Supporting Information

Stereoelectronic and Dynamical Effects Dictate Nitrogen Inversion during Valence Isomerism in Benzene Imine

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1. **DFT methods:**

The suitable choice of DFT functional and basis set is important to locate the saddle points and minima on the potential energy landscape. The M06-2X functional shows better agreements with the experimental results and is extensively used to investigate various thermal pericyclic reactions. Table S1 shows the relative free energies and activation energies for the valence isomerism in benzene imine (Endo–1a) at various levels of theory. In our study, we found M06-2X/6-31+G(d,p) method is better suited to investigate the quantum mechanical and non-statistical effects involved in the valence isomerism assisted N-inversion reaction (Endo–1 → Endo–2, Exo–2).

**Table ST1:** Relative free energies and activation energies (in kcal/mol) for valence isomerism assisted N-inversion (Endo–1 → Endo–2 → Exo–2) and N-inversion followed by valence isomerism (Endo–1 → Exo–1 → Exo–2). The relative electronic energies are given at the ccsd(t)/def2-TZVP level (blue colored values).

|   | B3LYP-GD3BJ/6-31+G(d,p) | M06-2X/6-31+G(d,p) | M06-2X-D3/def2-TZVP | MP2/6-31+G(d,p) | CCSD(T)/def2-TZVP |
|---|-------------------------|------------------|----------------------|----------------|------------------|
| Endo-1a | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| ΔGᵢ exp(I) | 2.6 | 4.4 | 4.6 | 4.4 | 1.7 | 5.3 |
| Endo-2a | -4.1 | 0.3 | -0.6 | 0.1 | -1.1 | -1.4 |
| ΔGᵢ inv(I) | 1.0 | 1.4 | 1.1 | 1.4 | 0.9 | 3.0 |
| Exo-2a | -7.3 | -2.7 | -3.9 | -3.4 | -2.5 | -4.0 |
| ΔGᵢ inv(II) | 17.9 | 18.0 | 18.0 | 18.3 | – | 22.2 |
| Exo-1a | 3.9 | 3.7 | 3.6 | 3.6 | 3.6 | 3.5 |
| ΔGᵢ exp(II) | 3.5 | 5.5 | 5.5 | 5.5 | 2.7 | 6.8 |

S2
2. **Schematic Potential Energy Surfaces:**

The stereoelectronic induction at the N-site (as −F in 1b and its isolobal −CH₃ group in 1c) dictates the notable decrease in dihedral angle \( \phi(H13–C6–N7–R14) \), see Figure S1-S3 and Table ST1-ST3 for details. Therefore, the activation of the rate-limiting bridging (C1–C6) bond (ambimodal TS(1→2) structure) governs both the Valence (1 ⇌ 2) and Endo–Exo (2 ⇌ 3) dynamic equilibriums.

a) **Potential energy surface for (1a → 2a, 3a, 4a) pathways:**

![Diagram](image)

**Figure S1:** Reaction pathways and relative Gibbs free energy profile for valence isomerism assisted N-inversion (1a→2a→3a) and also connected with N-inversion followed by valence
isomerism ($1a\rightarrow 4a\rightarrow 3a$) or vice versa (M06-2X/6-31+G(d,p) level at 298.15 K). All these minima and saddle points are in $C_s$ symmetry.

**Table ST2:** Optimized distance ($d$) of rate-limiting bond ($C1$–$C6$), angle ($\theta$) of $C1$–$N7$–$C6$, and dihedral angle ($\phi$) of $H13$–$C6$–$N7$–$H14$ for $1a$ are shown at M06-2X/6-31+G(d,p) level of theory.

| Minima and Saddle Points | d($C1$–$C6$) (in Å) | $\theta$($C1$–$N7$–$C6$) (in degree) | $\Phi$($H13$–$C6$–$N7$–$H14$) (in degree) |
|--------------------------|-----------------------|--------------------------------------|--------------------------------------|
| $1a$                     | 1.54252               | 63.93740                             | 147.14239                            |
| $2a$                     | 2.29678               | 106.30204                            | 133.66294                            |
| $3a$                     | 2.41704               | 117.23269                            | 7.18013                              |
| $4a$                     | 1.52777               | 62.93756                             | 4.80234                              |
| TS($1a\rightarrow 2a$)   | 1.87817               | **82.35775**                         | **147.56230**                        |
| TS($2a\rightarrow 3a$)   | 2.43641               | 118.09088                            | 84.87024                             |
| TS($1a\rightarrow 4a$)   | 1.59343               | 69.66488                             | 70.40878                             |
| TS($4a\rightarrow 3a$)   | 1.85678               | 80.90686                             | 8.46895                              |
b) Potential energy surface for (1b → 2b, 3b, 4b) pathways:

**Figure S2:** Reaction pathways and relative Gibbs free energy profile for valence isomerism assisted N-inversion (1b → 2b → 3b) and further also associated with the valence isomerism dynamic equilibrium (3b ⇄ 4b) at M06-2X/6-31+G(d,p) level (at 298.15 K). All these minima and saddle points are in $C_s$ symmetry.
Table ST3: Optimized distance ($d$) of rate-limiting bond ($C1-C6$), angle ($\theta$) of $C1-N7-C6$, and dihedral angle ($\phi$) of $H13-C6-N7-F14$ for 1b are shown at M06-2X/6-31+G(d,p) level of theory.

| Saddle Points | Minima and Saddle Points | $d(C1-C6)$ (in Å) | $\theta(C1-N7-C6)$ (in degree) | $\Phi(H13-C6-N7-F14)$ (in degree) |
|---------------|--------------------------|-------------------|---------------------------------|-----------------------------------|
| 1b            |                          | 1.53278           | 62.63158                        | 144.03663                         |
| 2b            |                          | 2.35206           | 111.46321                       | 118.04864                         |
| 3b            |                          | 2.35439           | 110.87160                       | 4.67508                           |
| 4b            |                          | 1.52193           | 62.17213                        | 9.66296                           |
| TS(1b$\rightarrow$2b) |                | **1.88970**       | **82.91321**                    | **139.27730**                     |
| TS(2b$\rightarrow$3b) |                | 2.53426           | 132.03288                       | 42.50076                          |
| TS(4b$\rightarrow$3b) |                | 1.86993           | 81.28221                        | 3.93979                           |
c) Potential energy surface for \(1c \rightarrow 2c, 3c, 4c\) pathways:

**Figure S3:** Reaction pathways and relative Gibbs free energy profile for valence isomerism assisted N-inversion \((1c \rightarrow 2c \rightarrow 3c)\) and also connected with N-inversion followed by valence isomerism \((1c \rightarrow 4c \rightarrow 3c)\) or vice versa at (M06-2X/6-31+G(d,p) level at 298.15 K). All these minima and saddle points are in \(C_s\) symmetry.
Table ST4: Optimized distance (d) of rate-limiting bond (C1–C6), angle (θ) of C1–N7–C6, and dihedral angle (ϕ) of H13–C6–N7–C14 for 1c are shown at M06-2X/6-31+G(d,p) level of theory.

| Saddle Points | d(C1–C6) (in Å) | θ(C1–N7–C6) (in degree) | Φ(H13–C6–N7–C14) (in degree) |
|---------------|-----------------|--------------------------|-------------------------------|
| 1c            | 1.54944         | 64.49446                 | 137.62813                     |
| 2c            | 2.35185         | 110.72604                | 108.63644                     |
| 3c            | 2.37035         | 113.55525                | 15.52641                      |
| 4c            | 1.53783         | 63.94943                 | 0.45339                       |
| TS(1c→2c)     | **1.92129**     | **85.05517**             | **132.83223**                 |
| TS(2c→3c)     | 2.42577         | 117.44898                | 84.13946                      |
| TS(1c→4c)     | 1.60544         | 70.50890                 | 72.23281                      |

2. QCT Inputs:

The ambient temperature behavior of 1a, 1b, and 1c were investigated using post-transition state quasi-classical direct-MD simulations at 298.15 K in the gas phase. Reaction trajectories were simulated using the Progdyn–Gaussian16 interface from the sampled rate-determining TS(1→2) structures. The energies and derivatives were calculated on the fly with M06-2X/6-31+G(d,p) level. The typical input file for reaction trajectory simulations is shown below:

a) **Progdyn.conf:**

#This is the configuration file for PROGDYN. This file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
The programs won't read anything past the first blank line, and this file must end with a blank line.
The program has a number of default values but they are unlikely to be what you want.
Do not delete lines - rather, comment out lines for unwanted options.
The values here are read repeatedly and most can be changed in the middle of running jobs
The keywords are case sensitive. The following keywords should always be defined:

- **method**, charge, multiplicity, memory, processors, title
- **method** -- The following word is copied exactly to the gaussian input file.
  - method m062x/6-31+G(d,p)

To do a nonstandard route, make nonstandard 1. For normal calcs, use nonstandard 0 or else leave it out.
Then make a file called "nonstandard" containing the nonstandard route with no extra lines.
nonstandard 0

# NMRoptions As is NMRtype=1 will add a section for an NMR calc at every NMRevery intervals. If you want to combine the two use nonstandard

- **NMRtype**
  - NMRmethod2 B97D/6-31G*
  - NMRmethod LC-wPBE/6-31G*
  - NMRmethod3 B3LYP/cc-pvtz

- **NMRevery**
- **NMRrand**
- **NMRcc**
- **loadlimit**
- **geometry**
- **rotationmode**

- **method2** -- The options here are restricted, unrestricted, and read. restricted is the default
  - If the method is U..., put unrestricted here and the .com files will have in them guess=mix.
  - If you put read here, the .com files will contain guess=tcheck, which sometimes makes things faster, sometimes not.
  - The use of read requires a specifically defined checkpoint file name using the keyword checkpoint.
  - method2 restricted
  - charge 0
  - multiplicity 1
  - oniomchargemult 1 1
  - processors 16

- **memory**
  - memory 5gb

- **killcheck and checkpoint**
  - You can use a specifically defined checkpoint file name by putting
  - the name after the keyword checkpoint. This is necessary if you use the read option with method2.
  - Defined checkpoint names are an unnecessary modest hassle and if you do not want to bother, use killcheck 1
  - killcheck 1
  - checkpoint g16.chk

- **diagnostics**
  - 0 prints out nothing extra, 1 (default) prints out extra stuff to a file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
  - #4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical
calculations
diagnostics 0

### title -- the title keyword must be followed by exactly four words

**title** bo aze endo path

### initialdis -- 0 (default) turns off displacement of the normal modes, so that all trajectories start from the same place

# and only the energies and signs of the motion in the modes are randomized

# 1 gives a flat distribution of displacements where all of the possible values are equally likely

# 2 (recommended) gives a QM-like gaussian distribution of displacements, so that displacements in the middle are more likely that

# those at the end by 1/e

**initialdis** 2

### timestep -- this is the time between points in the trajectory. Typical values would be 1E-15 or 0.5E-15 or 0.25E-15

**timestep** 1E-15

### scaling -- this lets you scale the gaussian frequencies by a constant

**scaling** 1.0

**temperature** 298.15

### thermostat 1 puts in a damping factor so as to bring the classical temperature toward the desired temperature.

### use a thermostatmult between 0.95 and 1, typically 0.995, so the damping happens slowly - otherwise there will be

### overadjustment in response to random variation

### the thermostat is not exact. The second traj point ignores this, so it only applies to later points handled by progdynb.

**thermostat** 1

**thermostatmult** 0.999

### method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.

**method3** and **method4** add lines at the top of the input after the lines defining the method, and this is useful to implement things like the iop for mPW1k

**method5** and **method6** add lines after the geometry, after a blank line of course

only a single term with no spaces can be added, one per method line. Here are some examples to uncomment if needed

**method3** IOp(3/76=0572004280)

**method3** scrf=(pcm,solvent=ethanol)

**method3** scrf=(pcm,Solvent=dichloromethane)

#add the line below with big structures to get it to put out the distance matrix and the input orientation

**method4** iop(2/9=2000)

**method3** scf=(conver=5)

**method4** iop(3/124=3)

**method4** scrf=(pcm,Solvent=dmsoread)

**method5** radii=bondi

**method6**

### methodfile -- This keyword lets you add more complicated endings to gaussian input files such as a gen basis set. Put after the keyword the number of lines in a file you create called methodfile that contains the test you want to add to the end of the gaussian input methodfile 0

### numimag --This tells the program the number of imaginary frequencies in the starting
structure.  
#if 0, treats as ground state and direction of all modes is random  
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir  
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction  

numimag 1  

### searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.  
The choices are "negative" and "positive".  Positive moves in the direction defined in the gaussian frequency calculation  
for the imaginary frequency, while negative moves in the opposite direction.  The correct choice can be made either  
by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.  

searchdir positive  

### classical -- for quassiclassical dynamics, the default, use 0.  for classical dynamics, use 1  
#if there are no normal modes and the velocities are to be generated from scratch, use classical  
2  
classical 0  

### DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave it at 0 or comment it out  
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no  
#if DRP shows oscillations then decrease maxAtomMove  
#DRP 1  
#saddlepoint no  
#maxAtomMove 0.01  

classical 0  

### cannonball -- The program can "fire" a trajectory from a starting position toward a particular target, such as toward  
a ts.  To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the vector  
for firing the trajectory, relative to the starting geometry's standard orientation.  The number following cannonball sets  
the extra energy being put into the structure in kcal/mol  
cannonball 10  

### keepevery --This tells the program how often to write the gaussian output file to file dyn, after the first two points.  
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading time.  
keepevery 1  

### highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,  
#which must come before the medium level atoms.  Use some high value such as 999 if not using ONIOM  
#highlevel 9999  

### fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.  
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms  
#fixes one distance and fixing three has the effect of fixing three distances, not just two  
#in current form fixed atoms only are meant to work with no displacements, that is, initialdis=0  
#fixedatom1 16  
#fixedatom2 1  

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#fixedatom3 4  
#fixedatom4 20  
#applyforce 1 lets one push atoms together or apart - a positive force pushes them together  
#format is applyforce force - with the units on force the same as in the Gaussian output file  
#applyforce 2 or 3 or 4 applys a polynomials force centered at dist0. 2 is just harmonic, 3 is second order, 4 is third order  
#format is applyforce 4 forcecoefficient dist0 forcecoefficient2 forcecoefficient3  
#then use afatoms to chose the atoms with format afatoms firstatom secondatom [additional atoms]  
#applyforce 2 0.1 2.1  
#afatoms 1 6 1 2 3 4 5 6  
#applyforceB 2 0.01 5.2  
#afatomsB 8 15  
#applyforceC 2 0.01 5.2  
#afatomsC 8 15  
#zeroatom pushes the numbered atom toward the origin with a small harmonic potential - good with boxon when you want to keep the reaction in the center  
#zeroatom 16  
### boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the edge are reflected back toward the middle. Useful for dynamics with solvent molecules. This is a crude implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.  
#Set the box size so as to fit the entire initial molecule but not have too much extra room.  
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms  
#boxon 1  
#boxsize 11.2  
### sphereon and spheresize and sphereforce - uses a force to push atoms within a sphere. notice that if the atom is far outside of the sphere then the force is large unless sphereforce is set small  
#sphereon 1  
#spheresize 12.9  
#sphereforce .01  
#setting a value for empiricaldispersion sets its s6 value with the Grimme 2006 algorithm. Default is 0, with no empiricaldispersion  
#empiricaldispersion 0.0  
### displacements -- This keyword lets you set the initialdis of particular modes by using a series of lines of the format  
# displacements NumberOfMode InitialDisForThatMode, as in the example below. You should be able to do as many of these as you like  
# you might consider this for rotations where a straight-line displacement goes wrong at large displacements  
# The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same thing as 0 but is maintained for now because a previous version of the program had a bug that made 0 not work.  
#displacements 2 0  
#displacements 3 0  
#displacements 4 0  
#displacements 5 0  

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#displacements 6 0
#displacements 7 0
#displacements 8 0
#displacements 9 0
#displacements 10 0

### etolerance
This sets the allowable difference between the desired energy in a trajectory and the actual energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.

#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems. For very large and floppy molecules, a larger value may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 1

### controlphase
--It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
controlphase 2 positive

### damping
-- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities by the damping factor. A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range from 0.95 to 1.05. The use of damping lets one do simulated annealing - you add energy until the structure is moving enough to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1.000
#at a damping of 0.9995, the energy is cut in half in 693 points

### reversetraj
--This keyword sets the trajectories so that both directions from a transition state are explored.
reversetraj true

#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword classical
#updated Jan 2008 to include fixed atoms, ONIOM jobs, keeperevery, and box size
#updated Feb 2008 to include methodfile parameter
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# update Aug 2010 to include etolerance, damping controlphase and reversetraj

b) **Proganal code**: (for R = H)

Cut-offs are used based on the labeled atoms in the FreqinHP input file for QCT simulations:

```
#.................................................QCT Cut-offs.................................................
BEGIN {
  firsttitle=1
```
getline < "isomernumber"
isomer=$1
}
/ bo / {
  if (firsttitle==1) {
    printf("%s %s %s %s %s %s %s  ",\$1,$2,$3,$4,$6,$7,$8)
    printf(" %s %s %s  ",$6,$7,$8) >> "fullDistList"
    runpoint=$6
  }
  firsttitle++
}
/Standard orientation/,/Rotational constants/ {
  if (($1>.5) && ($1<99)) {
    A[$1]=$4;B[$1]=$5;C[$1]=$6
  }
}
#/before annihilation/ {
#   printf("%s %.5f ",$1,$6)
# }
END {
  C5C6=Distance(5,6)
  C1C2=Distance(1,2)
  C2C3=Distance(2,3)
  C5N13C6=Angle(5,13,6)
  H12C6N13H14=Dihedral(12,6,13,14)
  if ((C5C6<1.55) && (H12C6N13H14>135))
    custom1="Benzene_NH_endo"
  if ((C5C6>2.2) && (C5N13C6>100) && (H12C6N13H14>140))
    custom1="Azepine_endo"
  if ((C5C6>=2.4) && (C5N13C6>=118) && (H12C6N13H14<=90))
    custom1="TS"
  if ((C5C6>2.4) && (C5N13C6>110) && (H12C6N13H14<15))
    custom1="Azepine_exo"
  if (Distance(6,16)<meta)
    meta=Distance(6,16)
  #ortho=Distance(3,16)
  #if (Distance(5,16)<ortho) ortho=Distance(5,16)
  #ipso=Distance(4,16)
  #Opara=Distance(1,17)
  #if (Distance(1,18)<Opara) Opara=Distance(1,18)
  #Ometa=Distance(2,17)
  #if (Distance(2,18)<Ometa) Ometa=Distance(2,18)
  #if (Distance(6,17)<Ometa) Ometa=Distance(6,17)
  #if (Distance(6,18)<Ometa) Ometa=Distance(6,18)
  #Oortho=Distance(3,17)
  #if (Distance(3,18)<Oortho) Oortho=Distance(3,18)
  #if (Distance(5,17)<Oortho) Oortho=Distance(5,17)
  #if (Distance(5,18)<Oortho) Oortho=Distance(5,18)
  #Oipso=Distance(4,17)
  #if (Distance(4,18)<Oipso) Oipso=Distance(4,18)
#NitF=Distance(16,19)
#if (Distance(16,21)<NitF) NitF=Distance(16,21)
#if (Distance(16,22)<NitF) NitF=Distance(16,22)
#if (Distance(16,23)<NitF) NitF=Distance(16,23)

#BC=Distance(1,20)
#if (Distance(2,20)<BC) BC=Distance(2,20)
#if (Distance(3,20)<BC) BC=Distance(3,20)
#if (Distance(4,20)<BC) BC=Distance(4,20)
#if (Distance(5,20)<BC) BC=Distance(5,20)
#if (Distance(6,20)<BC) BC=Distance(6,20)
#if ((Opara<Ometa) && (Opara<Oortho) && (Opara<NitF)) choice=1
#if ((Ometa<Opara) && (Ometa<Oortho) && (Ometa<NitF)) choice=2
#if ((Oortho<Ometa) && (Oortho<Opara) && (Oortho<NitF)) choice=3
#if (choice==0) printf("p",para,"m",meta,"o",ortho,"i",ipso,"NitForNO",NitF,"BC",BC)
#if (choice==1) printf("p",para,"m",meta,"o",ortho,"i",ipso,"Opara",Opara,"BC",BC)
#if (choice==2) printf("p",para,"m",meta,"o",ortho,"i",ipso,"Ometa",Ometa,"BC",BC)
#if (choice==3) printf("p",para,"m1",Distance(2,16),"o1",Distance(3,16),"i",ipso,"o2",Distance(5,16),"m2" ,Distance(6,16)) >> "fullDistList"

printf("C5C6 %.3f C1C2 %.3f C2C3 %.3f Angle(5,13,6) %.3f Dihedral(12,6,13,14) %.3f Product Stage : %s",custom1) >> "fullDistList"

if (runpoint>=1000) {
  print "Too many points. XXXX"
  } else {
    if ((C5C6<1.55) && (H12C6N13H14>140))
      print "Benzene_NH_endo reached XXXX"
    if ((C5C6>2.4) && (C5N13C6>110) && (H12C6N13H14<15))
      print "desired Azepine_exo formed XXXX"
  }

system("date +\%b:\%d:\%Y \%T")
system("tail -l Echeck | grep XXXX")

function Distance(Atom1,Atom2) {
  return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-C[Atom2])^2 + (D[Atom1]-D[Atom2])^2 + (E[Atom1]-E[Atom2])^2 + (F[Atom1]-F[Atom2])^2 + (G[Atom1]-G[Atom2])^2 + (H[Atom1]-H[Atom2])^2 + (I[Atom1]-I[Atom2])^2 + (J[Atom1]-J[Atom2])^2 + (K[Atom1]-K[Atom2])^2 + (L[Atom1]-L[Atom2])^2 + (M[Atom1]-M[Atom2])^2 + (N[Atom1]-N[Atom2])^2 + (O[Atom1]-O[Atom2])^2 + (P[Atom1]-P[Atom2])^2 + (Q[Atom1]-Q[Atom2])^2 + (R[Atom1]-R[Atom2])^2 + (S[Atom1]-S[Atom2])^2 + (T[Atom1]-T[Atom2])^2 + (U[Atom1]-U[Atom2])^2 + (V[Atom1]-V[Atom2])^2 + (W[Atom1]-W[Atom2])^2 + (X[Atom1]-X[Atom2])^2 + (Y[Atom1]-Y[Atom2])^2 + (Z[Atom1]-Z[Atom2])^2)
}
function Angle(Atom1, Atom2, Atom3) {
    value = ((Distance(Atom1, Atom3)^2 + Distance(Atom1, Atom2)^2 + Distance(Atom2, Atom3)^2) / (2 * Distance(Atom1, Atom2) * Distance(Atom2, Atom3)))
    return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }
function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }
function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1, Atom2, Atom3, Atom4) {
    B1x = A[Atom2] - A[Atom1]
    B1y = B[Atom2] - B[Atom1]
    B1z = C[Atom2] - C[Atom1]
    B2x = A[Atom3] - A[Atom2]
    B2y = B[Atom3] - B[Atom2]
    B2z = C[Atom3] - C[Atom2]
    B3x = A[Atom4] - A[Atom3]
    B3y = B[Atom4] - B[Atom3]
    B3z = C[Atom4] - C[Atom3]
    modB2 = sqrt((B2x^2) + (B2y^2) + (B2z^2))
    # yAx is x-coord. etc of modulus of B2 times B1
    yAx = modB2 * (B1x)
    yAy = modB2 * (B1y)
    yAz = modB2 * (B1z)
    # CP2 is the crossproduct of B2 and B3
    CP2x = (B2y*B3z) - (B2z*B3y)
    CP2y = (B2z*B3x) - (B2x*B3z)
    CP2z = (B2x*B3y) - (B2y*B3x)
    termY = ((yAx*CP2x) + (yAy*CP2y) + (yAz*CP2z))
    # CP is the crossproduct of B1 and B2
    CPx = (B1y*B2z) - (B1z*B2y)
    CPy = (B1z*B2x) - (B1x*B2z)
    CPz = (B1x*B2y) - (B1y*B2x)
    termX = ((CPx*CP2x) + (CPy*CP2y) + (CPz*CP2z))
    dihed4 = (180/3.141592)*atan2(termY,termX)
    return dihed4
}

function killdyn(isomer) {
    system("rm -f dyn")
}

# ............................................................................................................................
3. Details of Reaction Trajectory Simulations:

a) **TS(1→2) sampling:**

To test the statistical convergence criteria, we have presented three plots for the sampled rate-limiting **TS(1a→2a)**, **TS(1b→2b)**, and **TS(1c→2c)** structures (see Figure S4). Each characteristic 3d plot of \(d(\text{C1−C6})\) in Å, \(\theta(\text{C1−N7−C6})\) in degree, and \(\phi(\text{H13−C6−N7−R14})\) in degree are depicted for the geometric variables of sampled **TS(1a→2a)**, **TS(1b→2b)**, and **TS(1c→2c)** structures, respectively. **Figure S4** shows the rate-limiting TS-zones for valence isomerism coupled N–R inversion.

**Figure S4:** Rate-limiting **TS(1→2)** samplings. Dynamical values of \(d, \theta, \phi\) geometric variables of the chameleonic **TS(1→2)** structures are depicted at the M06-2X/6-31+G(d,p) level at 298.15 K.
b) Ambimodal nature of TS(1→2) and flyby reaction trajectories:

Valence isomerism of *endo*-benzene imine (1) → *endo*-1H-azepine (2) and *exo*-1H-azepine (3) dictates the ring expansion coupled N-inversion event. Post-transition bifurcation pathways are elucidated for 1b and 1c in Figure S5. The ambimodal rate-limiting TSs are presented that govern the reaction trajectories during the dynamical fall out either to 2 or 3-product zone (Figure S5(a) and S5(c)) in case of 1b and 1c, respectively. Figure S5(b) and S5(d) elucidate the time-resolved variations of d(C1–C6) bond lengths (in Å) for both “normal” and “flyby” reaction trajectories. Normal reaction trajectories can afford 2 or 3 product zone (via 1→2→3) whereas, flyby trajectory directly pass through the N-inversion local minimum potential energy surface to reach the 3-product zone (1→3). Interestingly, a typical “normal” reaction pathway takes a longer path to produce the *exo*-1H-azepine whereas, dynamical paths are shorter.

*Figure S5:* Representative schematic potential energy landscapes and time-resolved d(C1–C6) bond lengths (in Å) variations of reaction trajectories represent the “bifurcation” phenomena.
near the rate-limiting $\text{TS}(1b\rightarrow2b)$ and $\text{TS}(1c\rightarrow2c)$ zones at the M06-2X/6-31+G(d,p) level at 298.15 K.

In Figure S5(b), the time-resolved variations of d(C1–C6) bond lengths reveal the bifurcation point and the ambimodal behavior of the transition state $\text{TS}(1b\rightarrow2b)$ that governs the stereoselectivity of $\text{endo-}1b \rightarrow \text{endo-}2b$ and $\text{exo-}3b$ isomerism. In contrast, the DFT-calculated minimum energy pathway shows that the activation barrier for N–F inversion ($2b\rightarrow3b$) is 6.7 kcal/mol and indicates the decoupled phenomena where $2b$ is the only product from the rate-limiting $\text{TS}(1b\rightarrow2b)$. However, the reaction dynamics simulations reveal the product outcome ($2b:3b$) is 2:1. Because $2b$ can evolve as an intermediate that is activated by converting the potential energy of the rate-limiting $\text{TS}(1b\rightarrow2b)$ into kinetic energy. Such types of reaction trajectories easily pass through the N-inversion and further dynamical fall out to the $\text{exo-}3b$ product zone. Therefore, the energized $2b$ molecules (behave like entropic intermediates) get converted into $3b$ compared to the time scale for intramolecular vibrational energy redistribution (IVR). With the significant energy release from the ambimodal $\text{TS}(1b\rightarrow2b)$, the potential for nonstatistical dynamics exists. Additionally, the activation of $2b$ molecules possesses the kinetic energy of the reaction coordinate that drives it onto the caldera-like potential surfaces of non-statistical pathways (see Figure S5(a) and S5(c)). In the case of 1b, reaction trajectories pass through the initial rate-limiting $\text{TS}(1b\rightarrow2b)$ then decided to bifurcate towards two stereoisomers ($2b$ and $3b$) within 63±24 fs. In such a short period, the reaction trajectories traverse to the post-bifurcation phase and are entropically pre-decided to dynamically fall out towards stereoisomers.

Further, Figure S5(d) depicts time-resolved variations of d(C1–C6) bond lengths for “normal” and “flyby” reaction trajectories that can afford product $3c$-zone either through IRC-pathway (via product $2c$ zones) or dynamical (non-statistical) pathways traversing through the $\text{TS}(2c\rightarrow3c)$ dividing potential landscape.
c) **Methyl Rotation average time-scale at TS(2c→3c):**

![Histogram of Methyl Rotation average time-scale at TS(2c→3c)](image)

**Figure S6:** Timescale of dynamically stepwise trajectories at **TS(2c→3c)** zone.

### 3. **QMT Inputs:**

Quantum mechanical tunneling calculations are performed using the interface between Gaussian 16, Polyrate-17C, and Guassrate-17B. The CVT and CVT+SCT rates are computed at M06-2X/6-31+G(d,p) level of theory in the temperature range 10-300 K.

The input files are listed below:

- **nh.70**

  *GR|GENERAL
  GR|RESTART
  *GR|START
  CH|ARGE 0
  MU|LTIPICITY 1
  *GR|COMMON
GRENER
%mem=10GB
%nprocshared=16
%chk=guess.chk
%nproclinda=1
#N  m062x/6-31+g(d,p)
   SCF(direct,conver=9,maxcycle=2000)
   UNITS(AU) FCHK NOSYMM Integral(Grid=Ultrafine)
END

GRFIRST
%mem=10GB
%nprocshared=16
%chk=guess.chk
%nproclinda=1
#N  m062x/6-31+g(d,p)
   FORCE SCF(direct,conver=9,maxcycle=2000)
   UNITS(AU) FCHK NOSYMM Integral(Grid=Ultrafine)
END

GRSEC
%mem=10GB
%nprocshared=16
%chk=guess.chk
%nproclinda=1
#N  m062x/6-31+g(d,p)
   FREQ SCF(direct,conver=9,maxcycle=2000)
   UNITS(AU) FCHK NOSYMM Integral(Grid=Ultrafine)
END
nh.71

%mem=10GB
%nprocshared=16
%nproclinda=1

#N m062x/6-31+g(d,p) Opt FCHK NOSYMM SCF(conver=9,maxcycle=2000)

Product: endo-1H-azepine (endo-2)

|    |     |     |     |     |
|----|-----|-----|-----|-----|
| 0  | 1   |     |     |     |
| C  | 0.27921600 | -1.38676700 | 0.68119200 |
| C  | 0.27921600 | -1.38676700 | -0.68119200 |
| C  | -0.25782300 | -0.32325000 | -1.50566800 |
| C  | -0.25782300 | -0.32325000 | 1.50566800 |
| C  | -0.25782300 | 0.97694200 | -1.14839200 |
| C  | -0.25782300 | 0.97694200 | 1.14839200 |
| H  | 0.58298000 | -2.30064200 | 1.18598700 |
| H  | 0.58298000 | -2.30064200 | -1.18598700 |
| H  | -0.70642000 | -0.60056100 | -2.45671300 |
| H  | -0.70642000 | -0.60056100 | 2.45671300 |
| H  | -0.77288100 | 1.73316700 | -1.73517600 |
| H  | -0.77288100 | 1.73316700 | 1.73517600 |
| N  | 0.46350600 | 1.44639300 | 0.00000000 |
| H  | 1.38524600 | 1.00822500 | 0.00000000 |
%mem=10GB
%nprocshared=16
%nproclinda=1
#N m062x/6-31+g(d,p) Opt FCHK NOSYMM SCF(conver=9,maxcycle=2000)

Reactant - endo-benzene imine (R = H)

0 1
C   0.01383700 -1.44426900  0.72583500
C   0.23586700 -0.30762400  1.42299700
C   0.23586700  1.00724500  0.77126000
C   0.23586700  1.00724500 -0.77126000
C   0.23586700 -0.30762400 -1.42299700
C   0.01383700 -1.44426900 -0.72583500
H   -0.03735100 -2.39701200  1.24355200
H   0.43036400 -0.34458400  2.49075000
H   0.43036400 -0.34458400 -2.49075000
H   -0.03735100 -2.39701200 -1.24355200
H   0.73467100  1.82214400 -1.28756800
H   0.73467100  1.82214400  1.28756800
N   -0.92206700  1.43890500  0.00000000
H   -1.62773700  0.70234800  0.00000000
nh.75

%mem=10GB
%nprocshared=16
%nproclinda=1

#N  m062x/6-31+g(d,p)  FCHK  NOSYMM  SCF(conver=9,maxcycle=200)
Opt(TS,calcall,maxcycles=512,noeigentest)

TS : rate-limiting TS for valence isomerism

|   |          |          |          |
|---|----------|----------|----------|
|   |   0 1    |          |          |
|  C|          |          |          |
|  C| -0.07689100 | -1.41434700 | 0.70275700 |
|  C| -0.07689100 | -1.41434700 | -0.70275700 |
|  C| -0.31762700 | -0.25881200 | -1.44314100 |
|  C| -0.31762700 | -0.25881200 | 1.44314100 |
|  C| -0.07689100 | 1.02296700 | -0.93908600 |
|  C| -0.07689100 | 1.02296700 | 0.93908600 |
|  H| -0.11348800 | -2.37519100 | 1.20772000 |
|  H| -0.11348800 | -2.37519100 | -1.20772000 |
|  H| -0.76924800 | -0.34244500 | -2.42761300 |
|  H| -0.76924800 | -0.34244500 | 2.42761300 |
|  H| -0.48591900 | 1.90571900 | -1.42172900 |
|  H| -0.48591900 | 1.90571900 | 1.42172900 |
|  N| 0.96651800 | 1.27538800 | 0.00000000 |
|  H| 1.62858500 | 0.49841500 | 0.00000000 |
nh.dat

*General

TITLE
nh: Gaussrate Test Calculation
Test job
END

ATOMS
1  C
2  C
3  C
4  C
5  C
6  C
7  H
8  H
9  H
10 H
11 H
12 H
13 N
14 H
END

NOSUPERMOL

*OPTIMIZATION

OPTMIN  OHOOK
OPTTS OHOOK

*SECOND

HESSCAL HHOOK

*REACT1

INITGEO HOOKS

STATUS 0

GEOM
1
2
3
4
5
6
7
8
9
10
11
12
13
14

END
SPECIES NONLINRP

*PROD1

INITGEO HOOKS

STATUS 0

GEOM
1
2
3
4
5
6
7
8
9
10
11
12
13
14
END

SPECIES NONLINRP

*START

INITGEO HOOKS
STATUS  0

GEOM
1
2
3
4
5
6
7
8
9
10
11
12
13
14
END

SPECIES NONLINTS

*PATH

SCALEMASS  1.00000
SSTEP      0.0025
NSTEPS     99999
CURV       dgrad
INH        20
RODS

S28
SIGN          reactant
IDIRECT       -1

#RPM pagem

SRANGE
  slp     2.0
  slm    -2.0
END

#COORD curv3

PRPATH
coord 5 6
xmol
freq 26 27 28 29 30 31 32 33 34 35
END

INTDEF
1-2 1-4 1-7 2-8 2-3 3-5 3-9 4-6 5-6 4-10 5-11 5-13 6-12 6-13 13-14 1-2-3 1-2-8 1-4-10 1-4-6
2-3-5 2-1-7 2-3-9 2-1-4 3-5-11 3-5-13 3-2-8 4-1-7 4-6-12 4-6-13 5-3-9 5-13-14 5-13-6 6-13-14 6-4-10 11-5-13 12-6-13 14-13-6 14-13-5 1-2-3-5 1-2-3-9 1-4-6-13 1-4-6-12 2-3-5-11 2-3-5-13 2-1-4-10 2-1-4-6 3-2-1-4 3-2-1-7 3-5-13-14 3-5-13-6 4-6-13-14 4-1-2-8 4-6-13-5 5-13-6-12 6-13-5-11 7-1-2-8 7-1-4-10 8-2-3-9 9-3-5-11 10-4-6-12 11-5-13-6 11-5-13-14 12-6-13-14
12-6-13-5 13-5-3-9 13-6-4-10
END

*TUNNEL

ZCT
SCT

QRST
harmonic
mode 36
states all
END

*RATE

BOTHK

SIGMAF 1
SIGMAR 1

TST
CVT
CUS 2

PRDELG
PRPART rtp

TEMP
10
15
20
25
30
35
ANALYSIS
77
125
143
177
200
236
298
300
END

EACT
79. 81.
123. 127.
141. 143.
148. 150.
177. 198.
200. 220.
236. 240.
298. 300.
END

GTLOG
5. *CVT and CVT+SCT rates for Valence Isomerism*:

The CVT and CVT+SCT rates were calculated on the M06-2X/6-31+G(d,p) level potential energy surfaces in the temperature range 10-300 K. The details are shown below:

| Temperature (K) | k(CVT) (s⁻¹) | k(CVT+ SCT) (s⁻¹) |
|-----------------|--------------|-------------------|
| 10              | 7.34E-03     | 8.69E-12          |
| 15              | 1.56E-01     | 2.97E-08          |
| 20              | 7.85E-03     | 1.73E-06          |
| 25              | 2.18E-02     | 1.99E-05          |
| 30              | 4.44E-02     | 1.01E-04          |
| 35              | 1.46E-02     | 3.27E-04          |
| 40              | 3.63E-02     | 8.06E-04          |
| 45              | 1.61E-02     | 1.70E-03          |
| 50              | 2.14E-02     | 3.38E-03          |
| 60              | 3.34E-02     | 1.68E-02          |
| 75              | 5.42E-02     | 1.83E+00          |
| 77              | 1.17E+00     | 3.57E+00          |
| 79              | 2.44E+00     | 6.81E+00          |
| 80              | 3.47E+00     | 9.32E+00          |
| 81              | 4.89E+00     | 1.27E+01          |
| 98              | 5.89E+02     | 1.03E+03          |
| 100             | 9.30E+02     | 1.58E+03          |
| 123             | 6.30E+04     | 8.42E+04          |
| 125             | 8.46E+04     | 1.11E+05          |
| 127             | 1.13E+05     | 1.46E+05          |
| 141             | 6.65E+05     | 8.00E+05          |
| 143             | 8.33E+05     | 9.94E+05          |
| 145             | 1.04E+06     | 1.23E+06          |
| 148             | 1.43E+06     | 1.67E+06          |
| 150             | 1.76E+06     | 2.03E+06          |
| 177             | 1.81E+07     | 1.94E+07          |
| 198             | 7.23E+07     | 7.49E+07          |
| 200             | 8.13E+07     | 8.40E+07          |
| 220             | 2.34E+08     | 2.37E+08          |
| 236             | 4.81E+08     | 4.80E+08          |
| 240             | 5.68E+08     | 5.65E+08          |
| 273             | 1.86E+09     | 1.82E+09          |
| 298             | 3.86E+09     | 3.75E+09          |
| 300             | 4.07E+09     | 3.95E+09          |
## 1d→2d

| Temperature (K) | $k$(CVT) (S$^{-1}$) | $k$(CVT+ SCT) (S$^{-1}$) |
|----------------|---------------------|--------------------------|
| 10             | 2.77E-02            | 2.00E-11                  |
| 15             | 3.79E-01            | 1.02E-07                  |
| 20             | 1.53E-02            | 7.24E-06                  |
| 25             | 3.70E-01            | 9.37E-05                  |
| 30             | 6.91E-01            | 5.18E-04                  |
| 35             | 2.13E-00            | 1.77E-03                  |
| 40             | 5.06E-01            | 4.54E-03                  |
| 45             | 2.16E-00            | 9.84E-03                  |
| 50             | 2.79E-00            | 1.96E-02                  |
| 60             | 4.16E-00            | 8.06E-02                  |
| 75             | 6.46E-01            | 2.92E+00                  |
| 77             | 1.39E+00            | 5.21E+00                  |
| 79             | 2.88E+00            | 9.23E+00                  |
| 80             | 4.09E+00            | 1.22E+01                  |
| 81             | 5.75E+00            | 1.62E+01                  |
| 98             | 6.72E+00            | 1.01E+03                  |
| 100            | 1.06E+00            | 1.53E+03                  |
| 123            | 6.99E+00            | 7.43E+04                  |
| 125            | 9.37E+00            | 9.80E+04                  |
| 127            | 1.24E+01            | 1.28E+05                  |
| 141            | 7.27E+00            | 6.94E+05                  |
| 143            | 9.11E+00            | 8.62E+05                  |
| 145            | 1.13E+01            | 1.06E+06                  |
| 148            | 1.56E+01            | 1.45E+06                  |
| 150            | 1.91E+01            | 1.76E+06                  |
| 177            | 1.94E+01            | 1.70E+07                  |
| 198            | 7.69E+07            | 6.62E+07                  |
| 200            | 8.64E+07            | 7.43E+07                  |
| 220            | 2.47E+08            | 2.11E+08                  |
| 236            | 5.06E+08            | 4.32E+08                  |
| 240            | 5.97E+08            | 5.09E+08                  |
| 273            | 1.94E+09            | 1.66E+09                  |
| 298            | 4.01E+09            | 3.45E+09                  |
| 300            | 4.23E+09            | 3.64E+09                  |
6. NBO analyses:

Table ST5: The change in hybridization for Nitrogen for the valence isomerism in 1a at M06-2X/6-31+G(d,p) level of theory.

|                  | N-hybridization |                  |
|------------------|-----------------|------------------|
| 1a               |                 | TS(1a→2a)        |
| s(34.77%)        | p 1.87(65.03%)  | s(25.62%)        |
| d 0.01(0.20%)    |                 | d 0.01(0.20%)    |

7. Cartesian coordinates, Energies, and Harmonic Frequencies:

All the geometry minimizations, energy calculations, and harmonic frequencies determinations were performed using the following Gaussian 16 keywords at the M06-2X/6-31+G(d,p) level of theory in the gas phase at 298.15 K.

For Minima: #p opt freq m062x 6-31+g(d,p) int=grid=ultrafine symm=veryloose

For Saddle Points: # p opt=(ts,calcall,noeigentest) freq m062x 6-31+g(d,p) int=grid=ultrafine symm=veryloose

The optimized coordinates are presented with their corresponding energies and harmonic frequencies:

1a

|        | C               | C               | C               | C               | C               | C               | H               | H               | H               | N               | H               |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|        | 0.01383700      | -1.44426900     | 0.72583500      | 0.23586700      | -0.30762400     | 1.42299700      | -0.03735100    | -2.39701200    | 1.24355200     | -0.92206700    | -1.62773700    |
|        | 0.23586700      | 1.00724500      | 0.77126000      | 0.23586700      | -0.30762400     | -1.42299700     | 0.43036400     | -0.34458400    | 2.49075000     | 0.73467100     | 1.82214400     |
|        | 0.23586700      | 1.00724500      | -0.77126000     | 0.23586700      | -0.30762400     | -1.42299700     | 0.43036400     | -0.34458400    | -2.49075000    | 0.73467100     | 1.82214400     |
|        | 0.01383700      | -1.44426900     | -0.72583500     | -0.03735100     | -2.39701200     | 1.24355200      | 0.43036400     | -0.34458400    | 2.49075000     | -0.92206700    | 1.43890500     |
|        | -0.03735100     | -2.39701200     | 1.24355200      | 0.43036400      | -0.34458400     | 2.49075000      | 0.73467100     | 1.82214400     | 1.28756800     | -1.62773700    | 0.70234800     |
|        | -0.03735100     | -2.39701200     | -1.24355200     | 0.73467100      | 1.82214400      | 1.28756800      | -0.92206700    | 1.43890500     | 0.00000000     | 0.70234800     | 0.00000000     |

ENERGY = -287.4242593 (Hartree)

Thermochemistry:

Zero-point correction= 0.118437 (Hartree)
Thermal correction to Energy= 0.123645 (Hartree)
Thermal correction to Enthalpy = 0.124589 (Hartree)
Thermal correction to Gibbs Free Energy = 0.089803 (Hartree)
Sum of electronic and zero-point Energies = -287.305822 (Hartree)
Sum of electronic and thermal Energies = -287.300615 (Hartree)
Sum of electronic and thermal Enthalpies = -287.299670 (Hartree)
Sum of electronic and thermal Free Energies = -287.334456 (Hartree)

Frequencies (cm\(^{-1}\)):
258.6498, 303.6130, 462.3557, 527.5591, 614.4241, 633.8857, 707.0547, 768.6192, 801.0097, 886.5917, 936.5817, 942.1499, 979.9641, 1001.0097, 1142.7241, 1155.8152, 1189.0366, 1190.8265, 1226.9367, 1313.1410, 1365.9197, 1394.2224, 1447.2078, 1478.4589, 1638.4162, 1719.9870, 3190.6156, 3196.3220, 3209.4396, 3215.4709, 3227.0827, 3235.6515, 3522.8030

ENERGY = -287.418084 (Hartree)

Thermochemistry:
Zero-point correction = 0.118120 (Hartree)
Thermal correction to Energy = 0.123371 (Hartree)
Thermal correction to Enthalpy = 0.124315 (Hartree)
Thermal correction to Gibbs Free Energy = 0.089448 (Hartree)
Sum of electronic and zero-point Energies = -287.299964 (Hartree)
Sum of electronic and thermal Energies = -287.294714 (Hartree)
Sum of electronic and thermal Enthalpies = -287.293769 (Hartree)
Sum of electronic and thermal Free Energies = -287.328637 (Hartree)

Frequencies (cm\(^{-1}\)):
246.2257, 304.9518, 454.3909, 522.7693, 610.0590, 636.3867, 709.9226, 792.0032, 798.3669, 867.7043, 924.9839, 930.0415, 993.4035, 1005.3096, 1123.0332, 1150.8623, 1205.3715, 1209.1183, 1251.9642, 1366.4537, 1431.7995, 1455.1571, 1491.6251, 1660.4651, 1735.0353, 3175.2876, 3182.3036, 3204.9543, 3210.9208, 3223.7543, 3232.5549, 3554.4599

2a
C  0.27921600 -1.38676700  0.68119200
C  0.27921600 -1.38676700 -0.68119200
C -0.25782300 -0.32325000 -1.50566800
C -0.25782300 -0.32325000  1.50566800
C -0.25782300  0.97694200 -1.14839200
C -0.25782300  0.97694200  1.14839200
ENERGY = -287.4226241 (Hartree)

Thermochemistry:

Zero-point correction= 0.117575 (Hartree)
Thermal correction to Energy= 0.123180 (Hartree)
Thermal correction to Enthalpy= 0.124125 (Hartree)
Thermal correction to Gibbs Free Energy= 0.088582 (Hartree)
Sum of electronic and zero-point Energies= -287.305050 (Hartree)
Sum of electronic and thermal Energies= -287.299444 (Hartree)
Sum of electronic and thermal Enthalpies= -287.298500 (Hartree)
Sum of electronic and thermal Free Energies= -287.334042 (Hartree)

Frequencies (cm⁻¹):
249.1554, 264.7556, 360.9948, 425.7556, 444.8373, 631.7481, 706.6276, 765.4856, 792.1492, 829.9093, 881.0607, 896.9337, 978.8203, 983.8043, 989.4477, 1012.1235, 1023.8143, 1092.4987, 1125.0220, 1234.1845, 1248.9828, 1258.4232, 1359.7954, 1423.2265, 1424.7878, 1486.1707, 1605.7628, 1696.1046, 1699.5655, 3187.1054, 3194.8187, 3197.7715, 3208.7300, 3215.4912, 3219.8070, 3493.5924

ENERGY = -287.4267927 (Hartree)

Thermochemistry:

Zero-point correction= 0.117424 (Hartree)
Thermal correction to Energy= 0.123299 (Hartree)
Thermal correction to Enthalpy= 0.124243 (Hartree)
Thermal correction to Gibbs Free Energy= 0.088101 (Hartree)
Sum of electronic and zero-point Energies= -287.309369 (Hartree)
Sum of electronic and thermal Energies = -287.303494 (Hartree)
Sum of electronic and thermal Enthalpies = -287.302549 (Hartree)
Sum of electronic and thermal Free Energies = -287.338692 (Hartree)

Frequencies (cm\(^{-1}\)):
169.5645, 260.7813, 368.8234, 391.4298, 425.0446, 603.9315, 625.8652, 739.4565, 753.8918, 801.5064, 893.1835, 910.8110, 962.9890, 984.6410, 989.0197, 1012.5995, 1237.2872, 1244.3256, 1287.6313, 1372.6371, 1445.9481, 1484.8746, 1721.8196, 1724.0983, 1770.2439, 3180.6582, 3184.5298, 3184.6609, 3201.4742, 3220.2391, 3222.1713, 3660.5975

TS(1a→2a)

| Element | X1 | Y1 | Z1          |
|---------|----|----|-------------|
| C       | -0.07689100 | -1.41434700 | 0.70275700  |
| C       | -0.07689100 | -1.41434700 | -0.70275700 |
| C       | -0.31762700 | -0.25881200 | -1.44314100 |
| C       | -0.31762700 | -0.25881200 | 1.44314100  |
| C       | -0.07689100 | 1.02296700  | -0.93908600 |
| C       | -0.07689100 | 1.02296700  | 0.93908600  |
| H       | -0.11348800 | -2.37519100 | 1.20772000  |
| H       | -0.11348800 | -2.37519100 | -1.20772000 |
| H       | -0.76924800 | -0.34244500 | 2.42761300  |
| H       | -0.76924800 | -0.34244500 | -2.42761300 |
| H       | -0.48591900 | 1.90571900  | -1.42172900 |
| H       | -0.48591900 | 1.90571900  | 1.42172900  |
| N       | 0.96651800  | 1.27538800  | 0.00000000  |
| H       | 1.62858500  | 0.49841500  | 0.00000000  |

ENERGY = -287.4159216 (Hartree)

Thermochemistry:

| Term                          | Value (Hartree) |
|-------------------------------|-----------------|
| Zero-point correction        | 0.116914        |
| Thermal correction to Energy | 0.121900        |
| Thermal correction to Enthalpy| 0.122844        |
| Thermal correction to Gibbs Free Energy | 0.088433 (Hartree) |
| Sum of electronic and zero-point Energies | -287.299008 (Hartree) |
| Sum of electronic and thermal Energies | -287.294022 (Hartree) |
| Sum of electronic and thermal Enthalpies | -287.293077 (Hartree) |
| Sum of electronic and thermal Free Energies | -287.327488 (Hartree) |

Frequencies (cm\(^{-1}\)):
-398.7517, 319.5200, 338.4283, 469.7505, 479.0026, 647.7994, 705.7995, 739.7405, 812.4582, 859.9675, 888.7460, 955.5336, 972.4486, 983.1734, 998.6852, 1006.0040, 1046.6583, 1116.1854, 1134.2014, 1203.5114, 1218.7812, 1310.1988, 1311.5042, 1380.0553, 1415.7111, 1480.6940, 1500.5523, 1584.4334, 1645.2614, 3201.2361, 3206.2469, 3210.7744, 3218.9590, 3223.3768, 3230.3981, 3503.4829

TS(2a→3a)

| Element | X1          | Y1          | Z1          |
|---------|-------------|-------------|-------------|
| C       | 0.26875600  | -1.43265900 | 0.67448200  |
| C       | 0.26875600  | -1.43265900 | -0.67448200 |
| C       | -0.20788600 | -0.34880100 | -1.52703200 |
| C       | -0.20788600 | -0.34880100 | 1.52703200  |
| C       | -0.20788600 | 0.95653900  | -1.21820400 |
| C       | -0.20788600 | 0.95653900  | 1.21820400  |
| H       | 0.58040300  | -2.34207300 | 1.18321000  |

S38
ENERGY = -287.4188118 (Hartree)

Thermochemistry:
Zero-point correction= 0.116143 (Hartree)
Thermal correction to Energy= 0.121733 (Hartree)
Thermal correction to Enthalpy= 0.122677 (Hartree)
Thermal correction to Gibbs Free Energy= 0.086992 (Hartree)
Sum of electronic and zero-point Energies= -287.302669 (Hartree)
Sum of electronic and thermal Energies= -287.297079 (Hartree)
Sum of electronic and thermal Enthalpies= -287.296135 (Hartree)
Sum of electronic and thermal Free Energies= -287.331820 (Hartree)

Frequencies (cm\(^{-1}\)):
-354.4014, 210.8092, 226.8752, 376.1911, 435.4660, 469.5127, 624.8534, 763.1520, 767.5035, 796.2805, 857.9072, 910.7279, 946.2501, 980.0059, 983.2673, 1004.4454, 1020.1773, 1034.7961, 1050.9708, 1065.9708, 1071.4500, 1098.6059, 1151.0061, 1244.0526, 1256.6268, 1308.9077, 1318.1543, 1440.5555, 1446.1903, 1480.3644, 1695.9708, 1714.5102, 1737.8807, 3159.3775, 3163.3766, 3182.9823, 3195.3590, 3200.1467, 3208.8848, 3605.1480

TS(1a→4a)

|        |        |        |
|--------|--------|--------|
| C      | 0.01067200 | -1.45457700 |
| C      | 0.21998300 | -0.32844500 |
| C      | 0.21998300 | 1.00004200 |
| C      | 0.21998300 | -0.32844500 |
| C      | 0.01067200 | -1.45457700 |
| H      | -0.02465500 | -2.41436900 |
| H      | 0.42918700 | -0.38323400 |
| H      | 0.42918700 | -0.38323400 |
| H      | -0.02465500 | -2.41436900 |
| H      | 0.79501300 | 1.78739000 |
| H      | 0.79501300 | 1.78739000 |
| N      | -0.86011800 | 1.37987100 |
| H      | -1.78593400 | 1.75707800 |

ENERGY = -287.3931021 (Hartree)

Thermochemistry:
Zero-point correction= 0.115968 (Hartree)
Thermal correction to Energy= 0.121189 (Hartree)
Thermal correction to Enthalpy= 0.122133 (Hartree)
Thermal correction to Gibbs Free Energy= 0.087303 (Hartree)
Sum of electronic and zero-point Energies= -287.277134 (Hartree)
Sum of electronic and thermal Energies= -287.271913 (Hartree)
Sum of electronic and thermal Enthalpies = -287.270969 (Hartree)
Sum of electronic and thermal Free Energies = -287.305800 (Hartree)

Frequencies (cm⁻¹):
-909.2582,  249.5635,  309.4938,  458.0235,  526.3716,  566.7340,  639.4821,  701.5684,  748.0387,  776.3542,  782.0009,  833.0352,  860.9021,  895.6778,  956.3940,  988.2543,  1008.5507,  1024.5432,  1043.2242,  1096.3267,  1179.3785,  1198.6550,  1234.0172,  1319.2598,  1366.8170,  1428.4193,  1451.3875,  1502.3604,  1648.1292,  1724.7495,  3103.8365,  3110.0115,  3196.0459,  3200.8313,  3215.3989,  3225.8868,  3796.9893

TS(4a→3a)

C       0.19089700  -1.42208800   0.70397800
C       0.19089700  -1.42208800   -0.70397800
C       -0.25172300 -0.33562700   1.44573000
C       -0.25172300  0.96518500   -0.92839000
H       0.30525000  -2.38028500   1.20310200
H       0.30525000  -2.38028500     1.20310200
H       -0.71699200  -0.50178500  -2.41342100
H       -0.71699200  -0.50178500    2.41342100
H       -0.84763400   1.74660400   -1.39457000
H       -0.84763400   1.74660400     1.39457000
N       0.76803400   1.34672400     0.00000000
H       0.89309300   2.35423100     0.00000000

ENERGY = -287.4079435 (Hartree)

Thermochemistry:
Zero-point correction =  0.116590 (Hartree)
Thermal correction to Energy =  0.121613 (Hartree)
Thermal correction to Enthalpy =  0.122558 (Hartree)
Thermal correction to Gibbs Free Energy =  0.088086 (Hartree)
Sum of electronic and zero-point Energies = -287.291357 (Hartree)
Sum of electronic and thermal Energies = -287.286334 (Hartree)
Sum of electronic and thermal Enthalpies = -287.285389 (Hartree)
Sum of electronic and thermal Free Energies = -287.319861 (Hartree)

Frequencies (cm⁻¹):
-482.8170,  305.9606,  343.6094,  469.3884,  475.9735,  659.6996,  706.5749,  712.3293,  792.9138,  847.8765,  887.3548,  929.2657,  940.8313,  986.6100,  999.9664,  1003.4444,  1014.0006,  1080.5936,  1133.1724,  1210.6090,  1217.0826,  1240.7846,  1269.9128,  1370.8170,  1451.6470,  1500.8266,  1504.2950,  1598.0073,  1658.3719,  3185.7060,  3189.6195,  3200.2203,  3209.3580,  3217.4037,  3224.9899,  3578.4339

1b
C      -0.54946300   1.45168100   0.72512700
C      -0.54946300   0.29793000   1.42261300
C      -0.35646500  -0.99910600   0.76639200
C      -0.35646500  -0.99910600   -0.76639200
C      -0.54946300   0.29793000  -1.42261300
C      -0.54946300   1.45168100   -0.72512700
H      -0.65984900   2.39772700   1.24575200
H      -0.71006700   0.29435000   2.49546200
ENERGY = -386.56673 (Hartree)

Thermochemistry:
Zero-point correction = 0.109317 (Hartree)
Thermal correction to Energy = 0.115255 (Hartree)
Thermal correction to Enthalpy = 0.116199 (Hartree)
Thermal correction to Gibbs Free Energy = 0.079529 (Hartree)
Sum of electronic and zero-point Energies = -386.457422 (Hartree)
Sum of electronic and thermal Energies = -386.451484 (Hartree)
Sum of electronic and thermal Enthalpies = -386.450540 (Hartree)
Sum of electronic and thermal Free Energies = -386.487210 (Hartree)

Frequencies (cm⁻¹):
198.9900, 228.9230, 352.9999, 528.7530, 573.5600, 619.2933, 674.0990, 698.0683, 777.7570, 802.8403, 863.6175, 916.0549, 964.5290, 1001.9444, 1045.6717, 1060.1468, 1093.8973, 1140.7302, 1192.3289, 1211.5998, 1273.8591, 1357.7672, 1381.0790, 1435.8599, 1475.2913, 1653.9914, 1734.0220, 3198.3473, 3203.7014, 3213.9685, 3222.7025, 3235.2767, 3240.6089

ENERGY = -386.5655587 (Hartree)

Thermochemistry:
Zero-point correction = 0.108517 (Hartree)
Thermal correction to Energy = 0.114931 (Hartree)
Thermal correction to Enthalpy = 0.115875 (Hartree)
Thermal correction to Gibbs Free Energy = 0.078119 (Hartree)
Sum of electronic and zero-point Energies = -386.457042 (Hartree)
Sum of electronic and thermal Energies = -386.450628 (Hartree)
Sum of electronic and thermal Enthalpies = -386.449684 (Hartree)
Sum of electronic and thermal Free Energies = -386.487440 (Hartree)

Frequencies (cm⁻¹):
127.8957, 234.9266, 306.5399, 355.4003, 402.6720, 503.4847, 517.6195, 655.6041, 707.0937, 795.4266, 806.4330, 813.6768, 871.3685, 908.1460, 960.8154, 991.4783, 997.9419, 1022.4040, 1029.3472, 1037.6533, 1181.4654, 1244.9368, 1252.7469, 1326.0767, 1389.9368, 1434.0429, 1497.5786, 1586.3396, 1700.5702, 1709.9900, 3192.8054, 3196.4043, 3205.4346, 3219.3762, 3222.6100, 3227.0961
ENERGY = -386.5679107 (Hartree)

Thermochemistry:
Zero-point correction= 0.108042 (Hartree)
Thermal correction to Energy= 0.114505 (Hartree)
Thermal correction to Enthalpy= 0.115449 (Hartree)
Thermal correction to Gibbs Free Energy= 0.077596 (Hartree)
Sum of electronic and zero-point Energies= -386.459869 (Hartree)
Sum of electronic and thermal Energies= -386.453406 (Hartree)
Sum of electronic and thermal Enthalpies= -386.452462 (Hartree)
Sum of electronic and thermal Free Energies= -386.490315 (Hartree)

Frequencies (cm\(^{-1}\)):
134.4414, 281.2473, 324.4048, 378.0249, 395.1971, 437.3873, 454.9405, 624.8226, 704.0283, 723.4210, 741.2310, 816.2676, 897.9915, 916.4217, 954.4441, 959.8069, 988.1986, 1011.3722, 1029.7957, 1094.5853, 1145.0986, 1210.8723, 1236.1758, 1254.9081, 1352.2330, 1416.5977, 1466.1295, 1678.3636, 1713.3794, 1742.8656, 3193.0904, 3210.0879, 3220.3483, 3222.8301, 3240.3649, 3242.1371

ENERGY = -386.5669751 (Hartree)

Thermochemistry:
Zero-point correction= 0.108944 (Hartree)
Thermal correction to Energy= 0.115016 (Hartree)
Thermal correction to Enthalpy= 0.115961 (Hartree)
Thermal correction to Gibbs Free Energy= 0.078899 (Hartree)
Sum of electronic and zero-point Energies= -386.458031 (Hartree)
Sum of electronic and thermal Energies= -386.451959 (Hartree)
Sum of electronic and thermal Enthalpies$= -386.451015 \text{ (Hartree)}$

Sum of electronic and thermal Free Energies$= -386.488076 \text{ (Hartree)}$

Frequencies (cm$^{-1}$):
180.3201, 277.1661, 314.0481, 385.3073, 455.2930, 543.7889, 619.8777, 631.6090, 676.1274, 793.1834, 811.1491, 907.8441, 912.6167, 995.9773, 1003.9863, 1008.9374, 1028.9809, 1046.2795, 1087.2739, 1117.5533, 1189.1740, 1205.8534, 1241.4097, 1349.1216, 1396.0937, 1432.1567, 1470.5014, 1661.2997, 1734.8517, 3213.6346, 3220.5668, 3222.9217, 3228.2010, 3236.0461, 3241.5210

$\text{TS}(1b \rightarrow 2b)$

C 0.61810000 1.40752400 0.70086500
C 0.61810000 1.40752400 -0.70086500
C 0.61810000 0.23114700 -1.43473700
C 0.61810000 0.23114700 1.43473700
H 0.83089900 2.34029100 -1.21443900
H 0.83089900 2.34029100 1.21443900
H 1.02713200 0.23556400 -2.44069100
H 1.02713200 0.23556400 2.44069100
H 0.41181800 -1.92541200 -1.48208800
H 0.41181800 -1.92541200 1.48208800
N -0.86624100 -1.17671100 0.00000000
F -1.73232600 -0.06948400 0.00000000

ENERGY$= -386.5561368 \text{ (Hartree)}$

Thermochemistry:
Zero-point correction$= 0.107656 \text{ (Hartree)}$
Thermal correction to Energy$= 0.113387 \text{ (Hartree)}$
Thermal correction to Enthalpy$= 0.114331 \text{ (Hartree)}$
Thermal correction to Gibbs Free Energy$= 0.078019 \text{ (Hartree)}$

Sum of electronic and zero-point Energies$= -386.448481 \text{ (Hartree)}$
Sum of electronic and thermal Energies$= -386.442750 \text{ (Hartree)}$
Sum of electronic and thermal Enthalpies$= -386.441806 \text{ (Hartree)}$
Sum of electronic and thermal Free Energies$= -386.478117 \text{ (Hartree)}$

Frequencies (cm$^{-1}$):
-421.1720, 219.2778, 252.4982, 392.1540, 421.1367, 512.8878, 547.3421, 683.4650, 684.5907, 787.2638, 817.6951, 881.8120, 899.1167, 903.4299, 958.4936, 967.6013, 1004.5155, 1009.6335, 1010.8439, 1100.7540, 1154.7398, 1207.7860, 1240.0637, 1272.8882, 1367.3400, 1398.4325, 1490.4069, 1493.3003, 1594.2768, 1669.0528, 3204.8185, 3210.0993, 3215.8066, 3223.1709, 3226.1550, 3232.8377

$\text{TS}(2b \rightarrow 3b)$

C 0.50759700 1.74364000 0.67176400
C 0.50759700 1.74364000 -0.67176400
C 0.50759700 0.57678800 -1.56743100
C 0.50759700 0.57678800 1.56743100
C 0.05334800 -0.64705500 -1.26712800
C 0.05334800 -0.64705500 1.26712800
H 0.52723000 2.70901600 1.17191800
H 0.52723000 2.70901600 -1.17191800
H 0.91107500 0.71702600 -2.56564300
H 0.91107500 0.71702600 2.56564300
H 0.05498400 -1.45768000 -1.99336500
H 0.05498400 -1.45768000 1.99336500
N -0.36477500 -1.02515600 0.00000000
**ENERGY** = -386.55342 (Hartree)

**Thermochemistry:**
- Zero-point correction = 0.107442 (Hartree)
- Thermal correction to Energy = 0.113754 (Hartree)
- Thermal correction to Enthalpy = 0.114699 (Hartree)
- Thermal correction to Gibbs Free Energy = 0.076763 (Hartree)
- Sum of electronic and zero-point Energies = -386.445978 (Hartree)
- Sum of electronic and thermal Energies = -386.439666 (Hartree)
- Sum of electronic and thermal Enthalpies = -386.438721 (Hartree)
- Sum of electronic and thermal Free Energies = -386.476657 (Hartree)

**Frequencies (cm⁻¹):**
-294.6432, 99.1276, 225.6455, 336.6265, 377.3483, 394.1156, 445.9976, 619.8324, 690.5650, 742.5152, 765.5263, 836.3485, 861.5488, 915.2137, 951.9648, 956.5764, 978.3633, 997.0029, 1020.1459, 1126.0642, 1206.8631, 1244.4563, 1259.2583, 1376.5676, 1416.5116, 1445.6688, 1476.5669, 1692.8900, 1731.2107, 1751.2999, 3186.1945, 3189.8143, 3190.6857, 3206.9492, 3222.0268, 3224.1171

**TS(4b→3b)**

**ENERGY** = -386.5551371 (Hartree)

**Thermochemistry:**
- Zero-point correction = 0.107179 (Hartree)
- Thermal correction to Energy = 0.112994 (Hartree)
- Thermal correction to Enthalpy = 0.113938 (Hartree)
- Thermal correction to Gibbs Free Energy = 0.077358 (Hartree)
- Sum of electronic and zero-point Energies = -386.447958 (Hartree)
- Sum of electronic and thermal Energies = -386.442143 (Hartree)
- Sum of electronic and thermal Enthalpies = -386.441999 (Hartree)
- Sum of electronic and thermal Free Energies = -386.477779 (Hartree)

**Frequencies (cm⁻¹):**
-471.9734, 195.8014, 312.0077, 372.9110, 435.0566, 457.9695, 504.9130, 656.6465, 685.6430, 699.2063, 791.5707, 847.2442, 894.4167, 928.8751, 960.6020, 1001.5417, 1005.3075, 1035.0823, 1058.7712, 1099.5786, 1127.0017, 1207.2766, 1208.8725, 1224.3546, 1345.2956, 1409.2592, 1483.8574, 1486.9841, 1588.7997, 1649.1692, 3206.7047, 3217.6979, 3225.4577, 3231.0826, 3244.5029, 3246.7987

**1c**

C 0.36314600 -1.55541200 0.72525800
C 0.54740500 -0.41176300 1.42202100
ENERGY = -326.7117668 (Hartree)

Thermochemistry

Zero-point correction= 0.146196 (Hartree)
Thermal correction to Energy= 0.152844 (Hartree)
Thermal correction to Enthalpy= 0.153789 (Hartree)
Thermal correction to Gibbs Free Energy= 0.115804 (Hartree)
Sum of electronic and zero-point Energies= -326.565570 (Hartree)
Sum of electronic and thermal Energies= -326.558922 (Hartree)
Sum of electronic and thermal Enthalpies= -326.557978 (Hartree)
Sum of electronic and thermal Free Energies= -326.595963 (Hartree)

Frequencies (cm$^{-1}$):
138.4063, 225.0337, 258.6508, 353.8263, 403.5954, 501.6241, 551.3573, 604.4151, 647.8742, 684.1632, 768.8144, 804.0584, 890.1793, 907.0229, 967.3042, 975.1950, 996.6405, 1003.4709, 1023.7293, 1045.5383, 1100.5283, 1139.1301, 1165.1026, 1178.8422, 1197.4229, 1211.6564, 1360.6760, 1362.6767, 1403.7383, 1431.4066, 1452.2227, 1477.5730, 1494.7781, 1511.5036, 1642.7183, 1720.8655

2c

ENERGY = -326.7091504 (Hartree)

Thermochemistry:

Zero-point correction= 0.145241 (Hartree)
Thermal correction to Energy= 0.152437 (Hartree)
Thermal correction to Enthalpy= 0.153381 (Hartree)
Thermal correction to Gibbs Free Energy= 0.114212 (Hartree)
Sum of electronic and zero-point Energies= -326.563910 (Hartree)
Sum of electronic and thermal Energies= -326.556713 (Hartree)
Sum of electronic and thermal Enthalpies= -326.555769 (Hartree)
Sum of electronic and thermal Free Energies= -326.594938 (Hartree)

Frequencies (cm⁻¹):
117.2201, 203.8521, 296.3368, 355.7364, 462.4374, 464.6269, 526.2016, 743.8515, 1089.5824, 1149.4671, 1172.0243, 1211.9332, 1241.0709, 1286.5704, 1334.0725, 1379.6546, 1421.2325, 1459.8493, 1482.5739, 1491.7398, 1515.5582, 1574.6235, 1631.9608, 1705.2604, 1708.0191, 1708.0191, 3035.2819, 3116.2242, 3152.2449, 3165.5523, 3169.2313, 3187.3296, 3195.2078, 3199.5161, 3212.3713

3c

C  0.64058300  1.74884500  0.67426100
C  0.64058300  1.74884500
C  0.64058300  0.55018300
C  0.64058300  0.55018300  1.51103900
C  0.04009800  -0.60345600
C  0.04009800  -0.60345600  1.51103900
H  0.72227500  2.70351200  1.18934100
H  0.72227500  2.70351200
H  1.16988600  0.59267300
H  1.16988600  0.59267300  2.45870800
H  1.16988600  0.59267300  2.45870800
H  0.10674400  -1.47167300  1.84369200
H  0.10674400  -1.47167300
H  0.10674400  -1.47167300  1.84369200
N  -0.71943000  -0.78358700  0.00000000
C  -1.57103200  -1.95670300  0.00000000
H  -0.99833500  -2.89985700  0.00000000
H  -2.21196500  -1.93535100  0.88367900
H  -2.21196500  -1.93535100  -0.88367900

ENERGY = -326.7159121 (Hartree)

Thermochemistry:
Zero-point correction= 0.144997 (Hartree)
Thermal correction to Energy= 0.152285 (Hartree)
Thermal correction to Enthalpy= 0.153229 (Hartree)
Thermal correction to Gibbs Free Energy= 0.113843 (Hartree)
Sum of electronic and zero-point Energies= -326.570915 (Hartree)
Sum of electronic and thermal Energies= -326.563627 (Hartree)
Sum of electronic and thermal Enthalpies= -326.562683 (Hartree)
Sum of electronic and thermal Free Energies= -326.602069 (Hartree)

Frequencies (cm⁻¹):
126.6919, 185.9079, 240.3977, 266.9528, 362.3453, 381.0161, 393.8500, 448.7585, 632.2793, 715.8941, 752.4041, 755.1998, 825.9380, 889.4232, 907.3371, 962.0527, 963.7132, 984.0858, 996.9761, 1016.1149, 1076.6604, 1150.4835, 1213.7241, 1225.2859, 1238.1340, 1249.9114, 1351.7242, 1372.7450, 1434.5272, 1471.5963, 1472.4816, 1505.3465, 1511.0597, 1699.3064, 1704.1122, 1758.3072, 2992.3003, 3124.3480, 3146.0965, 3151.5589, 3171.5740, 3182.8429, 3201.0490, 3215.6964, 3218.0449
ENERGY = -326.7090966 (Hartree)

Thermochemistry:

Zero-point correction= 0.145786 (Hartree)
Thermal correction to Energy= 0.152491 (Hartree)
Thermal correction to Enthalpy= 0.153435 (Hartree)
Thermal correction to Gibbs Free Energy= 0.115330 (Hartree)
Sum of electronic and zero-point Energies= -326.563310 (Hartree)
Sum of electronic and thermal Energies= -326.556606 (Hartree)
Sum of electronic and thermal Enthalpies= -326.555662 (Hartree)
Sum of electronic and thermal Free Energies= -326.593767 (Hartree)

Frequencies (cm⁻¹):
176.5028, 209.0144, 273.7020, 328.0300, 352.9446, 451.6204, 549.6366, 610.0608, 640.2680, 674.9455, 789.6819, 792.1810, 891.9714, 917.8712, 977.1097, 986.0339, 989.6382, 1004.4204, 1038.8109, 1042.8000, 1117.3455, 1126.2574, 1171.6827, 1172.7786, 1208.4530, 1280.4550, 1362.6828, 1427.9186, 1441.2065, 1458.4500, 1489.0383, 1501.7284, 1504.4182, 1507.1565, 1508.2000, 1509.4182, 1655.3239, 1731.1722, 2998.0276, 3112.8346, 3148.9992, 3154.4994, 3154.7368, 3203.7419, 3209.8171, 3222.8471, 3231.5433

TS(1c→2c)

C -0.16021000 -1.56522800 0.72824900
C -0.16021000 -1.56522800 -0.72824900
C -0.55041100 -0.45368900 -1.44719400
C -0.55041100 -0.45368900 1.44719400
C -0.55041100 0.85587400 -0.96064600
C -0.55041100 0.85587400 0.96064600
H -0.05963900 -2.52085400 1.20724000
H -0.05963900 -2.52085400 -1.20724000
H -0.96919900 -0.61529500 -2.43737800
H -0.96919900 -0.61529500 2.43737800
H -1.14271100 1.62226000 -1.45657200
H -1.14271100 1.62226000 1.45657200
N 0.37525700 1.34585100 0.00000000
C 1.75113100 0.87048900 0.00000000
H 2.23686400 1.27935700 0.88900600
H 1.86817600 -0.21831200 0.00000000
H 2.23686400 1.27935700 -0.88900600
ENERGY = -326.7021832 (Hartree)

Thermochemistry:

Zero-point correction= 0.144588 (Hartree)
Thermal correction to Energy= 0.151039 (Hartree)
Thermal correction to Enthalpy= 0.151983 (Hartree)
Thermal correction to Gibbs Free Energy= 0.114400 (Hartree)
Sum of electronic and zero-point Energies= -326.557594 (Hartree)
Sum of electronic and thermal Energies= -326.551144 (Hartree)
Sum of electronic and thermal Enthalpies= -326.550200 (Hartree)
Sum of electronic and thermal Free Energies= -326.587783 (Hartree)

Frequencies (cm⁻¹):
-358.9666, 168.6407, 248.5794, 260.0830, 375.4701, 395.5302, 477.8345, 507.9874, 658.6071, 711.1703, 756.0678, 815.0838, 871.7403, 886.9207, 890.9457, 951.0973, 972.2316, 994.1298, 1004.7393, 1011.8638, 1118.1768, 1127.0730, 1165.0485, 1198.8321, 1210.3823, 1258.3137, 1369.3815, 1376.3137, 1423.3264, 1459.1207, 1484.8877, 1486.8709, 1496.0838, 1518.0973, 1594.7488, 1648.1455, 3069.9396, 3141.8006, 3164.4138, 3180.6510, 3184.1734, 3197.3637, 3202.8754, 3210.1809, 3222.1048

TS(2c→3c)

C                  0.64851600    1.60504700    0.67468000
C                  0.64851600    1.60504700    -0.67468000
C                  0.64851600    0.42518900    -1.53050000
C                  0.64851600    0.42518900    1.53050000
C                  0.17179300    -0.78929600    -1.21288500
C                  0.17179300    -0.78929600    1.21288500
H                  0.72707600    2.56383900    -1.18177300
H                  1.09231300    0.53748300    -2.51752600
H                  0.25263000    -1.59888400    -1.94014900
H                  0.25263000    -1.59888400    1.94014900
N                  -0.47156600    -1.14827900    0.00000000
C                  -1.92538800    -1.09505000    0.00000000
H                  -2.30339900    -1.61199200    -0.88734000
H                  -2.30339900    -1.61199200    0.88734000
H                  -2.30984100    -0.06391400    0.00000000

ENERGY = -326.7083362 -326.7021832 (Hartree)

Thermochemistry:

Zero-point correction= 0.144750 (Hartree)
Thermal correction to Energy= 0.151438 (Hartree)
Thermal correction to Enthalpy= 0.152382 (Hartree)
Thermal correction to Gibbs Free Energy= 0.114202 (Hartree)
Sum of electronic and zero-point Energies= -326.563587 (Hartree)
Sum of electronic and thermal Energies= -326.556899 (Hartree)
Sum of electronic and thermal Enthalpies= -326.555954 (Hartree)
Sum of electronic and thermal Free Energies= -326.594134 (Hartree)

Frequencies (cm⁻¹):
-80.2274, 187.9098, 211.1917, 221.9171, 342.2074, 354.1316, 439.5955, 442.0502, 642.3224, 719.2454, 761.7224, 794.4342, 853.6629, 866.7344, 911.2105, 963.9148, 984.4452, 996.2821, 998.4289, 1020.5285, 1091.4427, 1136.1475, 1204.1249, 1221.6587, 1247.2843, 1276.4235, 1382.1331, 1401.5463, 1428.9825, 1463.0126, 1497.9097, 1489.2202, 1520.0286, 1690.1865, 1708.9319, 1733.9916, 3017.5207, 3101.7449, 3141.1638, 3148.4553, 3152.8120, 3185.1880, 3194.0790, 3198.9359, 3211.0353
### TS(4c→3c)

| Element | X-axis | Y-axis | Z-axis |
|---------|--------|--------|--------|
| C       | 0.03552200 | -1.83265200 | 0.70483300 |
| C       | 0.03552200 | -1.83265200 | -0.70483300 |
| C       | -0.40301400 | -0.74652900 | -1.44783000 |
| C       | -0.40301400 | -0.74652900 | 1.44783000 |
| C       | -0.40301400 | 0.55404000 | 0.92481000 |
| C       | -0.40301400 | 0.55404000 | -0.92481000 |
| H       | 0.14672900 | -2.79190700 | 1.20281000 |
| H       | 0.14672900 | -2.79190700 | -1.20281000 |
| H       | -0.86507600 | -0.91098000 | 2.41730300 |
| H       | -0.86507600 | -0.91098000 | -2.41730300 |
| H       | -0.99706300 | 1.34667400 | -1.38268300 |
| H       | -0.99706300 | 1.34667400 | 1.38268300 |
| N       | 0.60572200 | 0.94568700 | 0.00000000 |
| C       | 0.90742400 | 2.36646300 | 0.00000000 |
| H       | 1.49647600 | 2.60085500 | -0.88951700 |
| H       | 1.49647600 | 2.60085500 | 0.00000000 |
| H       | 0.00000000 | 2.99382300 | 0.00000000 |

**ENERGY** = -326.7008262 (Hartree)

### Thermochemistry:

| Property                                | Value               |
|-----------------------------------------|---------------------|
| Zero-point correction                   | 0.144178 (Hartree)  |
| Thermal correction to Energy            | 0.150626 (Hartree)  |
| Thermal correction to Enthalpy          | 0.151570 (Hartree)  |
| Thermal correction to Gibbs Free Energy | 0.113942 (Hartree)  |
| Sum of electronic and zero-point Energies | -326.556648 (Hartree) |
| Sum of electronic and thermal Energies   | -326.550200 (Hartree) |
| Sum of electronic and thermal Enthalpies | -326.549256 (Hartree) |
| Sum of electronic and thermal Free Energies | -326.586884 (Hartree) |

### Frequencies (cm⁻¹):

-458.3500, 188.4247, 233.3359, 277.5236, 377.0674, 396.6475, 454.5437, 503.8294, 659.2956, 705.1025, 711.4169, 796.7005, 860.3133, 887.5645, 933.3132, 964.9630, 980.8876, 998.8373, 1007.0783, 1034.3535, 1122.5671, 1143.3978, 1162.0894, 1186.9814, 1211.5493, 1249.0254, 1292.8889, 1363.9914, 1438.6138, 1469.0847, 1489.7225, 1494.3435, 1500.5393, 1504.3356, 1595.0411, 1652.3717, 1662.7317, 2995.7193, 3121.7391, 3150.7616, 3156.0061, 3168.7068, 3198.1801, 3207.5512, 3216.2672, 3224.0076

### TS(1c→4c)

| Element | X-axis | Y-axis | Z-axis |
|---------|--------|--------|--------|
| C       | 0.32215400 | -1.71680600 | 0.72599100 |
| C       | 0.55121200 | -0.59395100 | 1.44283000 |
| C       | 0.55121200 | 0.73432000 | 0.80272000 |
| C       | 0.55121200 | 0.73432000 | -0.80272000 |
| C       | 0.55121200 | -0.59395100 | -1.44283000 |
| C       | 0.32215400 | -1.71680600 | -0.72599100 |
| H       | 0.28138100 | -2.67741100 | 1.23168600 |
| H       | 0.77630800 | -0.65675200 | 2.50474500 |
| H       | 0.77630800 | -0.65675200 | -2.50474500 |
| H       | 0.28138100 | -2.67741100 | -1.23168600 |
| H       | 1.12740100 | 1.52408800 | -1.29741800 |
| H       | 1.12740100 | 1.52408800 | 1.29741800 |
| N       | -0.52372000 | 1.10063800 | 0.00000000 |
| C       | -1.85484100 | 1.60836600 | 0.00000000 |
| H       | -2.38364500 | 1.23683600 | 0.88367900 |
| H       | -1.90313600 | 2.70832000 | 0.00000000 |
| H       | -2.38364500 | 1.23683600 | -0.88367900 |
ENERGY = -326.6820434 (Hartree)

**Thermochemistry:**
- Zero-point correction = 0.144160 (Hartree)
- Thermal correction to Energy = 0.150846 (Hartree)
- Thermal correction to Enthalpy = 0.151790 (Hartree)
- Thermal correction to Gibbs Free Energy = 0.113206 (Hartree)
- Sum of electronic and zero-point Energies = -326.537894 (Hartree)
- Sum of electronic and thermal Energies = -326.531208 (Hartree)
- Sum of electronic and thermal Enthalpies = -326.530264 (Hartree)
- Sum of electronic and thermal Free Energies = -326.568847 (Hartree)

**Frequencies (cm\(^{-1}\)):**
-298.8389, 85.8083, 185.7576, 205.9298, 394.3835, 419.8015, 513.0118, 522.8791, 652.0747, 660.5540, 747.3994, 808.9218, 888.3711, 905.3956, 965.3484, 971.3673, 983.9319, 1007.9693, 1014.7468, 1074.6581, 1080.5868, 1108.3210, 1137.9294, 1198.7412, 1201.7577, 1265.9890, 1265.3671, 1366.4091, 1427.0781, 1446.0062, 1468.0793, 1493.7939, 1517.4388, 1619.8707, 1648.8339, 1717.8060, 1771.8060, 1801.4489, 3074.0899, 3080.5733, 3086.2182, 3128.9158, 3194.7769, 3199.5624, 3214.0941, 3224.7378

9. **Codes:**

The awk-code to extract the \((d, \theta, \phi)\) geometrical variables for sampled TS structures and reaction trajectories \((1 \rightarrow 2, 3)\) is shown below:

a) **run.sh**

```
#!/usr/bin/env bash

echo -n "Enter the file name: 
read file

filedir=${pwd}
filename="${filedir}/${file}"
isomerlist=$(cat $filename | awk -F' ' '{print $3}' | sort -nu)
cd product_count
for isomer in $isomerlist
  do
cat $filename | awk -vx=$isomer '{if($3==x) print $0} > temp$isomer
header=$(awk '/Benzene_NH_endo/{print $0}' temp$isomer | wc -l)
footer=$(awk '/Azepine_exo/{print $0}' temp$isomer | wc -l)
footer_endo=$(awk '/Azepine_endo/{print $0}' temp$isomer | wc -l)
if [ $header -ge 1 -a $footer -ge 1 ];
  then
```

S50
tail -n $(echo $fileLength - $headLength - 1 | bc) temp$isomer | awk "%f%f%f\n", $5, $12, $15}' >> endo_endo_prod$isomer
eelif [ "$tailStart" == "TS" ];
  then
    head -n $headLength temp$isomer | sort -k 1 -nr | awk "%f%f%f\n", $5, $12, $15}' >> TS_endo_prod$isomer
tail -n $(echo $fileLength_endo - $headLength - 1 | bc) temp$isomer | awk "%f%f%f\n", $5, $12, $15}' >> TS_endo_prod$isomer
fi
eelif [ $header -gt 1 -a $footer -eq 0 ];
  then
cat temp$isomer > unprod_head_$isomer
eelif [ $header -eq 0 -a $footer -gt 1 ];
  then
cat temp$isomer > unprod_tail_$isomer
fi
#rm temp$isomer
done