

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)	ωb97-XD/ 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	0.0
$\Delta G_{\text{exp}}^{\ddagger}(\text{I})$	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
$\Delta G_{\text{inv}}^{\ddagger}(\text{I})$	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
$\Delta G_{\text{inv}}^{\ddagger}(\text{II})$	17.9	18.0	18.0	18.3	–	22.2
Exo-1a	3.9	3.7	3.6	3.6	3.6	3.5
$\Delta G_{\text{exp}}^{\ddagger}(\text{II})$	3.5	5.5	5.5	5.5	2.7	6.8

2. Schematic Potential Energy Surfaces:

The stereoelectronic induction at the N-site (as $-F$ in **1b** and its isolobal $-CH_3$ 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 ($1 \rightleftharpoons 2$) and *Endo-Exo* ($2 \rightleftharpoons 3$) dynamic equilibria.

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

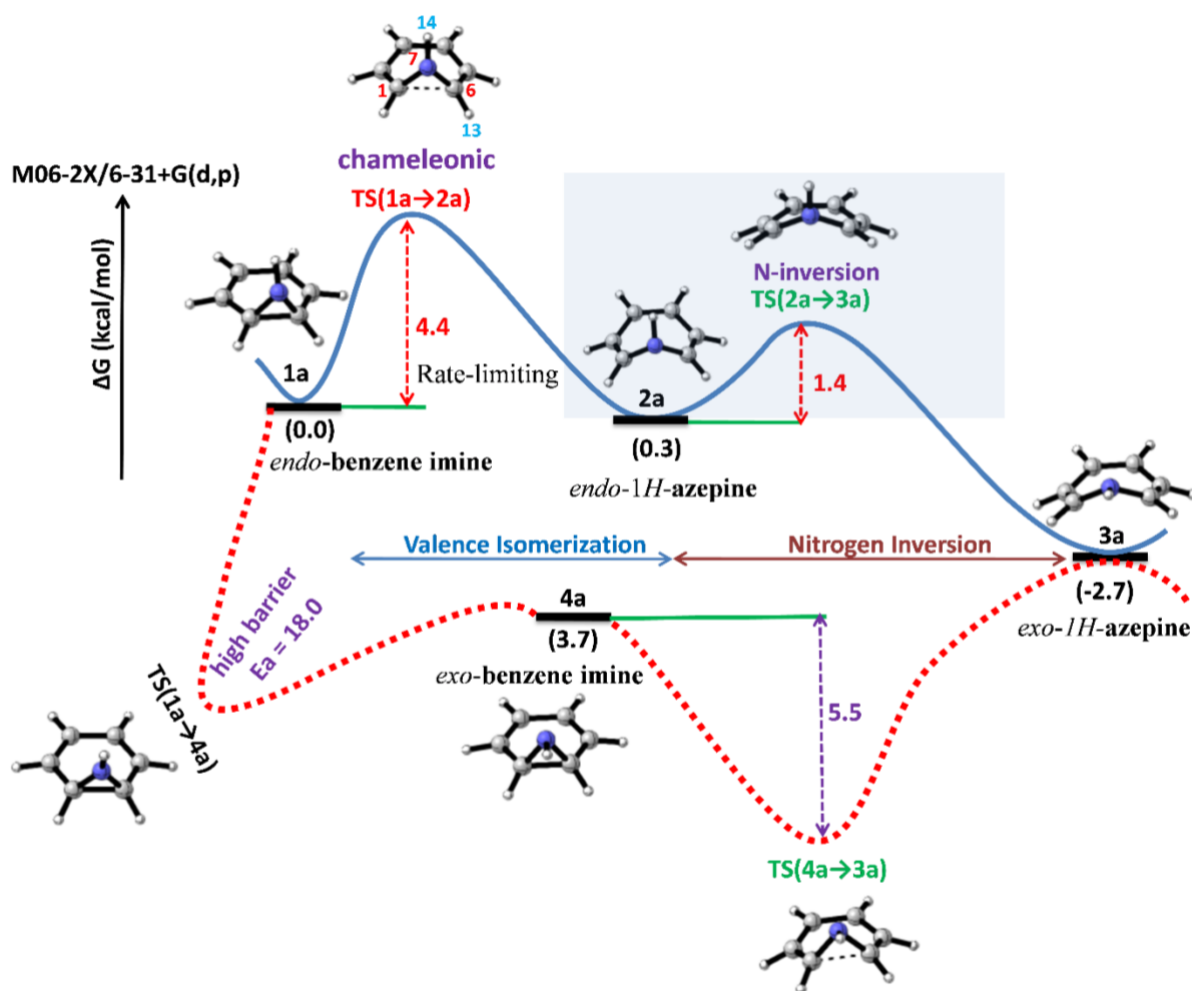


Figure S1: Reaction pathways and relative Gibbs free energy profile for valence isomerism assisted N-inversion ($1a \rightarrow 2a \rightarrow 3a$) and also connected with N-inversion followed by valence

isomerism (**1a**→**4a**→**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 (θ) of C1–N7–C6, and dihedral angle (ϕ) 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)	θ(C1–N7–C6) (in degree)	Φ(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→2a)	1.87817	82.35775	147.56230
TS(2a→3a)	2.43641	118.09088	84.87024
TS(1a→4a)	1.59343	69.66488	70.40878
TS(4a→3a)	1.85678	80.90686	8.46895

b) Potential energy surface for ($1b \rightarrow 2b, 3b, 4b$) pathways:

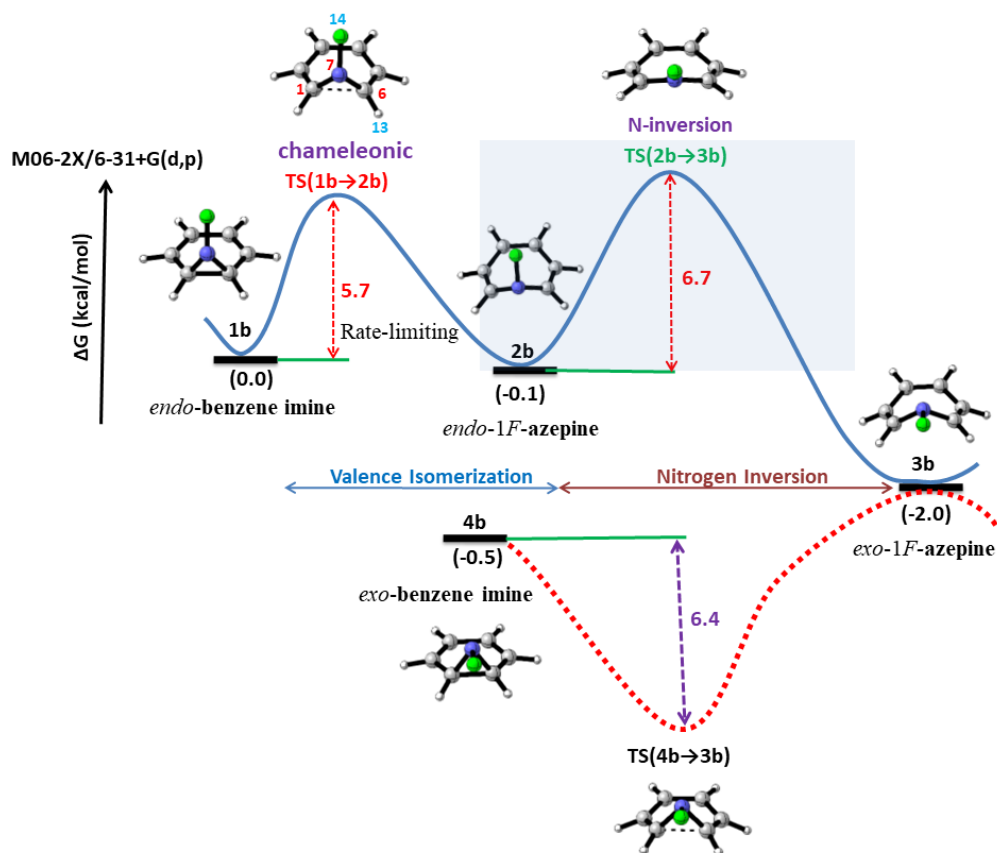


Figure S2: Reaction pathways and relative Gibbs free energy profile for valence isomerism assisted *N*-inversion ($1b \rightarrow 2b \rightarrow 3b$) and further also associated with the valence isomerism dynamic equilibrium ($3b \rightleftharpoons 4b$) at M06-2X/6-31+G(d,p) level (at 298.15 K). All these minima and saddle points are in C_s symmetry.

Table ST3: Optimized distance (d) of rate-limiting bond (C1–C6), angle (θ) of C1–N7–C6, and dihedral angle (ϕ) of H13–C6–N7–F14 for **1b** are shown at M06-2X/6-31+G(d,p) level of theory.

Minima and Saddle Points	d(C1–C6) (in Å)	θ(C1–N7–C6) (in degree)	Φ(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→2b)	1.88970	82.91321	139.27730
TS(2b→3b)	2.53426	132.03288	42.50076
TS(4b→3b)	1.86993	81.28221	3.93979

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

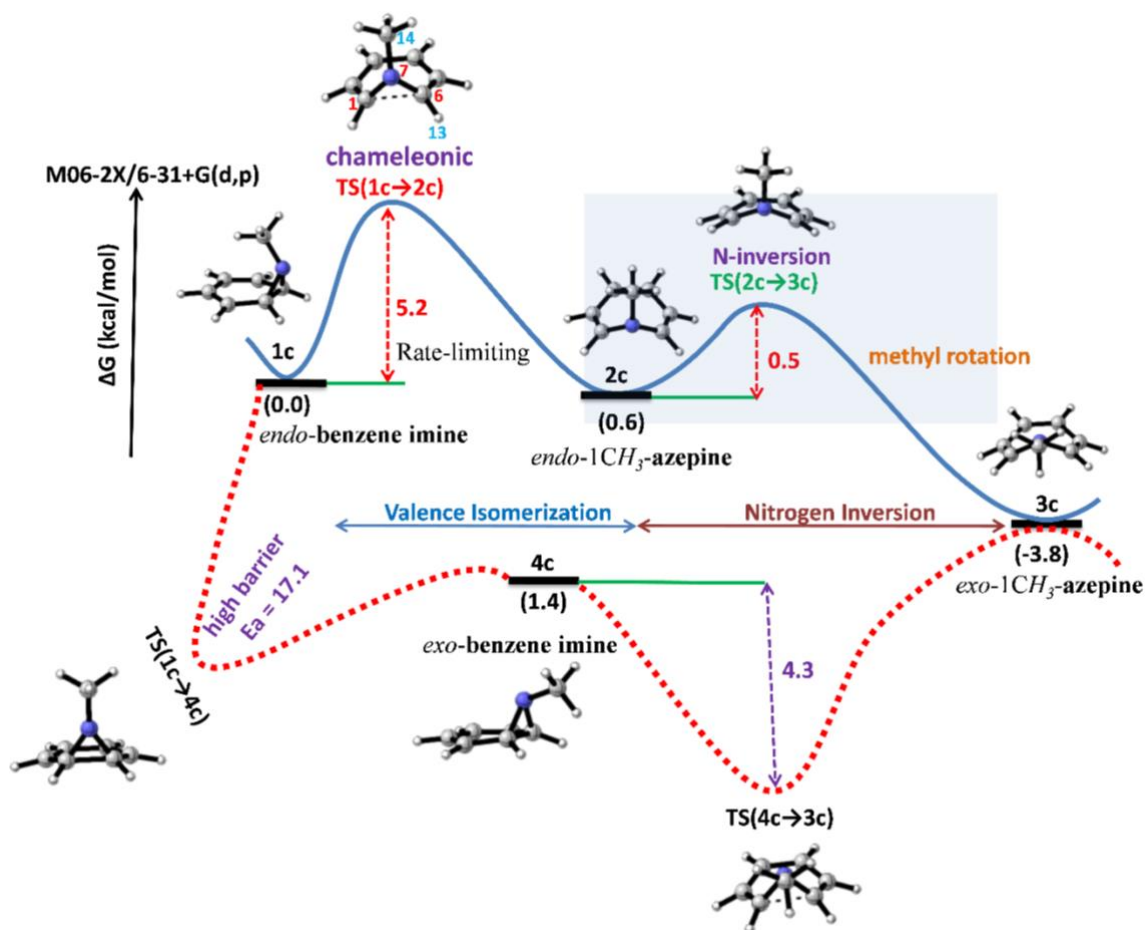


Figure S3: Reaction pathways and relative Gibbs free energy profile for valence isomerism assisted N-inversion ($1c \rightarrow 2c \rightarrow 3c$) and also connected with N-inversion followed by valence isomerism ($1c \rightarrow 4c \rightarrow 3c$) or vice versa at (M06-2X/6-31+G(d,p) level at 298.15 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.

Minima and 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 1
#NMRmethod2 B97D/6-31G*
#NMRmethod LC-wPBE/6-31G*
#NMRmethod3 B3LYP/cc-pvtz
#NMRevery 4
#NMRrand 1
#NMRcc 1
#loadlimit 10.0
#geometry linear
#rotationmode 0
**** 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 --The following "word" is copied exactly to the gaussian input file after %mem=.
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 than
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=dms0,read)
#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
**** 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

```

```

#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 applies a polynomial 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 16 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 sphereseize 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
#sphereseize 12.9
#sphereforce .01
#setting a value for empiricdispersion sets its s6 value with the Grimme 2006 algorithm.
Default is 0, with no empiricdispersion
#empiricdispersion 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

```

```

#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 .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, keepevery, and box size
#update 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 %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)

```



```

C[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.

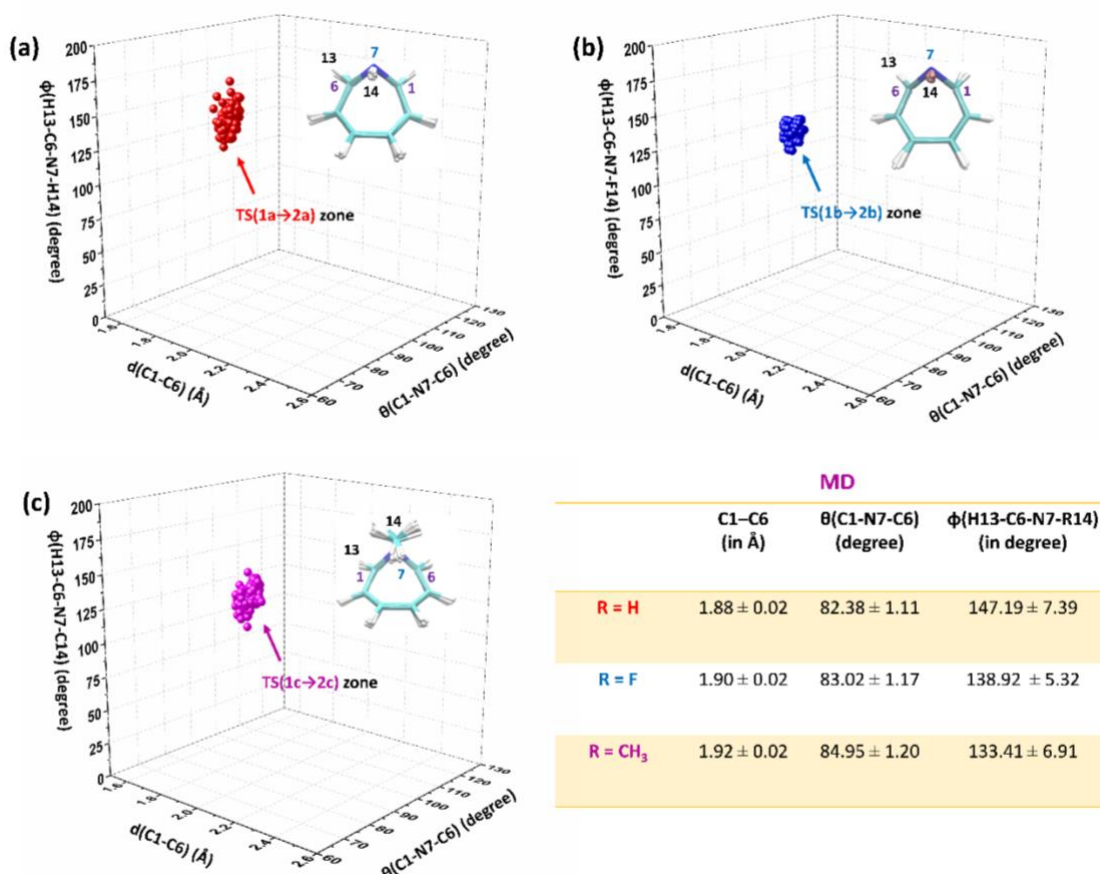


Figure S4: Rate-limiting **TS(1→2)** samplings. Dynamical values of d , θ , ϕ geometric variables of the chameleonic **TS(1→2)** structures are depicted at the M06-2X/6-31+G(d,p) level at 298.15 K.

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 $d(\text{C1-C6})$ 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.

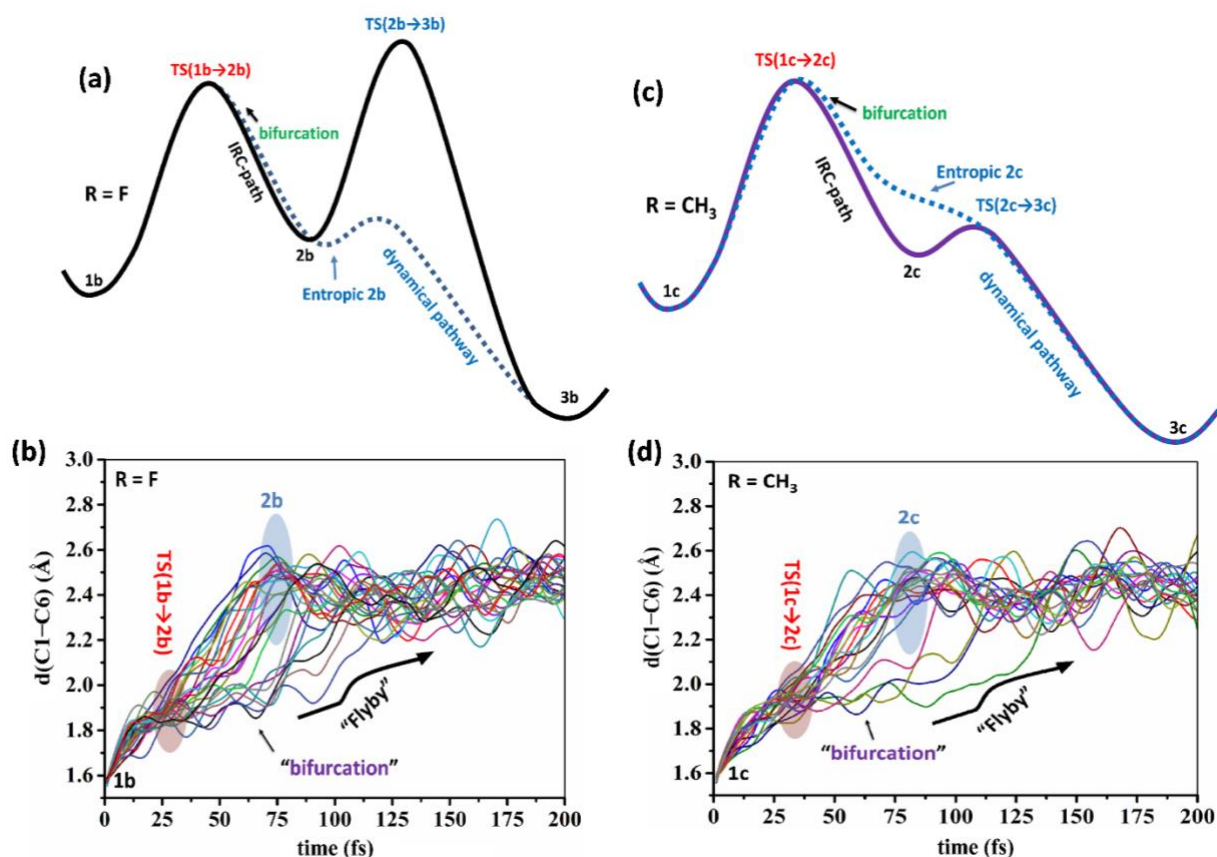


Figure S5: Representative schematic potential energy landscapes and time-resolved $d(\text{C1-C6})$ bond lengths (in Å) variations of reaction trajectories represent the “bifurcation” phenomena

near the rate-limiting $TS(1b \rightarrow 2b)$ and $TS(1c \rightarrow 2c)$ 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 $TS(1b \rightarrow 2b)$ that governs the stereoselectivity of $endo-1b \rightarrow endo-2b$ and $exo-3b$ isomerism. In contrast, the DFT-calculated minimum energy pathway shows that the activation barrier for N–F inversion ($2b \rightarrow 3b$) is 6.7 kcal/mol and indicates the decoupled phenomena where **2b** is the only product from the rate-limiting $TS(1b \rightarrow 2b)$. 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 $TS(1b \rightarrow 2b)$ into kinetic energy. Such types of reaction trajectories easily pass through the N-inversion and further dynamical fall out to the $exo-3b$ 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 $TS(1b \rightarrow 2b)$, 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 $TS(1b \rightarrow 2b)$ 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-satistical) pathways traversing through the $TS(2c \rightarrow 3c)$ dividing potential landscape.

c) Methyl Rotation average time-scale at TS(2c→3c):

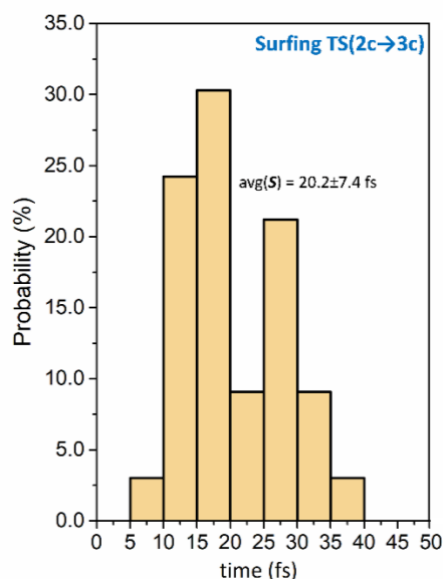


Figure S6: Timescale of dynamically stepwise trajectories at *TS(2c→3c)* zone.

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](#)

```
*GRGENERAL
GRRESTART
*GRSTART
CHARGE 0
MULTIPLICITY 1
*GRCOMMON
```

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

nh.73

%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	-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

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

40
45
50
60
75
77
79
80
81
98
100
123
125
127
141
143
145
148
150
177
198
200
220
236
240
273
298
300
END

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:

1a→2a		
Temperature (K)	k(CVT) (S⁻¹)	k(CVT+ SCT) (S⁻¹)
10	7.34E-83	8.69E-12
15	1.56E-51	2.97E-08
20	7.85E-36	1.73E-06
25	2.18E-26	1.99E-05
30	4.44E-20	1.01E-04
35	1.46E-15	3.27E-04
40	3.63E-12	8.06E-04
45	1.61E-09	1.70E-03
50	2.14E-07	3.38E-03
60	3.34E-04	1.68E-02
75	5.42E-01	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-82	2.00E-11
15	3.79E-51	1.02E-07
20	1.53E-35	7.24E-06
25	3.70E-26	9.37E-05
30	6.91E-20	5.18E-04
35	2.13E-15	1.77E-03
40	5.06E-12	4.54E-03
45	2.16E-09	9.84E-03
50	2.79E-07	1.96E-02
60	4.16E-04	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+02	1.01E+03
100	1.06E+03	1.53E+03
123	6.99E+04	7.43E+04
125	9.37E+04	9.80E+04
127	1.24E+05	1.28E+05
141	7.27E+05	6.94E+05
143	9.11E+05	8.62E+05
145	1.13E+06	1.06E+06
148	1.56E+06	1.45E+06
150	1.91E+06	1.76E+06
177	1.94E+07	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.*

1a→TS(1a→2a)	
N-hybridization	
1a	TS(1a→2a)
s(34.77%); p 1.87(65.03%); d 0.01(0.20%)	s(25.62%); p 2.90(74.18%); 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      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
```

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, 936.5842, 942.1499, 979.9641, 1001.0097, 1024.3222, 1029.1663, 1050.7423, 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

4a

C	0.03166400	-1.46219300	0.72838300
C	0.21962400	-0.32933800	1.43223500
C	0.21962400	0.98180200	0.76388700
C	0.21962400	0.98180200	-0.76388700
C	0.21962400	-0.32933800	-1.43223500
C	0.03166400	-1.46219300	-0.72838300
H	-0.00120000	-2.41891600	1.24084600
H	0.39953600	-0.36263100	2.50280600
H	0.39953600	-0.36263100	-2.50280600
H	-0.00120000	-2.41891600	-1.24084600
H	0.74192500	1.79247300	-1.26594900
H	0.74192500	1.79247300	1.26594900
N	-0.97728100	1.33551500	0.00000000
H	-1.09050000	2.34630200	0.00000000

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, 951.2978, 993.4035, 1005.3097, 1026.4647, 1031.3096, 1123.0332, 1159.6270, 1167.3392, 1207.3715, 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

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

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

3a

C	0.31943800	-1.43098800	0.67227800
C	0.31943800	-1.43098800	-0.67227800
C	-0.21570500	-0.36076200	-1.52070200
C	-0.21570500	-0.36076200	1.52070200
C	-0.21570500	0.94126400	-1.20851900
C	-0.21570500	0.94126400	1.20851900
H	0.70469700	-2.30792800	1.18796200
H	0.70469700	-2.30792800	-1.18796200
H	-0.62490100	-0.64011400	-2.48706400
H	-0.62490100	-0.64011400	2.48706400
H	-0.61900100	1.67210400	-1.90692200
H	-0.61900100	1.67210400	1.90692200
N	0.29944400	1.46861600	0.00000000
H	0.32597100	2.47738500	0.00000000

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, 603.3915, 625.8652, 739.4565, 753.8918, 801.5064, 893.1834, 910.8110, 940.4835, 960.7223, 962.9890, 984.6410, 989.0197, 1012.5995, 1136.3047, 1237.2872, 1244.3256, 1287.6313, 1372.6371, 1445.9481, 1469.3168, 1484.8746, 1721.8196, 1724.0983, 1770.2419, 3180.6582, 3184.5298, 3184.6609, 3201.4742, 3220.2391, 3222.1713, 3660.5975

TS(1a→2a)

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:

Zero-point correction= 0.116914 (Hartree)
Thermal correction to Energy= 0.121900 (Hartree)
Thermal correction to Enthalpy= 0.122844 (Hartree)
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)

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

H	0.58040300	-2.34207300	-1.18321000
H	-0.60314500	-0.62731400	-2.50166100
H	-0.60314500	-0.62731400	2.50166100
H	-0.61250200	1.67355300	-1.93256700
H	-0.61250200	1.67355300	1.93256700
N	0.26079600	1.51707100	0.00000000
H	1.20911300	1.87122500	0.00000000

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, 1151.0061, 1244.0526, 1256.6268, 1308.9077, 1381.1543, 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	0.72677300
C	0.21998300	-0.32844500	1.44070600
C	0.21998300	1.00004200	0.79671600
C	0.21998300	1.00004200	-0.79671600
C	0.21998300	-0.32844500	-1.44070600
C	0.01067200	-1.45457700	-0.72677300
H	-0.02465500	-2.41436900	1.23422100
H	0.42918700	-0.38323400	2.50616600
H	0.42918700	-0.38323400	-2.50616600
H	-0.02465500	-2.41436900	-1.23422100
H	0.79501300	1.78739000	-1.29100700
H	0.79501300	1.78739000	1.29100700
N	-0.86011800	1.37987100	0.00000000
H	-1.78593400	1.75707800	0.00000000

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, 761.4522, 804.1761, 897.9972, 940.0573, 956.3940, 988.2543, 1008.5507, 1024.5432, 1029.8094, 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	-0.33562700	1.44573000
C	-0.25172300	0.96518500	-0.92839000
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, 1048.3356, 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

H	-0.71006700	0.29435000	-2.49546200
H	-0.65984900	2.39772700	-1.24575200
H	-0.68814200	-1.88414600	-1.30041800
H	-0.68814200	-1.88414600	1.30041800
N	0.86960400	-1.28829000	0.00000000
F	1.72150800	-0.17821000	0.00000000

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, 352.9247, 422.3999, 528.7530, 573.5600, 619.2933, 674.0990, 698.0683, 777.7570, 802.8403, 863.6175, 916.0549, 964.5290, 980.8828, 1001.9444, 1009.0364, 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

2b

C	0.59998800	1.47185700	0.68002900
C	0.59998800	1.47185700	-0.68002900
C	0.59998800	0.29760800	-1.50785300
C	0.59998800	0.29760800	1.50785300
C	0.14189900	-0.93030600	-1.17603100
C	0.14189900	-0.93030600	1.17603100
H	0.72197500	2.42549000	1.18644300
H	0.72197500	2.42549000	-1.18644300
H	1.01091900	0.40481100	-2.50919200
H	1.01091900	0.40481100	2.50919200
H	0.24410400	-1.76445000	-1.86362800
H	0.24410400	-1.76445000	1.86362800
N	-0.59623900	-1.24208800	0.00000000
F	-1.76475900	-0.38966700	0.00000000

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, 503.4487, 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, 3196.4403, 3205.3446, 3219.3762, 3222.6100, 3227.0961

3b

C	0.61136500	1.71161800	0.67585900
C	0.61136500	1.71161800	-0.67585900
C	0.61136500	0.51287200	-1.50859800
C	0.61136500	0.51287200	1.50859800
C	-0.00031100	-0.63064400	-1.17719400
C	-0.00031100	-0.63064400	1.17719400
H	0.70979300	2.66451800	1.18985700
H	0.70979300	2.66451800	-1.18985700
H	1.15918600	0.53855000	-2.44536200
H	1.15918600	0.53855000	2.44536200
H	0.04249100	-1.54609000	-1.75892000
H	0.04249100	-1.54609000	1.75892000
N	-0.80908500	-0.69078000	0.00000000
F	-1.42537400	-1.95607300	0.00000000

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, 734.8204, 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

4b

C	0.18927100	-1.84355100	0.72988300
C	0.36875000	-0.71173400	1.43605200
C	0.36875000	0.59447600	0.76096400
C	0.36875000	0.59447600	-0.76096400
C	0.36875000	-0.71173400	-1.43605200
C	0.18927100	-1.84355100	-0.72988300
H	0.15913400	-2.80081700	1.24069100
H	0.53981600	-0.73672800	2.50713200
H	0.53981600	-0.73672800	-2.50713200
H	0.15913400	-2.80081700	-1.24069100
H	0.80885500	1.44875200	-1.26340100
H	0.80885500	1.44875200	1.26340100
N	-0.84677700	0.93438500	0.00000000
F	-0.91215800	2.35184400	0.00000000

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 (Hartree)
Sum of electronic and thermal Free Energies= -386.488076 (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, 907.8841, 912.6167, 980.1631, 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

TS(1b→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
C	0.19004600	-1.00855100	-0.94484900
C	0.19004600	-1.00855100	0.94484900
H	0.83088900	2.34029100	1.21443900
H	0.83088900	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 (Hartree)

Thermochemistry:

Zero-point correction= 0.107656 (Hartree)
Thermal correction to Energy= 0.113387 (Hartree)
Thermal correction to Enthalpy= 0.114331 (Hartree)
Thermal correction to Gibbs Free Energy= 0.078019 (Hartree)
Sum of electronic and zero-point Energies= -386.448481 (Hartree)
Sum of electronic and thermal Energies= -386.442750 (Hartree)
Sum of electronic and thermal Enthalpies= -386.441806 (Hartree)
Sum of electronic and thermal Free Energies= -386.478117 (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, 3210.0093, 3215.8066, 3223.1709, 3226.1550, 3232.8377

TS(2b→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

F -1.47285200 -1.87123400 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)

C	-0.07622700	-1.79791200	0.70358400
C	0.37188000	-0.71534600	1.45234200
C	0.37188000	0.57951500	0.93496600
C	0.37188000	0.57951500	-0.93496600
C	0.37188000	-0.71534600	-1.45234200
C	-0.07622700	-1.79791200	-0.70358400
H	-0.20175200	-2.75494300	1.20146500
H	0.83883400	-0.88132800	2.41800300
H	0.83883400	-0.88132800	-2.41800300
H	-0.20175200	-2.75494300	-1.20146500
H	0.90923300	1.41327700	-1.37360000
H	0.90923300	1.41327700	1.37360000
N	-0.65806300	0.93406700	0.00000000
F	-0.72184200	2.34582500	0.00000000

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=	-386.441199 (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

C	0.54740500	0.90587300	0.77472200
C	0.54740500	0.90587300	-0.77472200
C	0.54740500	-0.41176300	-1.42202100
C	0.36314600	-1.55541200	-0.72525800
H	0.33252000	-2.50824300	1.24539300
H	0.72711100	-0.44681000	2.49272900
H	0.72711100	-0.44681000	-2.49272900
H	0.33252000	-2.50824300	-1.24539300
H	1.07568400	1.70427200	-1.29018600
H	1.07568400	1.70427200	1.29018600
N	-0.58402000	1.38320000	0.00000000
C	-1.84926100	0.66934300	0.00000000
H	-2.40378900	0.98123600	0.88899600
H	-2.40378900	0.98123600	-0.88899600
H	-1.77482100	-0.42374300	0.00000000

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

C	0.67135100	1.48309200	0.67856300
C	0.67135100	1.48309200	-0.67856300
C	0.67135100	0.30031600	-1.51523800
C	0.67135100	0.30031600	1.51523800
C	0.17060100	-0.90402400	-1.17592500
C	0.17060100	-0.90402400	1.17592500
H	0.79273100	2.43812900	1.18406600
H	0.79273100	2.43812900	-1.18406600
H	1.15282800	0.38636800	-2.48744500
H	1.15282800	0.38636800	2.48744500
H	0.31571400	-1.75836500	-1.83648700
H	0.31571400	-1.75836500	1.83648700
N	-0.60175900	-1.15572100	0.00000000
C	-1.93476600	-0.55556900	0.00000000
H	-2.47149300	-0.90244300	-0.88709300
H	-2.47149300	-0.90244300	0.88709300
H	-1.91829000	0.54348700	0.00000000

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, 203.8534, 228.5221, 296.3368, 331.6247, 355.7364, 462.4374, 464.6269, 652.3016, 743.8551, 758.2630, 798.5767, 853.5075, 869.9627, 907.8500, 975.6046, 992.8562, 993.5039, 1002.2565, 1020.8695, 1089.5824, 1149.4671, 1172.0243, 1211.9332, 1241.0709, 1286.5704, 1344.0725, 1379.6548, 1421.2235, 1459.8493, 1482.5739, 1491.7398, 1515.5582, 1631.9608, 1705.2604, 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	-0.67426100
C	0.64058300	0.55018300	-1.51103900
C	0.64058300	0.55018300	1.51103900
C	0.04009800	-0.60345600	-1.18517500
C	0.04009800	-0.60345600	1.18517500
H	0.72227500	2.70351200	1.18934100
H	0.72227500	2.70351200	-1.18934100
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	1.84369200
N	-0.71493000	-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

4c

C	0.20019700	-1.87125400	0.72824900
C	0.40012400	-0.74113900	1.43467700
C	0.40012400	0.56990200	0.76891600
C	0.40012400	0.56990200	-0.76891600
C	0.40012400	-0.74113900	-1.43467700
C	0.20019700	-1.87125400	-0.72824900
H	0.16588900	-2.82903700	1.23881200
H	0.59503900	-0.77951500	2.50248800
H	0.59503900	-0.77951500	-2.50248800
H	0.16588900	-2.82903700	-1.23881200
H	0.92267000	1.38761800	-1.26519700
H	0.92267000	1.38761800	1.26519700
N	-0.77489600	0.93935000	0.00000000
C	-1.07450300	2.36320500	0.00000000
H	-1.66555500	2.60140100	-0.88825500
H	-1.66555500	2.60140100	0.88825500
H	-0.17014400	2.99428000	0.00000000

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, 1208.6757, 1209.4163, 1280.4530, 1362.6828, 1427.9186, 1441.2065, 1458.4500, 1489.0383, 1501.7284, 1504.4182, 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	0.70010300
C	-0.16021000	-1.56522800	-0.70010300
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, 1376.2660, 1423.3264, 1459.1207, 1484.8877, 1486.8709, 1496.0696, 1518.0842, 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	0.72707600	2.56383900	-1.18177300
H	1.09231300	0.53748300	-2.51752600
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, 1479.7097, 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)

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	-0.88951700
H	0.00000000	2.99382300	0.00000000

ENERGY= -326.7008262 (Hartree)

Thermochemistry:

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, 2995.7193, 3121.7391, 3150.7616, 3156.0061, 3168.7068, 3198.1801, 3207.5512, 3216.2672, 3224.0076

TS(1c→4c)

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, 1365.3671, 1366.4091, 1427.0781, 1446.0062, 1468.0793, 1493.7939, 1517.4388, 1619.8707, 1648.8339, 1717.8060, 3001.4489, 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, θ , and ϕ) geometrical variables for sampled TS structures and reaction trajectories (**1**→**2**, **3**) is shown below:

a) [run.sh](#)

```
#.....  
# TS Sampled Structures & Trajectory Analyses  
# input fullDistList  
# Nilangshu Mandal, IACS, 15th August, 2021  
#.....  
#!/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
```

```

headLength=$(awk '/Benzene_NH_endo/{print $0}' temp$sisomer | tail -n 1 | awk -F ' ' '{print
$1}')
footLength_exo=$(awk '/Azepine_exo/{print $0}' temp$sisomer | tail -n 1 | awk -F ' ' '{print
$1}')
footLength_endo=$(awk '/Azepine_endo/{print $0}' temp$sisomer | tail -n 1 | awk -F ' ' '{print
$1}')
tailStart=$(tail -n $footLength_exo temp$sisomer | awk -F ' ' '{print $19}' | awk NF | head -n 1)

if [ "$tailStart" == "Azepine_endo" ];
then
    head -n $headLength temp$sisomer | sort -k 1 -nr | awk -F ' ' '{printf "%f\t%f\t%s\n",
$5, $12, $15}' >> endo_exo_prod$sisomer
    head -n $headLength temp$sisomer | sort -k 1 -nr | awk '{if($1 == "1") print $0 }' >>
TS_sampling.dat
    tail -n $(echo $footLength_exo - 1 | bc) temp$sisomer | awk -F ' ' '{printf
"%f\t%f\t%s\n", $5, $12, $15}' >> endo_exo_prod$sisomer

    elif [ "$tailStart" == "TS" ];
    then
        head -n $headLength temp$sisomer | sort -k 1 -nr | awk -F ' ' '{printf "%f\t%f\t%s\n",
$5, $12, $15}' >> TS_exo_prod$sisomer
        tail -n $(echo $footLength_exo - 1 | bc) temp$sisomer | awk -F ' ' '{printf
"%f\t%f\t%s\n", $5, $12, $15}' >> TS_exo_prod$sisomer
    fi
    elif [ $header -ge 1 -a $footer_endo -ge 1 ];
    then
        awk '/Benzene_NH_endo/{print $0}' temp$sisomer > headFile

        if [ $(wc -l headFile | awk '{print $1}') -gt 1 ];
        then
            start=$(cat headFile | head -n 1 | awk -F ' ' '{print $1}')
            while read line;
            do
                temp=$(echo $line | awk -F ' ' '{print $1}')
                if [ $(echo $temp - $start | bc) -gt 1 ];
                then
                    headLength=$start
                    break
                fi
                start=$temp
            done < headFile
            elif [ $(wc -l headFile | awk '{print $1}') -eq 1 ];
            then
                headLength=$(cat headFile | tail -n 1 | awk -F ' ' '{print $1}')
            fi
            fileLength=$(wc -l temp$sisomer | awk '{print $1}')
            tail -n $(echo $fileLength - $headLength | bc) temp$sisomer | awk -F ' ' '{print $19}' | awk NF >
tailFile

            tailEnd=$(cat tailFile | tail -n 1)
            tailStart=$(cat tailFile | head -n 1)
            echo $fileLength, $headLength, $tailEnd, $tailStart, $sisomer

            if [ "$tailEnd" == "Benzene_NH_endo" ];
            then
                cat temp$sisomer >> unprod_head_$sisomer

                elif [ "$tailStart" == "Azepine_endo" ];
                then
                    head -n $headLength temp$sisomer | sort -k 1 -nr | awk -F ' ' '{printf "%f\t%f\t%s\n",
$5, $12, $15}' >> endo_endo_prod$sisomer

```

```

        tail -n $(echo $fileLength - $headLength - 1 | bc) temp$sisomer | awk -F' '{printf
"%f\t%f\t%s\n", $5, $12, $15}' >> endo_endo_prod$sisomer
        elif [ "$tailStart" == "TS" ];
        then
            head -n $headLength temp$sisomer | sort -k 1 -nr | awk -F' '{printf "%f\t%f\t%s\n",
$5, $12, $15}' >> TS_endo_prod$sisomer
            tail -n $(echo $fileLength_endo - $headLength - 1 | bc) temp$sisomer | awk -F'
'{printf "%f\t%f\t%s\n", $5, $12, $15}' >> TS_endo_prod$sisomer
            fi

        elif [ $header -gt 1 -a $footer -eq 0 ];
        then
            cat temp$sisomer > unprod_head_$sisomer
        elif [ $header -eq 0 -a $footer -gt 1 ];
        then
            cat temp$sisomer > unprod_tail_$sisomer
        fi
        #rm temp$sisomer
done

```