Supplementary Materials

Photochemical Isomerization
Reactions of Acrylonitrile.
A Mechanistic Study

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
(1) 1 (Acrylonitrile)

| Atomic Number | X     | Y     | Z     |
|---------------|-------|-------|-------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 6             | 0.000000 | 0.000000 | 1.073894 |
| 6             | 1.150698 | 0.000000 | 1.754928 |
| 1             | 2.113382 | 0.000000 | 1.228753 |
| 1             | -0.953532 | 0.000000 | 1.568559 |
| 6             | 1.206300 | 0.000000 | 3.198030 |
| 7             | 1.251278 | 0.000000 | 4.365393 |

CASSCF(12,11)/6-311G(d,p) = -169.974955478
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p)= -169.9951085

(2) FC

CASSCF(12,11)/6-311G(d,p) = -169.6845266
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p)= -169.7200179

(3) S1/S0-CI

| Atomic Number | X     | Y     | Z     |
|---------------|-------|-------|-------|
| 1             | -0.402997 | -0.717679 | 0.029489 |
| 6             | -0.275306 | 0.108375 | 0.702642 |
| 6             | 0.738983 | 0.187611 | 1.565099 |
| 1             | 1.545826 | -0.312469 | 2.020291 |
| 1             | -0.995719 | 0.908705 | 0.674658 |
| 6             | 0.893847 | 0.556914 | 4.626453 |
| 7             | 1.661599 | -0.330225 | 3.835883 |

Derivative Coupling

| -1     | -0.0006894774 | 0.0009277660 | 0.0020458626 |
| -2     | 0.0020082252 | -0.0019575224 | 0.0025365995 |
| -3     | -0.0074703749 | 0.0035887462 | -0.0151570861 |
| -4     | -0.0008835638 | 0.0024543504 | 0.0014335271 |
| -5     | 0.0025017349 | -0.0006002592 | -0.0003041061 |
| -6     | 0.0240038720 | -0.0270279516 | -0.0219132153 |
| -7     | -0.0194704159 | 0.0226148706 | 0.0313584183 |

Unscaled Gradient Difference

| -1     | 0.0002594426 | -0.0010290998 | -0.0019055180 |
| -2     | -0.0010438218 | 0.0015574800 | 0.0002869697 |
\begin{table}
\centering
\begin{tabular}{llll}
   & Atomic & Number & Coordinates (Angstroms) \\
   & & & X & Y & Z \\
1 & & 0.000000 & 0.000000 & 0.000000 \\
6 & & 0.000000 & 0.000000 & 1.072912 \\
6 & 1 & 1.155747 & 0.000000 & 1.738709 \\
1 & 1 & 2.129673 & 0.000000 & 1.238284 \\
1 & 1 & -0.944837 & 0.000000 & 1.582242 \\
7 & & 1.220509 & 0.000000 & 3.126897 \\
6 & & 1.275653 & 0.000000 & 4.308941 \\
\end{tabular}
\caption{(4) Int-1 (isocyanate)}
\end{table}

\begin{table}
\centering
\begin{tabular}{llll}
   & Atomic & Number & Coordinates (Angstroms) \\
   & & & X & Y & Z \\
1 & & 0.000000 & 0.000000 & 0.000000 \\
6 & & 0.000000 & 0.000000 & 1.059648 \\
6 & 1 & 1.054224 & 0.000000 & 1.906249 \\
1 & 1 & 2.018133 & 0.300297 & 2.244455 \\
1 & 1 & -0.474040 & 0.198484 & 2.449639 \\
6 & & -0.057036 & -0.308010 & 3.527387 \\
7 & & -0.731580 & -0.445024 & 4.490621 \\
\end{tabular}
\caption{(5) TS1}
\end{table}

CASSCF(12,11)/6-311G(d,p) = -169.7010426
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p) = -169.7311529

(4) \textbf{Int-1 (isocyanate)}

\begin{table}
\centering
\begin{tabular}{llll}
   & Atomic & Number & Coordinates (Angstroms) \\
   & & & X & Y & Z \\
1 & & 0.000000 & 0.000000 & 0.000000 \\
6 & & 0.000000 & 0.000000 & 1.072912 \\
6 & 1 & 1.155747 & 0.000000 & 1.738709 \\
1 & 1 & 2.129673 & 0.000000 & 1.238284 \\
1 & 1 & -0.944837 & 0.000000 & 1.582242 \\
7 & & 1.220509 & 0.000000 & 3.126897 \\
6 & & 1.275653 & 0.000000 & 4.308941 \\
\end{tabular}
\caption{(4) Int-1 (isacrylonitrile)}
\end{table}

CASSCF(12,11)/6-311G(d,p) = -169.83597251

S-3
(6) TS2

| Atomic Number | X      | Y      | Z      |
|---------------|--------|--------|--------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 6             | 0.000000 | 0.000000 | 1.060081 |
| 6             | 0.385291 | 0.262777 | 2.179750 |
| 1             | 0.843161 | 0.459367 | 3.107144 |
| 1             | -0.988648 | -0.458756 | 2.108033 |
| 7             | -1.133834 | -0.466376 | 3.129892 |
| 6             | -1.341899 | -0.523473 | 4.298116 |

CASSCF(12,11)/6-311G(d,p) = -169.8055265
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p) = -169.8265658

(7) HCCH + HCN (monomer)

| Atomic Number | X      | Y      | Z      |
|---------------|--------|--------|--------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 6             | 0.000000 | 0.000000 | 1.055679 |
| 6             | 0.000000 | 0.000000 | 2.273363 |
| 1             | 0.000000 | 0.000000 | 3.329041 |

| Atomic Number | X      | Y      | Z      |
|---------------|--------|--------|--------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 6             | 0.000000 | 0.000000 | 1.057614 |
| 7             | 0.000000 | 0.000000 | 2.209371 |

CASSCF(12,11)/6-311G(d,p) = -169.9197985
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p) = -169.9377115

(8) HCCH + HCN (linear)

| Atomic Number | X      | Y      | Z      |
|---------------|--------|--------|--------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 6             | 0.000000 | 0.000000 | 1.055679 |
| 6             | 0.000000 | 0.000000 | 2.273363 |
| 1             | 0.000000 | 0.000000 | 3.329041 |

CASSCF(12,11)/6-311G(d,p) = -169.9197985
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p) = -169.9377115
| Atomic Number | X      | Y      | Z      |
|--------------|--------|--------|--------|
| 6            | 0.000000 | 0.000000 | 0.609255 |
| 1            | 2.846769 | 0.000000 | 0.000000 |
| 6            | 0.000000 | 0.000000 | -0.609255 |
| 1            | 0.000000 | 0.000000 | -1.665501 |
| 1            | 0.000000 | 0.000000 | 1.665501 |
| 6            | 3.905719 | 0.000000 | 0.000000 |
| 7            | 5.057726 | 0.000000 | 0.000000 |

CASSCF(12,11)/6-311G(d,p) = -169.9225599
MP2(12,11)/6-311++G(3df,3pd)/CASSCF(12,11)/6-311G(d,p) = -169.9455159

(9) HCCH + HCN (T-shape; T-int-2)
(11) HCC(CN) + H2

| Atomic Number | X     | Y     | Z     |
|---------------|-------|-------|-------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 6             | 0.000000 | 0.000000 | 1.055681 |
| 6             | 0.000000 | 0.000000 | 2.249202 |
| 6             | 0.000000 | 0.000000 | 3.631560 |
| 7             | 0.000000 | 0.000000 | 4.800493 |

CASSCF(12,11)/6-311G(d,p) = -169.8805359
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p) = -169.8997115

(12) HCCH + HNC (monomer)

| Atomic Number | X     | Y     | Z     |
|---------------|-------|-------|-------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 6             | 0.000000 | 0.000000 | 1.055679 |
| 6             | 0.000000 | 0.000000 | 2.273363 |
| 1             | 0.000000 | 0.000000 | 3.329041 |

| Atomic Number | X     | Y     | Z     |
|---------------|-------|-------|-------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 7             | 0.000000 | 0.000000 | 0.983676 |
| 6             | 0.000000 | 0.000000 | 2.152315 |

CASSCF(12,11)/6-311G(d,p) = -169.8887559
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p) = -169.9077115

(13) HCCH + HNC (linear)

| Atomic Number | X     | Y     | Z     |
|---------------|-------|-------|-------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 7             | 0.000000 | 0.000000 | 0.984382 |
| 6             | 0.000000 | 0.000000 | 2.163775 |
| 1             | 0.000000 | 0.000000 | 4.906940 |
| 6             | 0.000000 | 0.000000 | 5.964342 |
| 6             | 0.000000 | 0.000000 | 7.171013 |
CASSCF(12,11)/6-311G(d,p) = -169.8955773
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p)= -169.9214689

(14) HCCH + HNC (T-shape; T-int-3)

| Atomic Number | X     | Y     | Z    |
|---------------|-------|-------|------|
| 6             | 0.000000 | 0.000000 | 0.603417 |
| 1             | 2.571855 | 0.000000 | 0.000000 |
| 6             | 0.000000 | 0.000000 | -0.603417 |
| 1             | 0.000000 | 0.000000 | 1.659208 |
| 1             | 0.000000 | 0.000000 | 1.659208 |
| 7             | 3.558805 | 0.000000 | 0.000000 |
| 6             | 4.739413 | 0.000000 | 0.000000 |

CASSCF(12,11)/6-311G(d,p) = -169.896582
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p)= -169.9224676

(15) TS4

| Atomic Number | X     | Y     | Z    |
|---------------|-------|-------|------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 6             | 0.000000 | 0.000000 | 1.055839 |
| 6             | 0.000000 | 0.000000 | 2.260992 |
| 1             | 0.213163 | 0.000000 | 3.897840 |
| 1             | -0.819304 | 0.000000 | 4.687785 |
| 7             | -1.888340 | 0.000000 | 5.953845 |
| 6             | -2.538358 | 0.000006 | 6.941883 |
| -1            | 0.000000 | 0.000000 | -0.010000 |
| -2            | 0.000000 | 0.000000 | -0.010000 |
| -3            | 0.000000 | 0.000000 | -0.020000 |
| -4            | 0.060000 | 0.000000 | 0.310000 |
| -5            | 0.630000 | 0.000000 | -0.710000 |
| -6            | -0.030000 | 0.000000 | 0.030000 |
| -7            | -0.020000 | 0.000000 | 0.030000 |

CASSCF(12,11)/6-311G(d,p) = -169.9225599
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p)= -169.7520363

(16) Pro

| Atomic Number | X     | Y     | Z    |
|---------------|-------|-------|------|
| S-7           |       |       |      |
1                   0.000000    0.000000    1.055681
6                   0.000000    0.000000    2.249202
6                   0.000000    0.000000    3.631560
7                   0.000000    0.000000    4.800493

CASSCF(12,11)/6-311G(d,p) = -169.8805359
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p)= -169.8587115

(17) **TS5 (dark)**

| Atomic Number | X      | Y      | Z      |
|---------------|--------|--------|--------|
| 1             | 0.000000 | 0.000000 | 0.000000 |
| 6             | 1.157232 | 0.000000 | 1.737224 |
| 1             | 2.123677 | 0.011187 | 1.282436 |
| 1             | 0.944313 | -0.069230 | 1.577677 |
| 7             | 1.471666 | -0.825620 | 3.307666 |
| 6             | 1.260571 | 0.373093 | 3.405101 |

CASSCF(12,11)/6-311G(d,p) = -169.8753205
MP2(12,11)/6-311++G(3df,3pd)//CASSCF(12,11)/6-311G(d,p)= -169.8968823