Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2015

# Supplementary Materials

## A Model Study on The Photochemical Isomerizations of Cyclic Silenes

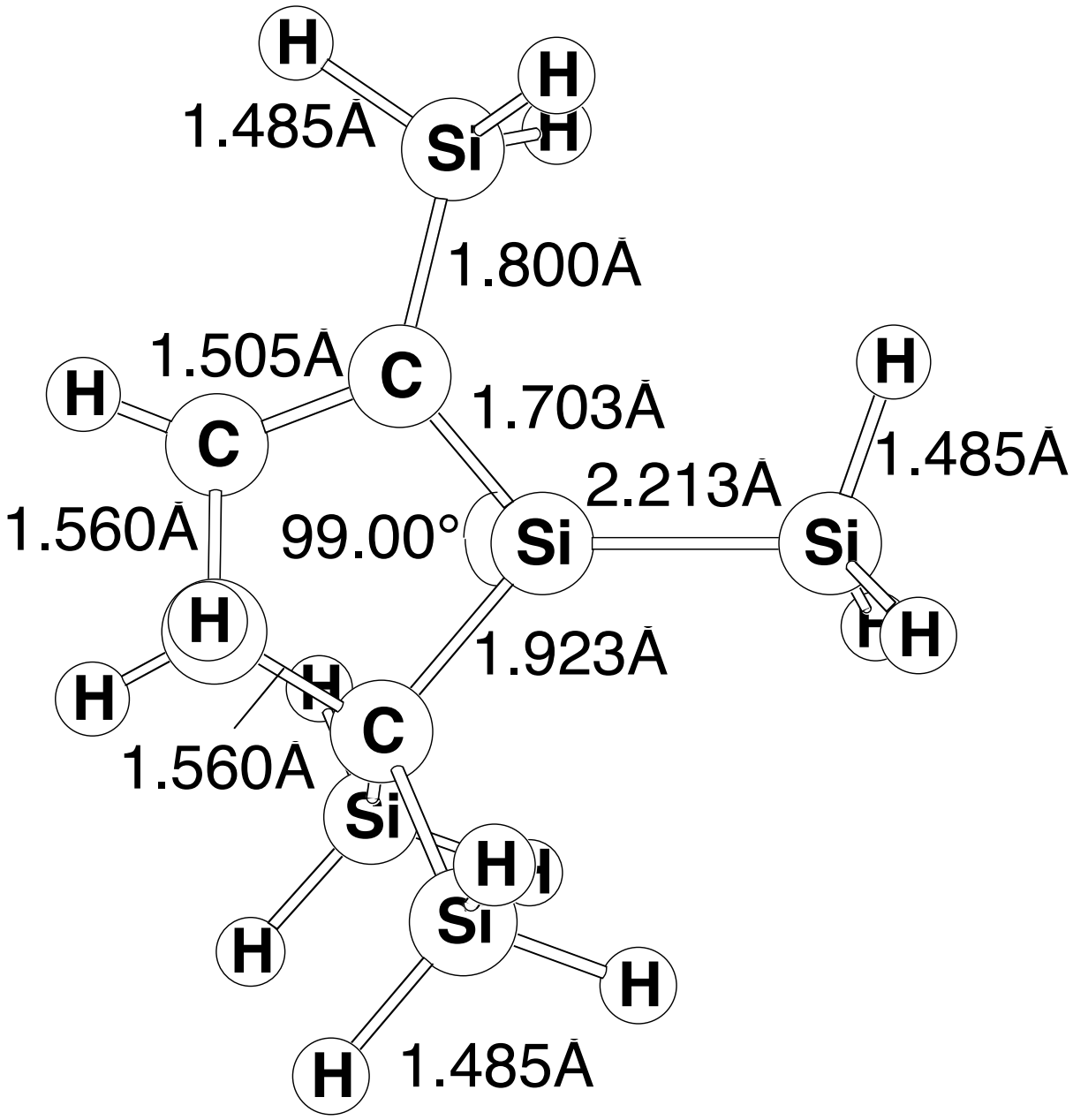
Ming-Der Su[1,2]*

[1]Department of Applied Chemistry, National Chiayi University, Chiayi 60004, Taiwan

[2]Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

*E-mail: midesu@mail.ncyu.edu.tw

**The fixed geometrical parameters are shown below:**



# (All geometries were calculated CASSCF(8,8)/6-311G*)

## (1) **Rea-3**

| Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| 14 | 0.000000 | 0.000000 | 0.000000 |
| 6 | 0.000000 | 0.000000 | 1.707676 |
| 6 | 1.464981 | 0.000000 | 2.166735 |
| 6 | 2.375017 | -0.499655 | 1.021559 |
| 6 | 1.851883 | -0.026063 | -0.391151 |
| 14 | -1.765040 | 0.108261 | -1.561919 |
| 14 | -1.400086 | 0.066280 | 2.910995 |
| 14 | 2.486993 | 1.718112 | -0.792048 |
| 14 | 2.348237 | -1.250022 | -1.742007 |
| 1 | 1.613944 | -0.639158 | 3.033925 |
| 1 | 2.369098 | -1.586657 | 1.050353 |
| 1 | 3.404571 | -0.189683 | 1.185327 |
| 1 | -1.530229 | 1.244107 | -2.476240 |
| 1 | -1.809546 | -1.141850 | -2.346728 |
| 1 | -3.033106 | 0.294979 | -0.834449 |
| 1 | -2.693402 | -0.037451 | 2.196500 |
| 1 | -1.317269 | -1.038158 | 3.898328 |
| 1 | -1.408043 | 1.330094 | 3.689651 |
| 1 | 3.960293 | 1.701102 | -0.935424 |
| 1 | 1.897762 | 2.197763 | -2.063166 |
| 1 | 2.127785 | 2.672229 | 0.278137 |
| 1 | 1.756045 | -0.854249 | -3.040870 |
| 1 | 3.818905 | -1.304536 | -1.897920 |
| 1 | 1.861555 | -2.604552 | -1.395785 |
| 1 | 1.755124 | 1.004291 | 2.474416 |

CASSCF(8,8)/6-311G(d) = -1605.456023
MP2(8,8)/6-311++G(3df,3pd)//CASSCF(8,8)/6-311G(d)= -1607.555703

## (2) **FC**

CASSCF(8,8)/6-311G(d) = -1605.253715
MP2(8,8)/6-311++G(3df,3pd)//CASSCF(8,8)/6-311G(d)= -1607.371557

## (3) **S1/S0 CI**

| Atomic Number | . | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 14 | | -0.266289 | 0.187136 | -0.218131 |

| | | | |
|---|---|---|---|
| 6 | 0.123824 | 0.822848 | 1.481760 |
| 6 | 1.562107 | 0.867826 | 1.633775 |
| 6 | 2.392939 | 0.176763 | 0.566881 |
| 6 | 1.578830 | 0.037623 | -0.780364 |
| 14 | -1.758421 | -1.652673 | -0.335688 |
| 14 | -1.031161 | 1.082072 | 2.940716 |
| 14 | 1.982032 | 1.496893 | -1.932499 |
| 14 | 2.038161 | -1.593911 | -1.624784 |
| 1 | 2.029996 | 1.204089 | 2.543587 |
| 1 | 2.670716 | -0.805487 | 0.958633 |
| 1 | 3.335862 | 0.695719 | 0.409195 |
| 1 | -2.422174 | 1.187853 | 2.450708 |
| 1 | -0.928843 | -0.072589 | 3.864294 |
| 1 | -0.684145 | 2.307717 | 3.690472 |
| 1 | -3.093335 | -1.193870 | 0.104047 |
| 1 | -1.852457 | -2.105786 | -1.740758 |
| 1 | -1.349085 | -2.799848 | 0.506083 |
| 1 | 3.418053 | 1.461055 | -2.301820 |
| 1 | 1.179018 | 1.421004 | -3.171358 |
| 1 | 1.711216 | 2.782250 | -1.258318 |
| 1 | 1.443566 | -1.689105 | -2.979288 |
| 1 | 3.511135 | -1.709653 | -1.747204 |
| 1 | 1.561048 | -2.740812 | -0.818198 |
| 1 | 0.624392 | 2.461485 | 1.182024 |

---

Derivative Coupling

| | | | |
|---|---|---|---|
| -1 | 0.0004731585 | -0.0001931899 | 0.0168077260 |
| -2 | -0.0162972620 | -0.0578376432 | -0.0071412751 |
| -3 | -0.0268828699 | 0.0350143255 | -0.0125378819 |
| -4 | 0.0002654837 | 0.0046836739 | -0.0056163860 |
| -5 | 0.0020490011 | -0.0011543530 | 0.0010174242 |
| -6 | -0.0001149901 | 0.0023917107 | 0.0002312968 |
| -7 | 0.0000169041 | -0.0018385177 | -0.0033299669 |
| -8 | -0.0006870984 | 0.0006248103 | 0.0000706901 |
| -9 | -0.0002835411 | -0.0000153979 | -0.0002607724 |
| -10 | 0.0000698558 | -0.0006762861 | 0.0006504147 |
| -11 | -0.0020380974 | 0.0012354776 | 0.0032140980 |
| -12 | -0.0000712265 | -0.0001065885 | 0.0010486216 |
| -13 | 0.0001177231 | -0.0001324539 | 0.0002797254 |
| -14 | 0.0003542354 | 0.0008792111 | 0.0004753813 |

| | | | |
|---|---|---|---|
| -15 | 0.0000778478 | 0.0011349831 | 0.0000569668 |
| -16 | 0.0000145100 | -0.0001801569 | 0.0000108790 |
| -17 | -0.0000826573 | -0.0003083874 | 0.0000672264 |
| -18 | 0.0000391051 | 0.0001428161 | -0.0005216314 |
| -19 | 0.0001072954 | 0.0001118132 | -0.0000166449 |
| -20 | 0.0002077979 | -0.0002847075 | 0.0001415898 |
| -21 | -0.0000620026 | -0.0000619791 | -0.0003221870 |
| -22 | 0.0000782890 | 0.0001193472 | 0.0001300417 |
| -23 | 0.0002014964 | -0.0001179602 | 0.0000166311 |
| -24 | 0.0001594415 | 0.0000096949 | 0.0000489451 |
| -25 | 0.0422876004 | 0.0165597578 | 0.0054790876 |

Unscaled Gradient Difference

| | | | |
|---|---|---|---|
| -1 | -0.0067654167 | 0.0148778148 | 0.0161443600 |
| -2 | -0.1077357807 | 0.0212208375 | -0.0380800112 |
| -3 | 0.1019430417 | 0.0741982163 | 0.0028874937 |
| -4 | -0.0025712800 | -0.0081030484 | 0.0044289426 |
| -5 | 0.0047575545 | 0.0016643132 | -0.0005651728 |
| -6 | -0.0001558981 | 0.0036612850 | 0.0014550136 |
| -7 | -0.0014948610 | -0.0105162845 | -0.0040183891 |
| -8 | -0.0014734866 | -0.0035663991 | 0.0004511936 |
| -9 | 0.0001639539 | 0.0012633744 | 0.0005054703 |
| -10 | -0.0005514561 | -0.0016283380 | -0.0008588049 |
| -11 | 0.0005636646 | -0.0041614050 | 0.0008573461 |
| -12 | -0.0013378295 | -0.0008369583 | 0.0006378675 |
| -13 | 0.0006325342 | 0.0005887889 | -0.0000798486 |
| -14 | 0.0008766033 | 0.0005557920 | 0.0023403786 |
| -15 | 0.0005221560 | 0.0009146677 | 0.0002230805 |
| -16 | -0.0000300283 | -0.0003856184 | -0.0000158305 |
| -17 | 0.0002244621 | -0.0000604044 | 0.0001907532 |
| -18 | -0.0000206316 | 0.0000757922 | -0.0007190518 |
| -19 | 0.0000865566 | 0.0007440092 | 0.0000095432 |
| -20 | 0.0000813871 | 0.0007537687 | 0.0000123569 |
| -21 | -0.0003637742 | 0.0011996447 | 0.0006155663 |
| -22 | -0.0000628493 | -0.0002451919 | -0.0003246242 |
| -23 | 0.0003332586 | -0.0002676992 | 0.0000086457 |
| -24 | -0.0000035541 | -0.0000885704 | -0.0001585187 |
| -25 | 0.0123816737 | -0.0918583870 | 0.0140522402 |

---

CASSCF(8,8)/6-311G(d) = -1605.2724932964

MP2(8,8)/6-311++G(3df,3pd)//CASSCF(8,8)/6-311G(d)= -1607.383225
MP2(8,8)/6-311++G(3df,3pd)//CASSCF(8,8)/6-311G(d)= -1607.385615

## (4) **Pro-4**

| Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| 14 | 0.000000 | 0.000000 | 0.000000 |
| 6 | 0.000000 | 0.000000 | 1.879521 |
| 6 | 1.288372 | 0.000000 | 2.284686 |
| 6 | 2.420431 | 0.000866 | 1.276907 |
| 6 | 1.878456 | 0.333389 | -0.162671 |
| 14 | -0.877767 | -2.016091 | -0.900747 |
| 14 | -1.430112 | -0.016231 | 3.082402 |
| 14 | 2.134501 | 2.183097 | -0.501845 |
| 14 | 2.772050 | -0.700392 | -1.464840 |
| 1 | 1.569962 | -0.035610 | 3.350824 |
| 1 | 2.896717 | -0.979019 | 1.306635 |
| 1 | 3.192879 | 0.700936 | 1.590337 |
| 1 | -2.368233 | -1.112525 | 2.753074 |
| 1 | -0.929617 | -0.207637 | 4.461789 |
| 1 | -2.180907 | 1.256804 | 3.016258 |
| 1 | -2.332793 | -2.059015 | -0.626164 |
| 1 | -0.677892 | -2.081313 | -2.366500 |
| 1 | -0.245920 | -3.202566 | -0.282221 |
| 1 | 3.581965 | 2.498906 | -0.497553 |
| 1 | 1.573195 | 2.562875 | -1.815941 |
| 1 | 1.484259 | 2.991534 | 0.552543 |
| 1 | 2.264941 | -0.392385 | -2.820425 |
| 1 | 4.228375 | -0.435331 | -1.436189 |
| 1 | 2.564691 | -2.141805 | -1.197462 |
| 1 | -0.803597 | 1.106950 | -0.579767 |

CASSCF(8,8)/6-311G(d) = -1605.5211230004
MP2(8,8)/6-311++G(3df,3pd)//CASSCF(8,8)/6-311G(d)= -1607.575212

## (5) **TS**

| Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| 14 | -0.265288 | 0.181868 | -0.216522 |
| 6 | 0.123869 | 0.818762 | 1.483551 |
| 6 | 1.563677 | 0.865730 | 1.637757 |
| 6 | 2.397374 | 0.176677 | 0.570872 |

| | | | |
|---|---|---|---|
| 6 | 1.579893 | 0.035822 | -0.777157 |
| 14 | -1.758799 | -1.656939 | -0.333466 |
| 14 | -1.036807 | 1.086201 | 2.936781 |
| 14 | 1.979090 | 1.495809 | -1.930588 |
| 14 | 2.042297 | -1.591903 | -1.625895 |
| 1 | 2.028742 | 1.202260 | 2.548667 |
| 1 | 2.678821 | -0.802620 | 0.966718 |
| 1 | 3.338797 | 0.699306 | 0.417176 |
| 1 | -2.422718 | 1.202592 | 2.433773 |
| 1 | -0.944761 | -0.069664 | 3.864044 |
| 1 | -0.686740 | 2.311761 | 3.682673 |
| 1 | -3.083486 | -1.198220 | 0.134028 |
| 1 | -1.880829 | -2.089291 | -1.743478 |
| 1 | -1.340548 | -2.816257 | 0.486628 |
| 1 | 3.414063 | 1.446068 | -2.315525 |
| 1 | 1.165123 | 1.426789 | -3.163957 |
| 1 | 1.723839 | 2.782134 | -1.252684 |
| 1 | 1.446676 | -1.686403 | -2.974721 |
| 1 | 3.512022 | -1.697716 | -1.759374 |
| 1 | 1.575912 | -2.746186 | -0.822047 |
| 1 | 0.626767 | 2.452018 | 1.176507 |

---

| | | | |
|---|---|---|---|
| -1 | 0.00 | 0.00 | 0.00 |
| -2 | 0.00 | 0.02 | -0.01 |
| -3 | 0.03 | -0.07 | 0.02 |
| -4 | 0.01 | -0.01 | 0.00 |
| -5 | 0.00 | 0.00 | 0.00 |
| -6 | 0.00 | 0.00 | 0.00 |
| -7 | 0.00 | 0.00 | 0.00 |
| -8 | 0.00 | 0.00 | 0.00 |
| -9 | 0.00 | 0.00 | 0.00 |
| -10 | 0.04 | 0.09 | -0.05 |
| -11 | 0.04 | -0.02 | -0.04 |
| -12 | 0.00 | 0.01 | 0.01 |
| -13 | 0.00 | 0.00 | 0.00 |
| -14 | 0.00 | -0.01 | -0.01 |
| -15 | -0.01 | -0.01 | 0.01 |
| -16 | 0.00 | 0.00 | 0.00 |
| -17 | 0.00 | 0.00 | 0.00 |
| -18 | 0.01 | 0.01 | 0.00 |

| | | | |
|---|---|---|---|
| -19 | 0.00 | 0.00 | 0.00 |
| -20 | 0.00 | 0.00 | 0.00 |
| -21 | 0.00 | 0.00 | 0.00 |
| -22 | 0.00 | 0.00 | 0.00 |
| -23 | 0.00 | 0.00 | 0.00 |
| -24 | 0.00 | 0.00 | 0.00 |
| -25 | -0.60 | 0.78 | -0.12 |

---

CASSCF(8,8)/6-311G(d) = --1605.315988
MP2(8,8)/6-311++G(3df,3pd)//CASSCF(8,8)/6-311G(d)= -1607.3889661