

1. Position of equilibrium of allene → propyne at 298.15 K (by DFT using a 6-31G(d) basis set, m062x functional).

The equilibrium constant and thus position of equilibrium needs to take into account both **enthalpy** (which is related to the difference in total energy for the two gas phase molecules), and **entropy** (which relates to internal motions, particularly rotation and vibration). Statistical mechanics is used to convert energy levels of internal motions into entropy. See: Mohammad M. Ghahremanpour, Paul J. van Maaren, Jonas C. Ditz, Roland Lindh and David van der Spoel, J. Chem. Phys. 145, 114305 (2016) for a detailed discussion of how well various codes in Gaussian predict thermodynamic properties.

The reference article in the Gaussian manual is <http://gaussian.com/thermo/> (accessed 4 Jan 219) guides you to the lines in the *.log file and also gives useful advice on how to do successful calculations. It can be accessed from Help~Gaussian in GaussView.

For each molecule, $\Delta G_f^\circ = \Delta H_f^\circ - T \Delta S_f^\circ$ and $\Delta G_{\text{rxn}}^\circ = \Delta G_f^\circ(\text{propyne}) - \Delta G_f^\circ(\text{allene})$ $K_{\text{eq}} = \exp(-\Delta G_{\text{rxn}}^\circ/RT)$

Calculation			Total Energy (hartrees = h)		Gibbs Energy (hartrees) (*)		ΔG_{rxn} (kJ/mol)	K_{eq} (298 K)
Method (all DFT)	Job type	Symmetry	Allene	Propyne	Allene	Propyne		
m062 6-31G(d)	Opt/ freq	D2d / C3v	-116.657 67	-116.653 27	-116.592 27	-116.658 82	10.636	0.0135

(*) includes correction for thermal energy $P_{\text{allene}} / P_{\text{propyne}} = K = 0.0135$

The **Gibbs free energies** predicted for propyne and allene at the M06-2X/6-31G(d) levels of theory are -116.658 82 h and -116.592 27 h, respectively. That makes allene more stable than propyne by 11.1 kJ/mol. **At 298.15 K that's a ratio of 1.4 to 98.6 propyne:allene.** Allene is more stable.

The requested functional was accessed by adding #p opt=m062x to the Add. Inp. tab. Placing this keyword int the “Additional Keywords” field below all the tabs does not seem to activate that functional.

NB In my initial calculations, I got a WARNING:

Warning -- **explicit consideration of 2 degrees of freedom as vibrations may cause significant error**

According to the Gaussian help file: If you see the following warning, it can be a sign that one of two things is happening. First, it often shows up if your structure is not a minimum with respect to all non-imaginary modes. You should go back and re-optimize your structure, since all the thermochemistry based on this structure is likely to be wrong. Second, it may indicate that there are internal rotations in your system. You should correct for errors caused by this situation.

In this case, allene does not have internal DoF, so the problem could be that the structure is not a true minimum geometry (although there were no negative frequencies). For propyne 4 DoF were problematic – probably related to internal rotation of the CH₃.

Allene (D2D)

(NB the thermodynamic information is in the log file, not the out file)

Total E (in summary): **-116.657 67348**

Enthalpy: -116.597487 hartree Gibbs free energy: -116.624970 hartree

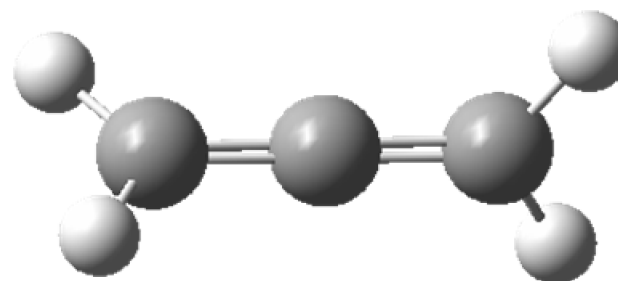
Entropy @ 298.15) : $\Delta S_f^\circ = (\Delta G_f^\circ - \Delta H_f^\circ) / T = -9.21784E-05$ hartree/K

```
Stoichiometry C3H4
Framework group D2D[0(C),C2(C,C),2SGD(H2)]
Deg. of freedom 3
Full point group D2D NOp 8
Largest Abelian subgroup C2V NOp 4
Largest concise Abelian subgroup C2V NOp 4
Standard orientation:
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.306850
3	1	0	0.000000	0.927372	1.876306
4	1	0	0.000000	-0.927372	1.876306
5	6	0	0.000000	0.000000	-1.306850
6	1	0	-0.927372	0.000000	-1.876306
7	1	0	0.927372	0.000000	-1.876306

```
Rotational constants (GHZ): 145.7687819 8.8796395 8.8796395
```

```
Zero-point correction= 0.055485 (Hartree/Particle)
Thermal correction to Energy= 0.059242
Thermal correction to Enthalpy= 0.060186
Thermal correction to Gibbs Free Energy= 0.032703
Sum of electronic and zero-point Energies= -116.602189
Sum of electronic and thermal Energies= -116.598431
Sum of electronic and thermal Enthalpies= -116.597487
Sum of electronic and thermal Free Energies= -116.624970
```



NB still had the warning ! (2 DoF) even after making sure the geometry was optimized

Propyne (C3v)

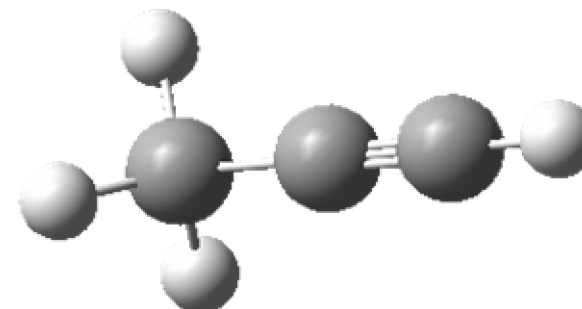
Total E (in summary): **-116.653 27 009** hartree

Enthalpy: -116.597487 hartree Gibbs free energy: -116.620743

Entropy @ 298.15) : $\Delta S_f^\circ = (\Delta G_f^\circ - \Delta H_f^\circ) / T = -9.43585E-05$ hartree/K

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000000	0.000000	-1.241376
2	1	0	0.000000	1.022334	-1.637961
3	1	0	-0.885367	-0.511167	-1.637961
4	1	0	0.885367	-0.511167	-1.637961
5	6	0	0.000000	0.000000	0.218929
6	6	0	0.000000	0.000000	1.426073
7	1	0	0.000000	0.000000	2.492127

Rotational constants (GHZ): 159.9282515 8.5255224 8.5255224
Zero-point correction= 0.055718 (Hartree/Particle)
Thermal correction to Energy= 0.059716
Thermal correction to Enthalpy= 0.060660
Thermal correction to Gibbs Free Energy= 0.032527
Sum of electronic and zero-point Energies= -116.597552
Sum of electronic and thermal Energies= -116.593554
Sum of electronic and thermal Enthalpies= -116.592610
Sum of electronic and thermal Free Energies= -116.620743



NB had the warning ! (4 DoF)

$$\frac{\Delta G(T_1)}{T_1} = \frac{\Delta G(T_2)}{T_2} - \Delta H(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

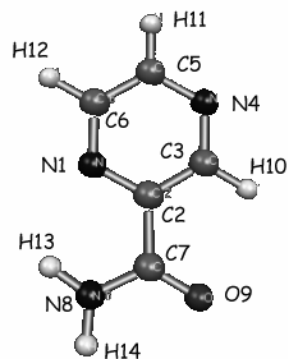
Comparison to experiment

Lifshitz et al, (J. Chem. Phys 79 (1975) 1148) reports $K_{\text{exp}} = 2.3$ at 1100K, for allene \leftrightarrow propyne and computes a value of **3.45** from tabulated Gibbs Free Energy. Using the Gibbs-Helmholtz equation (see p. 121, Engel&Read(2006) -

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) - \text{these } K(1100\text{K}) \text{ values predict } \mathbf{K = 1.00 \text{ at } 298 \text{ K.}}$$

My calculated K(298) disagrees by factor of 100 with K projected from experimental measurements at 1100 K

2. nmr calculation for pyrazinamide – used NMR/ GIAO Method after RHF/6-31G(d) geometry optimization calc.
 If you use salvation the answer is much more accurate than if you do not (which gives gas phase vauiies)
 from my RHF/6-31G(d) calc

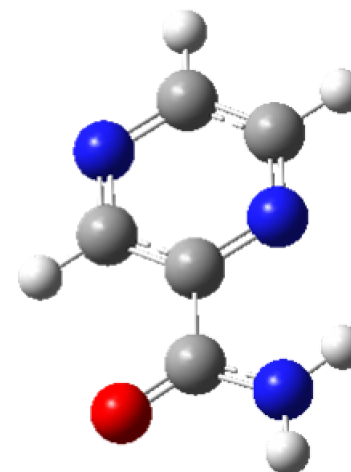


nucleus	Chemical shift		
	Experiment	Lit. Calc (*)	My calculation
C2	146.4	138.3	140.6
C3	145.0	140.7	144.0
C5	144.4	140.8	145.1
C6	148.2	135.4	137.7
C7	165.1	159.9	159.9
H10	9.2	9.6	9.65
H11	8.7	8.6	8.68
H12	8.5	8.3	8.97
H13	7.9	6.7	6.36
H14	8.3	4.0	4.67

(*) Chis et al. Chem. Phys 316 (2005) 153 ; B3LYP/6-31G(d) for C-1 monomer (see below)

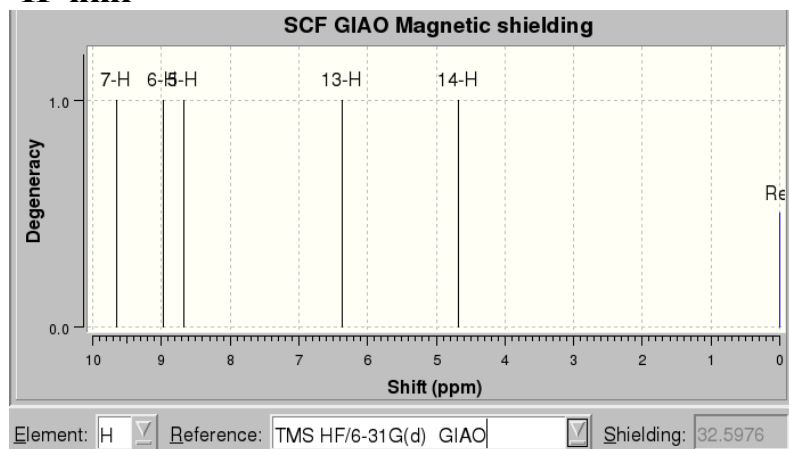
Geometry optimization calculation using RHF 6-31G(d) took 16 min and 24 sec on ripper

Geometry	C1	dipole moment	4.2655 Debye	E(RHF) = -430.486952369 h	after 16 cycles
1	C5	-1.695371	1.206687	0.035732	
2	C6	-2.462896	0.051340	-0.024010	
3	C3	-0.595800	-1.203571	-0.009493	
4	C2	0.174575	-0.048455	0.050310	
5	H12	-2.152060	2.178934	0.053529	
6	H11	-3.535735	0.103615	-0.053910	
7	H10	-0.129191	-2.168344	-0.026769	
8	N4	-1.913704	-1.146921	-0.046391	
9	N1	-0.380426	1.148927	0.072512	
10	N8	2.332225	1.016320	0.148286	
11	C7	1.676572	-0.153363	0.091105	
12	O	2.217892	-1.226797	0.072308	
13	H13	1.844169	1.882144	0.161946	
14	H140	3.326835	1.003586	0.177257	

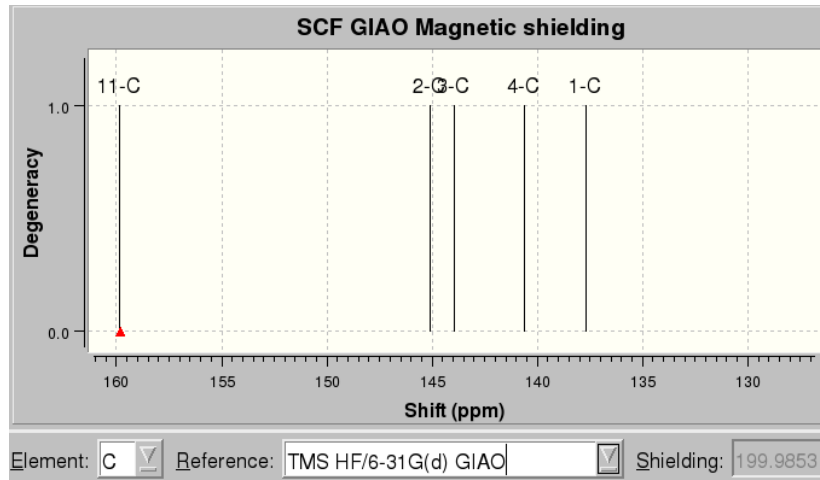


I then changed the job type to NMR, selected GIAO method, and , on the Solvation tab, selected 'default' and chloroform from the menu of possible solvents. The calculation took 3 min 4 sec.

¹H nmr



¹³C nmr



The poor agreement of the predicted ¹H chemical shifts for H13 and H14 with experiment are because **this molecule likes to dimerize by forming H-bonds between H14-O9** (see V. Chis et al. Chemical Phys. 316 (2005) 153). Note that the Chis et al calculations also show **BOTH H-13 and H-14 too low**, even though only H-14 is implicated in the H-bonding.

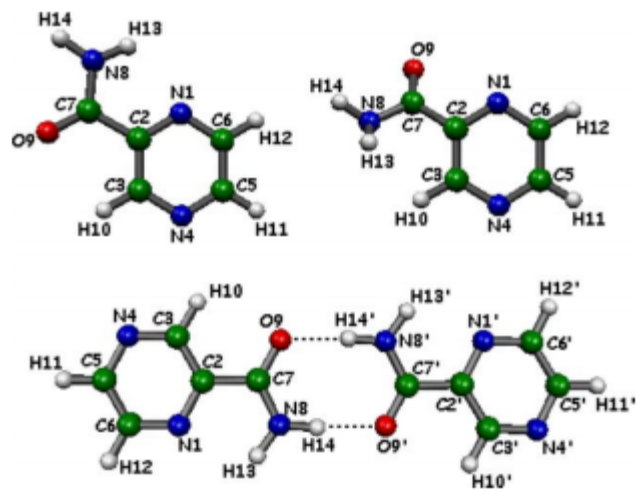


Fig. 1. Molecular structure and atom numbering scheme for the two conformers of pyrazinamide (C1 – top left, C2 – top right) and pyrazinamide dimer (bottom).

Calculated	
B3LYP/6-31G(d)	
Monomer C1	Dimer
138.3	138.9
140.7	140.5
140.8	140.8
135.4	135.6
151.6	155.6
9.4	9.4
8.6	8.6
8.3	8.3
6.7	6.9
4.0	8.9

3. Diels-Alder reaction – PM3 semi-empirical calculation

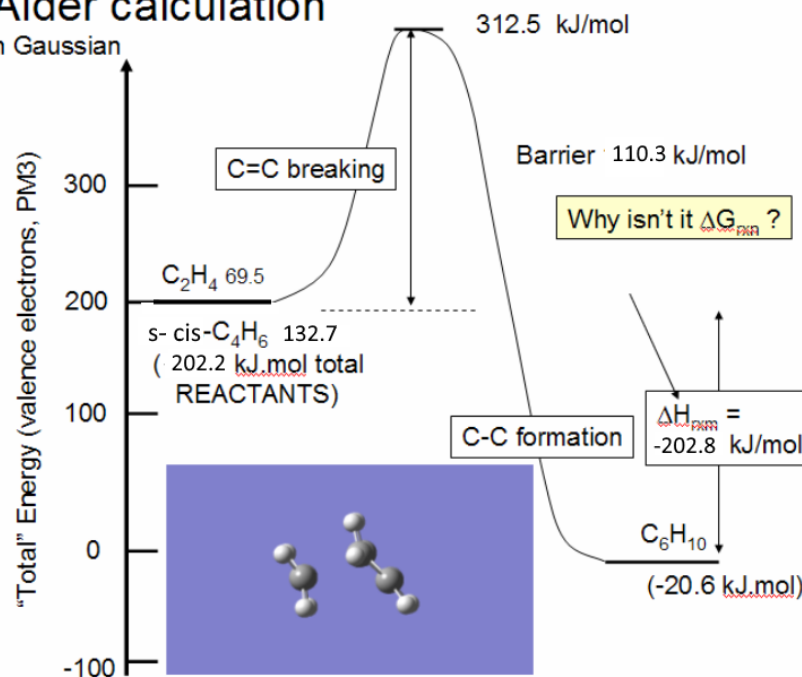
Use PM3; TS (Beryn) , calculate force constants once, opt=noeigen in Additional Keywords; guess default

1 h = 262.5 kJ/mol	pm3		HF 3-21G	
Molecule	Total energy (h)	E (kJ/mol)	Total energy (h)	E (10 ⁵ kJ/mol)
1,3-Butadiene - cis	0.0505507	132.7	-154.05394316	-4.0447
1,3-Butadiene - trans	0.0493885	129.7		-4.005
Ethene	0.0264660	69.5	-77.60098814	-2.0374
REACTANTS		202.2	-231.6549313	-6.0821
Cyclohexene	-0.0078478	-20.6	-231.72915120	-6.0840
Transition state	0.119012	312.5	-229.3658351	-6.0221
Barrier		110.3		600 kJ/mol
ΔH_{rxn}		-202.8		-190.3 kJ/mol

NB the individual energies are very different since PM3 does not include energies of core electrons. But the enthalpy of reaction is similar.

Diels Alder calculation

pm3 in Gaussian



Cis-Butadiene

NB the starting geometry was not carefully done. Perhaps should do an MM optimization first ?
(Spartan had a 'clean-up' procedure in its input process; Gaussian has the same – Edit~Clean)

For butadiene – there are multiple “SCF done” cycles – have to get to the LAST ONE to get final optimized energy

```
line 248/4645 SCF Done: E(RPM3) = 0.970178385728 A.U. after 20 cycles
line 479/4645 SCF Done: E(RPM3) = 0.890625711311 A.U. after 16 cycles
line 652/4645 SCF Done: E(RPM3) = 0.746143927805 A.U. after 16 cycles
line 826/4645 SCF Done: E(RPM3) = 0.493109134248 A.U. after 14 cycles
line 998/4645 SCF Done: E(RPM3) = 0.230827211676 A.U. after 13 cycles
line 1172/4645 SCF Done: E(RPM3) = 0.147369903695 A.U. after 12 cycles
line 1343/4645 SCF Done: E(RPM3) = 0.901137937061E-01 A.U. after 12 cycles
...
line 4371/4645 SCF Done: E(RPM3) = 0.505509506176E-01 A.U. after 13 cycles
```

geometry restored to original

===== used clean , and then the default input file, not the Harvey modified one

```
line 248/1774 SCF Done: E(RPM3) = 0.601296417956E-01 A.U. after 12 cycles
```

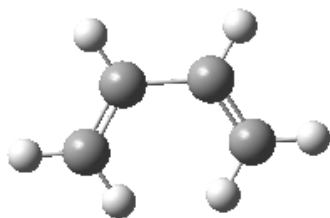
...

```
line 1503/1774 SCF Done: E(RPM3) = 0.505507341102E-01 A.U. after 13 cycles
```

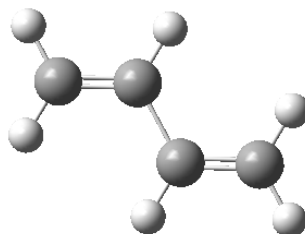
===== using the Harvey format, get same answer

```
line 1503/1774 SCF Done: E(RPM3) = 0.505507341102E-01 A.U. after 13 cycles
```

=====
Cis-Butadiene



Trans butadiene



Trans butadiene

line 993/1278 SCF Done: E(RPM3) = 0.493884530507E-01 A.U. after 13 cycles

Energy difference (cis – trans) = 3.05 kJ/mol

<http://chemistry.umeche.maine.edu/Modeling/donmolmech.html>

[literature says trans is more stable than cis by 3.21 kcal/mol, or 0.77 kJ/mol]

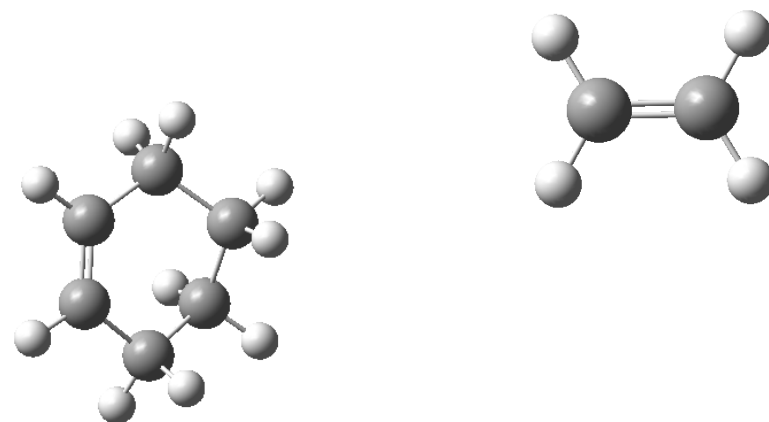
Thus pm3 method over-estimates the Thermochemistry by ~*4

Ethene

SCF Done: E(RPM3) = 0.264660251344E-01 A.U. after 7 cycles

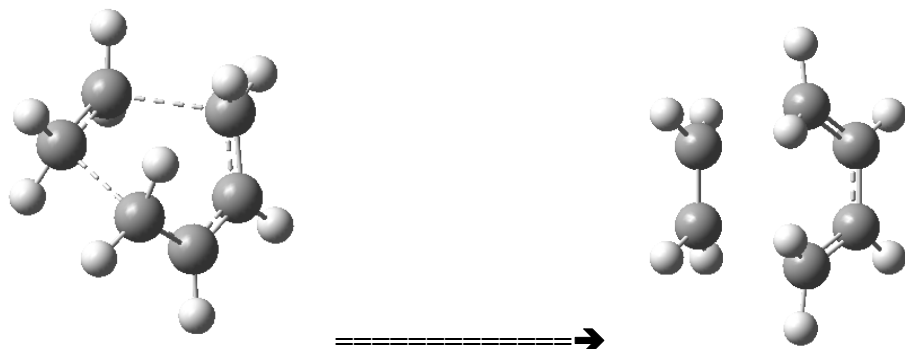
Cyclohexene

SCF Done: E(RPM3) = -0.784776827086E-02



Diels Alder Thermochemistry





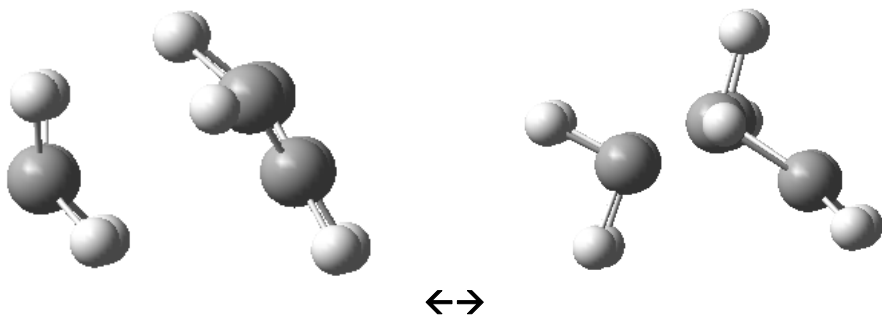
using the supplied 'hint' geometry, but had to rebond in a sensible manner

1st try, I used just OPT & TS (Berny) → structure reverted to two non-bonded molecules with delocalized bonding in the butadiene

2nd try, I added partial bonds to make the D-A adduct, and then used OPT&FREQ

line 3212/4218 SCF Done: E(RPM3) = 0.119012226305 A.U. after 2 cycles is LAST of the SCF Done

imaginary frequency (the ethane moving against the cis butadiene) = - 934 cm⁻¹



**Movie made of the motion along the reaction co-ordinate
(the imaginary frequency)**

