Supporting Information

Does Tetrahydrofuran (THF) Behave like a Solvent or a Reactant in the Photolysis of Thionyl Chloride (Cl_2SO) in Cyclohexane? A Transient Infrared Difference Study.

*Meng-Chen Shih and Li-Kang Chu**

Department of Chemistry, National Tsing Hua University, 101, Section 2, Kuang-Fu Road, Hsinchu, Taiwan 30013

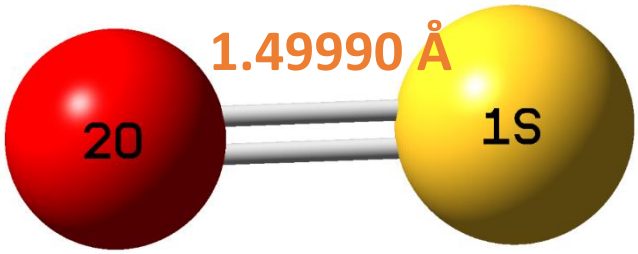
Corresponding Author

* To whom correspondence should be addressed. Phone: 886-3-5715131 ext. 33396. Fax: 886-3-5711082. E-mail: lkchu@mx.nthu.edu.tw.

Geometries of relevant species

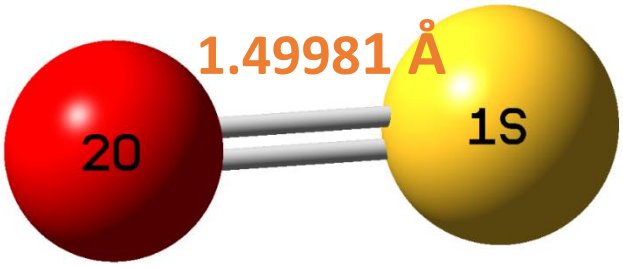
The optimized molecular structures of the relevant species at the electronically ground state were predicted with B3LYP method using basis sets aug-cc-pVTZ. The solvent effect was taken into consideration using c-PCM model. The isolated molecules included triplet SO, singlet SO, SO_2, SSO, ClSO, Cl_2S, SO_3, Cl_2SO, SSO_2, $(SO)_2$, $(ClSO)_2$, and THF. The complexes which contained THF included triplet SO-THF, singlet SO-THF, SO_2-THF, Cl_2S-THF, ClSO-THF, SSO_2-THF, and Cl_2SO-THF. The absolute energies and harmonic vibrational wavenumbers of the SO associated vibrations and C–O–C asymmetric stretch of the THF moiety in the complexes for the aforementioned molecules were listed in **Table 1**.

1. S=O (Triplet)



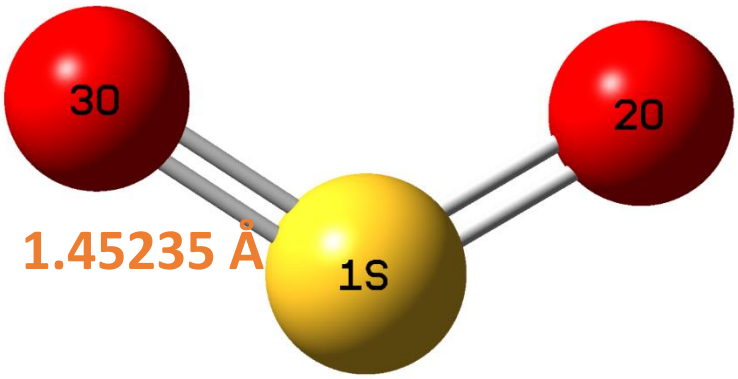
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	0.000000	0.000000	0.499966
2	8	0.000000	0.000000	-0.999932

2. S=O (Singlet)



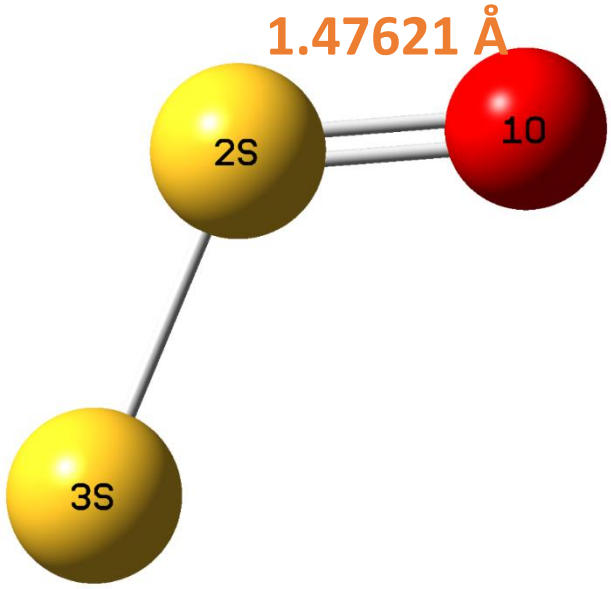
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	0.000000	0.000000	0.499936
2	8	0.000000	0.000000	-0.999872

3. O=S=O



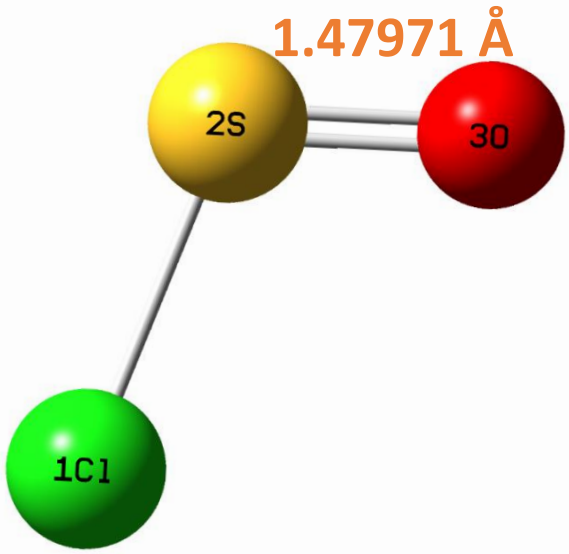
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	0.000000	0.000000	0.376141
2	8	0.000000	1.242334	-0.376141
3	8	0.000000	-1.242334	-0.376141

4. S-S=O



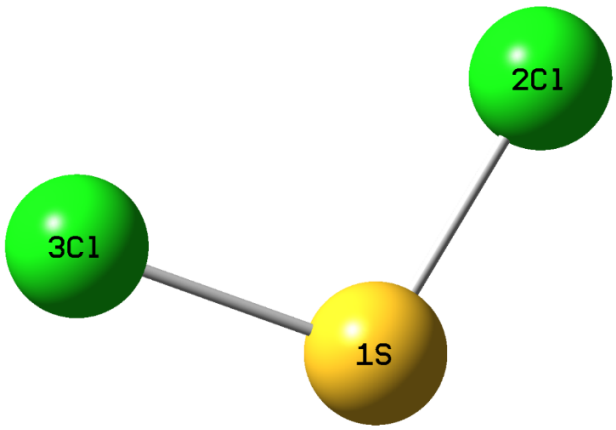
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	1.471811	0.795239	0.000000
2	16	0.000000	0.681306	0.000000
3	16	-0.735905	-1.078925	0.000000

5. ClSO



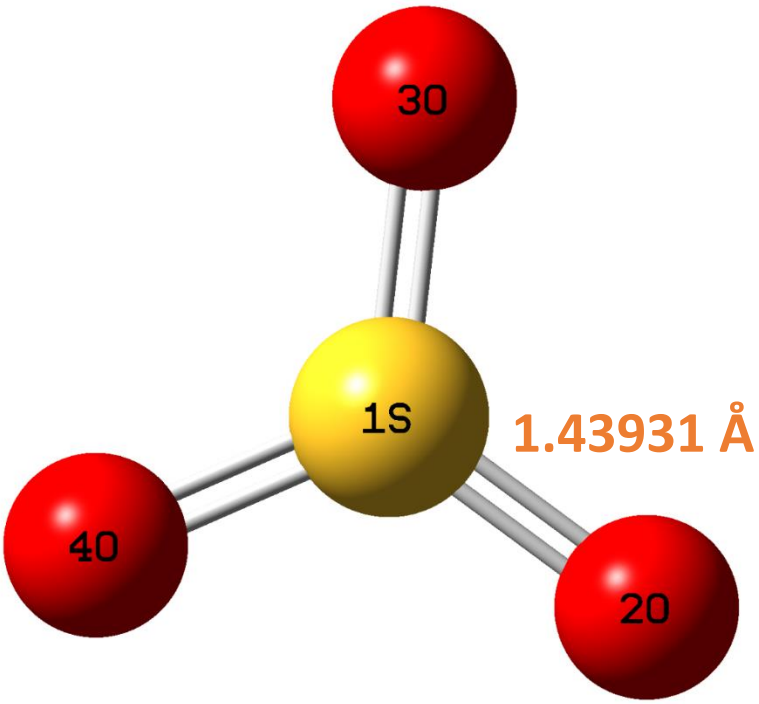
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	17	-0.696330	-1.161300	0.000000
2	16	0.000000	0.821016	0.000000
3	8	1.479701	0.825731	0.000000

6. Cl_2S



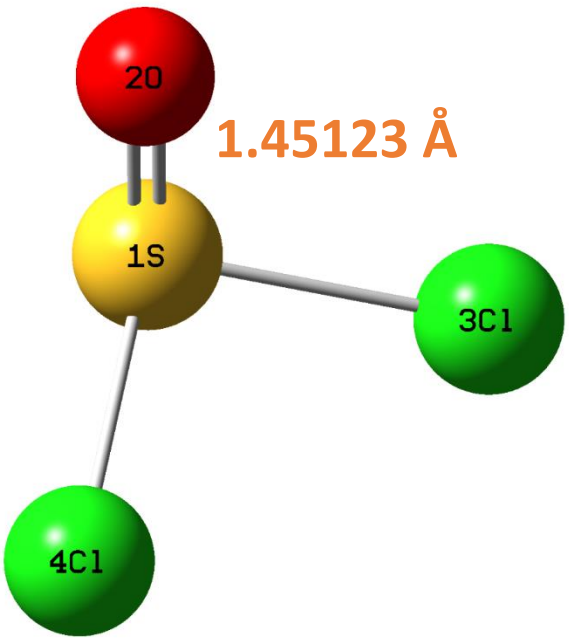
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	0.000000	0.000000	0.861861
2	17	0.000000	1.612962	-0.405582
3	17	0.000000	-1.612962	-0.405582

7. SO_3



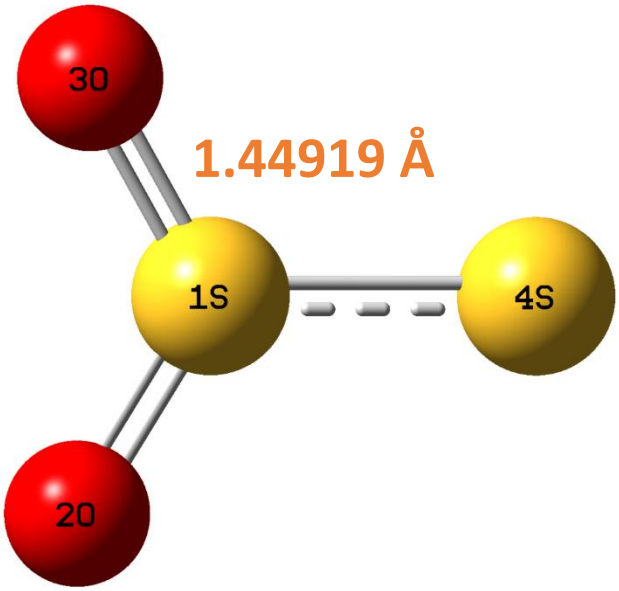
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	0.000000	0.000000	0.000033
2	8	0.000000	0.000000	1.439347
3	8	0.000000	1.246432	-0.719707
4	8	0.000000	-1.246432	-0.719707

8. Cl_2SO



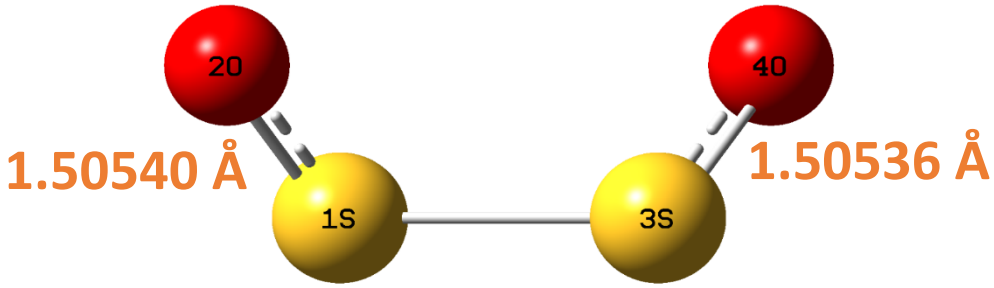
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	0.178096	0.728135	0.000000
2	8	-1.113103	1.390602	0.000000
3	17	0.178096	-0.669852	1.608189
4	17	0.178096	-0.669852	-1.608189

9. S–S=O_2



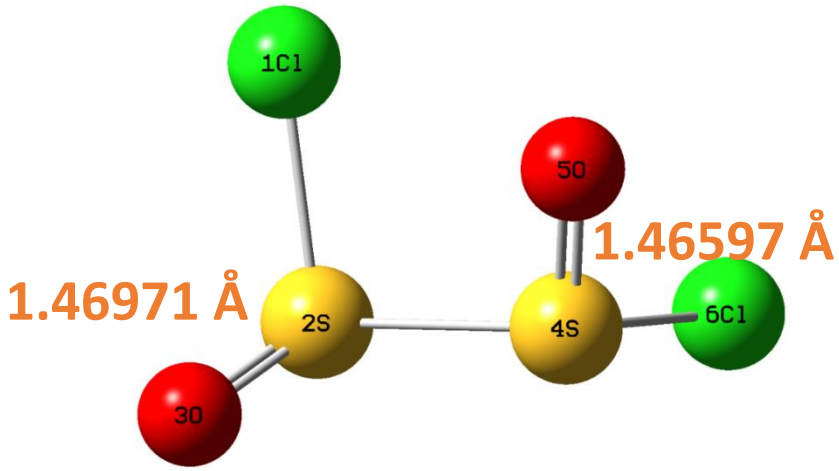
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	-0.385757	-0.000027	-0.000035
2	8	-1.124383	-1.246832	0.000025
3	8	-1.123846	1.247126	0.000025
4	16	1.509871	-0.000119	0.000010

10. O=S–S=O



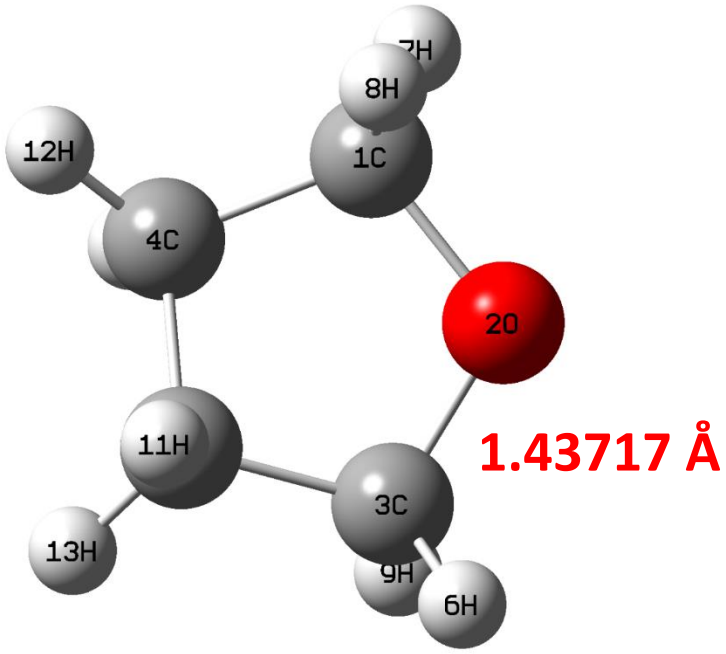
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	-1.055349	-0.349367	-0.363105
2	8	-1.791731	0.698717	0.427774
3	16	1.055394	-0.349387	0.363083
4	8	1.791642	0.698791	-0.427730

11. $(ClSO)_2$



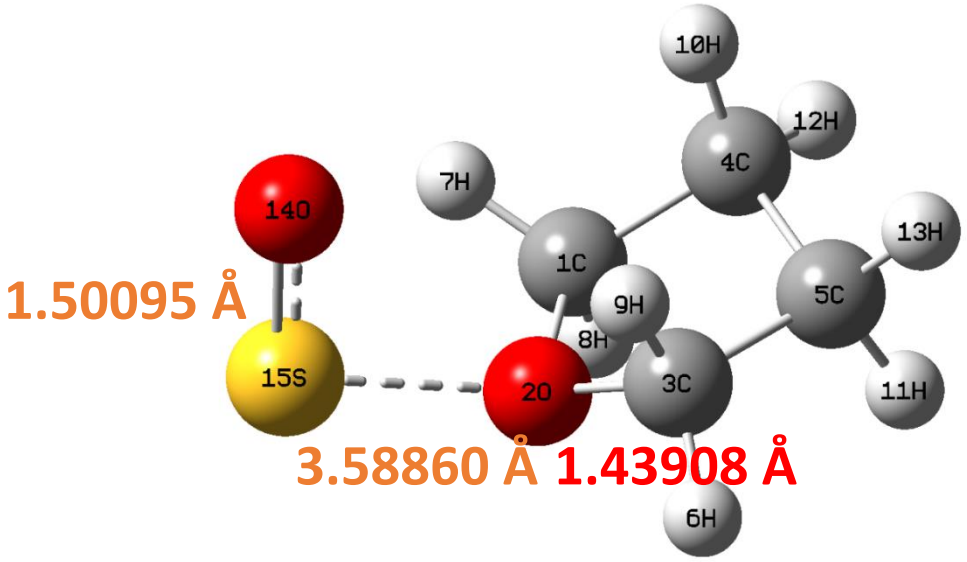
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	17	-1.673324	1.188385	-0.524351
2	16	-1.020079	-0.797821	-0.337952
3	8	-1.824586	-1.492647	0.676953
4	16	1.002913	-0.134344	0.874609
5	8	0.843702	1.258216	1.304145
6	17	2.151073	-0.200733	-0.913019

12. THF



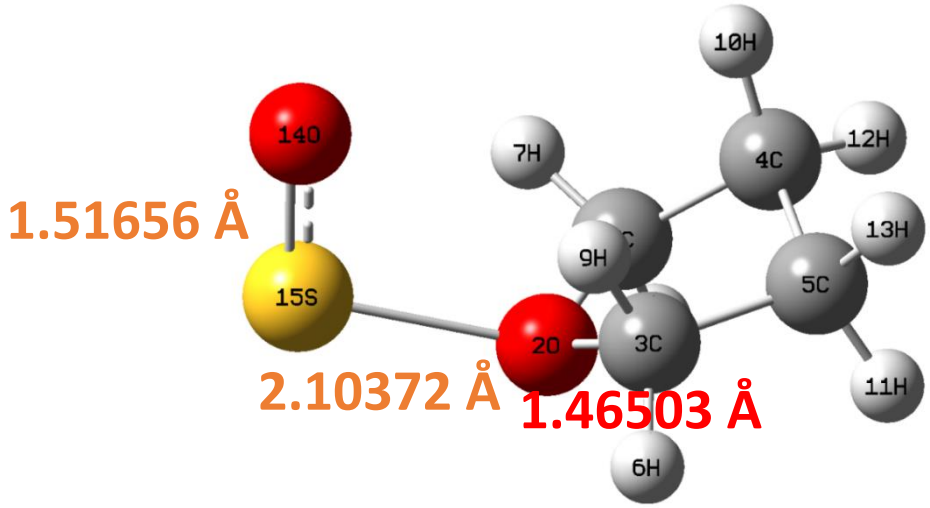
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	1.177138	0.427115
2	8	0.000000	0.000000	1.251623
3	6	0.000000	-1.177138	0.427115
4	6	0.301578	0.704456	-0.993954
5	6	-0.301578	-0.704456	-0.993954
6	1	-0.743406	-1.872923	0.817588
7	1	0.743406	1.872923	0.817588
8	1	-0.983939	1.653712	0.486393
9	1	0.983939	-1.653712	0.486393
10	1	1.379223	0.656252	-1.158862
11	1	-1.379223	-0.656252	-1.158862
12	1	-0.129233	1.358366	-1.750575
13	1	0.129233	-1.358366	-1.750575

13. S=O-THF (Triplet)



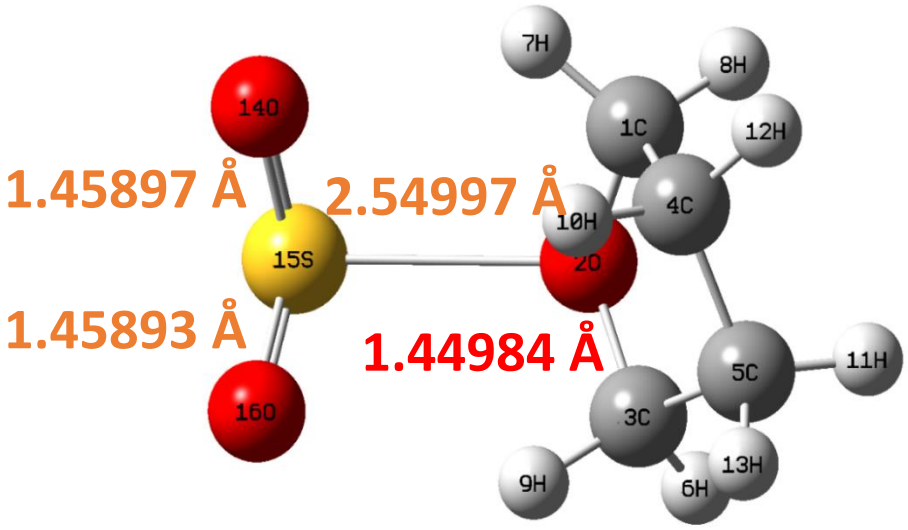
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.613214	1.273647	0.044228
2	8	0.712646	0.514373	-0.779443
3	6	1.034725	-0.885855	-0.698330
4	6	2.347970	0.260916	0.919621
5	6	2.384088	-0.973846	0.011682
6	1	1.052390	-1.294895	-1.709129
7	1	1.031458	1.997517	0.615922
8	1	2.309987	1.820942	-0.599143
9	1	0.251175	-1.396794	-0.130881
10	1	1.773973	0.050900	1.823617
11	1	3.200772	-0.892512	-0.707684
12	1	3.336681	0.606934	1.217036
13	1	2.505473	-1.907433	0.558741
14	8	-2.565270	-0.910277	0.627069
15	16	-2.807556	0.383337	-0.094543

14. S=O-THF (Singlet)



Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.860657	1.214030	-0.322640
2	8	0.116912	0.015054	-0.745091
3	6	0.761463	-1.183301	-0.202118
4	6	1.952678	0.709384	0.610790
5	6	2.171127	-0.734200	0.137977
6	1	0.691853	-1.949566	-0.968705
7	1	0.152629	1.893075	0.142953
8	1	1.255241	1.661265	-1.233550
9	1	0.206290	-1.491898	0.684326
10	1	1.604688	0.721306	1.643429
11	1	2.805702	-0.758821	-0.748520
12	1	2.852422	1.317761	0.545351
13	1	2.621702	-1.365777	0.901215
14	8	-2.052107	-0.114755	1.155087
15	16	-1.949033	0.045924	-0.349407

15. SO_2–THF



Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.181833	1.194117	-0.387664
2	8	0.537661	-0.020326	-0.843372
3	6	1.247754	-1.177582	-0.334886
4	6	2.136460	0.766431	0.719907
5	6	2.541777	-0.642240	0.270819
6	1	1.402304	-1.865001	-1.165220
7	1	0.406274	1.884150	-0.058982
8	1	1.712308	1.633584	-1.235688
9	1	0.619685	-1.664122	0.414700
10	1	1.614796	0.728044	1.677011
11	1	3.324962	-0.589538	-0.486824
12	1	2.982354	1.444281	0.819147
13	1	2.899743	-1.266734	1.087244
14	8	-1.992140	1.246338	0.349078
15	16	-1.942537	-0.081180	-0.254099
16	8	-1.861619	-1.207280	0.669936

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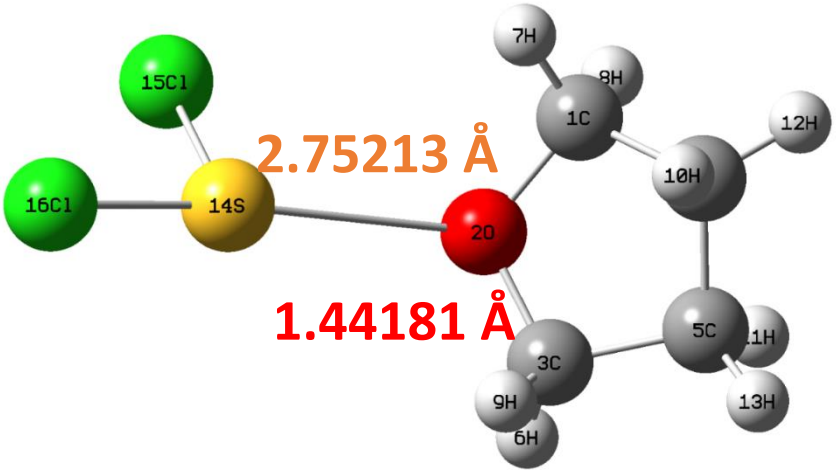
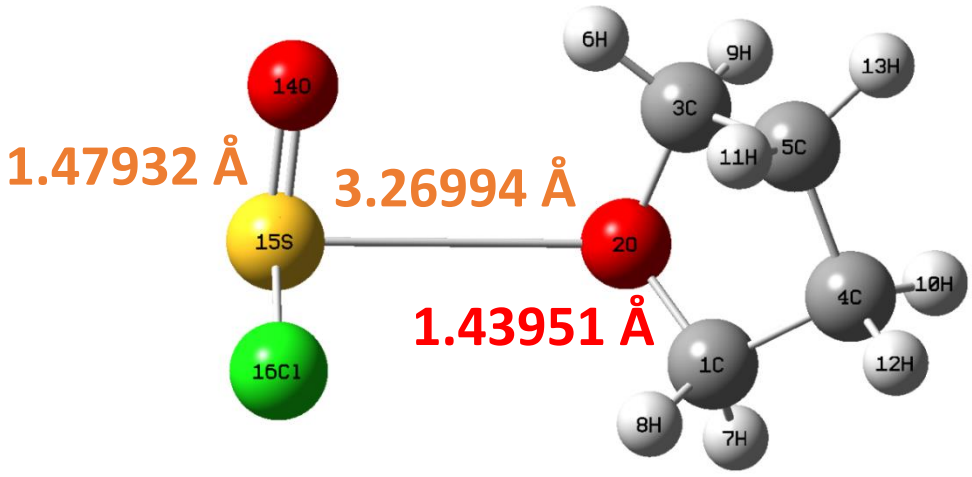
16. Cl_2S–THF



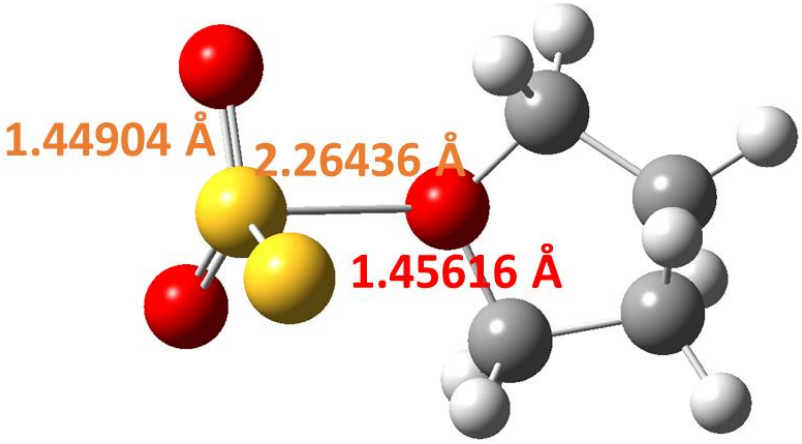
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.112255	0.835608	0.753613
2	8	1.423884	0.364168	-0.424110
3	6	2.169493	-0.708321	-1.034554
4	6	3.208731	-0.186215	1.039778
5	6	3.540470	-0.703159	-0.364775
6	1	2.207289	-0.528306	-2.108491
7	1	1.386225	0.931453	1.560362
8	1	2.529420	1.823458	0.539992
9	1	1.643671	-1.651900	-0.858319
10	1	2.823001	-0.995493	1.661729
11	1	4.211371	-0.011404	-0.876433
12	1	4.063834	0.255186	1.548831
13	1	4.004238	-1.688118	-0.363195
14	16	-1.216330	-0.319331	-0.054899
15	17	-1.680600	1.676186	-0.227347
16	17	-3.083197	-1.168327	0.274548

17. ClSO–THF



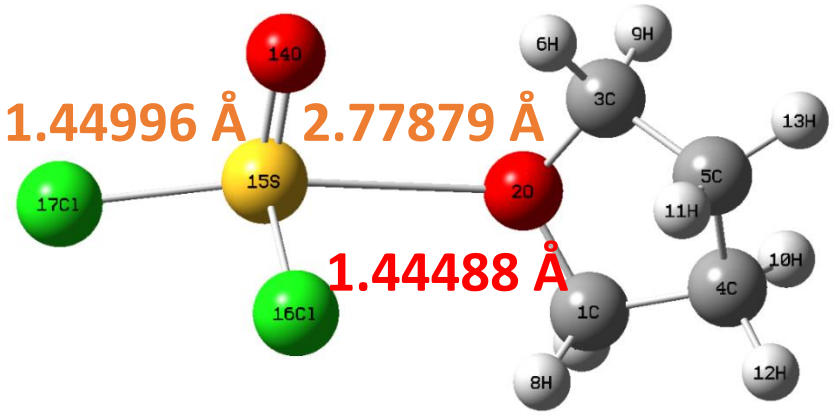
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.864085	-0.930106	-0.863006
2	8	1.249067	0.371347	-0.850680
3	6	1.830664	1.180295	0.187714
4	6	3.069957	-0.843799	0.070714
5	6	2.622071	0.223830	1.075335
6	1	1.025277	1.695149	0.711436
7	1	2.132028	-1.176526	-1.891061
8	1	1.137887	-1.667670	-0.507950
9	1	2.483767	1.930778	-0.269516
10	1	3.951707	-0.504430	-0.475356
11	1	1.972982	-0.214994	1.834860
12	1	3.305442	-1.800590	0.534002
13	1	3.452235	0.715079	1.580462
14	8	-1.772008	1.621776	0.460024
15	16	-2.001033	0.560452	-0.544726
16	17	-2.328349	-1.274725	0.441144

18. S–S=O_2–THF



Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	1.471873	-0.305080	0.093398
2	8	1.637234	-1.387862	-0.855204
3	8	1.673477	-0.566389	1.504347
4	16	1.525292	1.504519	-0.536954
5	6	-1.471419	0.162587	1.228538
6	8	-0.760343	-0.652691	0.247342
7	6	-1.480642	-0.653063	-1.018190
8	6	-2.616679	0.819114	0.466724
9	6	-2.882166	-0.177221	-0.668526
10	1	-1.429467	-1.661709	-1.418387
11	1	-0.764234	0.868828	1.658371
12	1	-1.819630	-0.513976	2.008290
13	1	-0.979189	0.035927	-1.701339
14	1	-2.302684	1.781737	0.062839
15	1	-3.489583	-1.010833	-0.314711
16	1	-3.484660	0.982808	1.102119
17	1	-3.382704	0.273219	-1.523447

19. $Cl_2S{=}O{-}THF$



Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.210992	0.508796	1.195072
2	8	1.476103	-0.560818	0.559827
3	6	2.260899	-1.129093	-0.508800
4	6	3.608021	0.496890	0.574857
5	6	3.347647	-0.105030	-0.810825
6	1	1.595374	-1.329438	-1.346851
7	1	2.216715	0.332183	2.270829
8	1	1.691040	1.449196	0.997430
9	1	2.689073	-2.076664	-0.167989
10	1	4.274981	-0.148409	1.148365
11	1	2.971721	0.656672	-1.495419
12	1	4.049209	1.491342	0.536929
13	1	4.232864	-0.557029	-1.255173
14	8	-1.122461	-1.330262	-0.942412
15	16	-1.265723	-0.381920	0.145024
16	17	-1.019256	1.579811	-0.687923
17	17	-3.384502	-0.239098	0.532062