20	-0.20	0.05	-0.13
-21	-0.02	0.02	-0.01
-22	0.05	0.03	0.04
-23	-0.16	-0.12	-0.06
-24	-0.06	0.05	-0.05
-25	-0.03	-0.02	-0.00
-26	-0.06	-0.22	-0.08
-27	-0.14	-0.02	-0.09
-28	-0.06	-0.20	-0.06

MP2-CAS-(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -2902.687391

(7) C-Rea-S_0

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.000000	0.000000	0.000000
6	0.000000	0.000000	1.352717
6	-1.450668	-0.005030	-0.072824
6	-1.548802	0.000801	1.323720
14	-2.225683	1.519148	2.287377
1	-1.925179	1.332203	3.717124
1	-3.691301	1.637721	2.135389
1	-1.605286	2.780283	1.849643
14	-2.219695	-1.511810	2.301859
1	-1.589766	-2.773508	1.880348

1	-3.684246	-1.642211	2.147427
1	-1.924853	-1.307155	3.730368
14	-2.104403	-1.520983	-1.076292
1	-1.797086	-1.331455	-2.504412
1	-3.568993	-1.639882	-0.923946
1	-1.473291	-2.776683	-0.638712
14	-2.106255	1.500578	-1.091636
1	-1.485804	2.763343	-0.658698
1	-3.573250	1.614560	-0.961342
1	-1.779768	1.297847	-2.513826
14	1.311459	0.004284	2.692108
1	1.164445	1.199910	3.543869
1	2.649613	0.005309	2.078771
1	1.167819	-1.189047	3.547688
14	1.375121	-0.002452	-1.285460
1	1.269715	1.196216	-2.139357
1	1.255782	-1.193857	-2.147894
1	2.684919	-0.013151	-0.616023

MP2-CAS-(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -1897.453892

(8) C-FC-S_1

CAS-MP2(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -1897.267792

(9) C-FC-T_1

CAS-MP2(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -1897.259792

(10) C-CI

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z

6	-0.199486	-0.289407	-0.028153
6	-0.133393	-1.039680	1.240622
6	-1.570220	0.210388	0.072879
6	-1.982918	1.275677	1.042184
14	-1.216792	2.975716	0.833524
1	0.229856	2.884381	0.553080
1	-1.428440	3.786529	2.047735
1	-1.862950	3.660000	-0.305865

14	-3.303867	0.955681	2.333624
1	-2.687580	0.326006	3.518516
1	-4.350162	0.047110	1.830670
1	-3.929622	2.225525	2.752285
14	-0.649733	-2.845692	1.283197
1	0.525114	-3.723284	1.090416
1	-1.620875	-3.130531	0.211353
1	-1.253031	-3.171415	2.589987
14	-2.813857	-0.296779	-1.267495
1	-3.035530	0.841673	-2.184286
1	-4.111714	-0.694662	-0.699247
1	-2.248568	-1.421683	-2.037561
14	0.741219	-0.261693	2.724210
1	0.072702	0.952740	3.224662
1	2.112999	0.108759	2.316037
1	0.816480	-1.248314	3.821520
14	0.916679	-0.520189	-1.503644
1	0.422814	0.322548	-2.608532
1	0.955516	-1.930823	-1.939396
1	2.287164	-0.114957	-1.142680

Derivative Coupling

-1	-0.0295081406	-0.0042458587	0.0139884434
-2	0.0111502933	0.0041471510	0.0074324499
-3	0.0223927742	-0.0049054038	-0.0253083028
-4	-0.0081839660	0.0004683065	0.0142837148
-5	-0.0018460714	0.0013651489	-0.0021066136
-6	-0.0000191059	-0.0005177033	0.0001137429
-7	-0.0001665783	-0.0001960343	0.0000424737
-8	0.0000423310	0.0001679717	-0.0002610196
-9	0.0022879256	0.0000369792	0.0015569046
-10	-0.0000919552	-0.0001461173	0.0000014358
-11	-0.0000381336	0.0001758179	0.0001800979
-12	0.0000289916	0.0000859597	-0.0000544482
-13	0.0013892475	0.0015143537	0.0000047402
-14	0.0001012524	0.0000349630	-0.0000350743
-15	0.0000035814	0.0002146001	0.0001370077
-16	0.0000099133	0.0001530186	-0.0000610783
-17	0.0044850807	0.0064463690	-0.0056245278
-18	-0.0006226059	-0.0001553905	-0.0003398119
-19	0.0005795856	0.0000181545	0.0002644703

-20	-0.0001228119	0.0001179067	0.0001530122
-21	-0.0003866781	-0.0019499493	-0.0007837099
-22	0.0000344246	-0.0001272881	-0.0001186607
-23	-0.0001733911	0.0000511451	0.0001239183
-24	-0.0000218007	0.0000960220	-0.0000191922
-25	-0.0011422417	-0.0029446470	-0.0037787243
-26	-0.0000952363	0.0000424093	-0.0000447790
-27	0.0001265284	-0.0001548499	-0.0002002387
-28	-0.0002132129	0.0002069653	0.0004537699

Unscaled Gradient Difference

-1	-0.0103664136	0.0027594370	0.0045361046
-2	0.0347275170	-0.0193249379	0.0209286249
-3	-0.0349805841	0.0464639882	-0.0008588740
-4	0.0103523424	-0.0253097606	-0.0257592387
-5	0.0062170014	-0.0033485042	0.0045937110
-6	-0.0000694803	0.0002312258	-0.0002051487
-7	0.0000697821	0.0004560083	-0.0001747037
-8	-0.0003447373	-0.0002182185	0.0004701877
-9	-0.0061621367	0.0016613634	-0.0054546269
-10	0.0001523623	0.0002836707	-0.0003420029
-11	0.0002166405	-0.0003053690	-0.0000919174
-12	-0.0001289807	0.0000597254	0.0003176294
-13	0.0032082502	-0.0004746170	0.0016194209
-14	-0.0001805553	-0.0003301231	-0.0002995182
-15	-0.0003271152	0.0002920405	-0.0001240314
-16	-0.0001129874	0.0003229758	0.0002829332
-17	-0.0022716699	-0.0013064935	0.0049103738
-18	0.0001003506	-0.0005864151	-0.0005299912
-19	-0.0001138766	0.0001314410	0.0005168947
-20	-0.0005617836	0.0004129228	-0.0003464349
-21	-0.0007481750	-0.0011336855	-0.0010822808
-22	-0.0001479207	0.0001235042	-0.0001831629
-23	-0.0000707757	0.0000517847	0.0002904302
-24	-0.0001549750	0.0001478248	-0.0001572051
-25	0.0011547534	-0.0009943095	-0.0020330524
-26	0.0000788993	0.0001671802	-0.0005485055
-27	0.0000436365	-0.0004549186	-0.0002198364
-28	0.0004206314	0.0002222596	-0.0000557795

CAS-MP2(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -1897.387805

(11) C-Pro-S_0

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.000000	0.000000	0.000000
6	0.000000	0.000000	1.494110
6	1.336580	0.000000	0.746269
6	-0.724200	-1.121988	0.748281
14	-2.631477	-0.989987	0.709236
1	-3.040264	0.408539	0.467662
1	-3.205902	-1.437516	1.990570
1	-3.155275	-1.845209	-0.373429
14	-0.294247	-2.972787	0.876063
1	-1.470089	-3.609519	1.508880
1	0.857729	-3.257231	1.746774
1	-0.097660	-3.596857	-0.445263
14	-0.613324	1.134584	-1.367701
1	-1.588811	0.402295	-2.196155
1	0.536356	1.530253	-2.200594
1	-1.259440	2.353453	-0.844756
14	2.253772	1.677852	0.777289
1	1.286953	2.777100	0.974643
1	2.975447	1.898803	-0.488205
1	3.226568	1.678221	1.887183
14	2.662031	-1.363919	0.635853
1	3.847448	-0.720881	0.027854
1	2.287400	-2.477843	-0.251736
1	3.053943	-1.877565	1.960441
14	-0.608038	1.106193	2.887322
1	0.555442	1.671448	3.594100
1	-1.407400	0.294056	3.822107
1	-1.442606	2.219892	2.396935

CAS-MP2(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -1897.437639

(12) C-TS-S_0

Atomic Number	Coordinates (Angstroms) X	Y	Z

6	-0.19949	-0.28941	-0.02815
6	-0.13339	-1.03968	1.24062
6	-1.57022	0.21039	0.07288
6	-1.98292	1.27568	1.04218
14	-1.21679	2.97572	0.83352
1	0.22986	2.88438	0.55308
1	-1.42844	3.78653	2.04773
1	-1.86295	3.66	-0.30587
14	-3.30387	0.95568	2.33362
1	-2.68758	0.32601	3.51852
1	-4.35016	0.04711	1.83067
1	-3.92962	2.22553	2.75229
14	-0.64973	-2.84569	1.2832
1	0.52511	-3.72328	1.09042
1	-1.62088	-3.13053	0.21135
1	-1.25303	-3.17142	2.58999
14	-2.81386	-0.29678	-1.2675
1	-3.03553	0.84167	-2.18429
1	-4.11171	-0.69466	-0.69925
1	-2.24857	-1.42168	-2.03756
14	0.74122	-0.26169	2.72421
1	0.0727	0.95274	3.22466
1	2.113	0.10876	2.31604
1	0.81648	-1.24831	3.82152
14	0.91668	-0.52019	-1.50364
1	0.42281	0.32255	-2.60853
1	0.95552	-1.93082	-1.9394
1	2.28716	-0.11496	-1.14268

-1	-0.31	-0.12	0.13
-2	0.35	-0.08	0.13
-3	-0.03	0.34	-0.25
-4	-0.00	-0.12	-0.00
-5	0.01	-0.02	0.01
-6	0.01	0.00	-0.02
-7	-0.02	0.01	-0.01
-8	-0.04	-0.05	0.03
-9	-0.02	0.01	-0.01
-10	0.06	0.01	-0.05
-11	-0.04	-0.03	0.08

-12	-0.01	-0.01	0.04
-13	0.05	-0.01	0.00
-14	-0.15	-0.25	-0.05
-15	-0.06	0.21	0.03
-16	-0.02	0.14	0.01
-17	0.00	0.05	-0.04
-18	-0.28	-0.16	-0.24
-19	0.14	-0.04	0.21
-20	-0.01	-0.02	0.03
-21	0.01	0.00	0.02
-22	-0.02	0.03	-0.03
-23	0.01	0.04	0.06
-24	0.03	0.05	0.07
-25	-0.04	-0.03	0.00
-26	-0.00	0.01	0.04
-27	0.13	-0.01	-0.04
-28	-0.16	0.13	0.20

CAS-MP2(6,6)/6-311++G(3df,3pd)//CAS(6,6)/6-311G(d) = -1897.413472