CH504 - Computational Chemistry
Lab Assignment 2

Nikhil Manjrekar (200050088)

January 30, 2023

Question: 1

Aim:

To investigate the properties of the given two organic π-conjugated molecules using quantum chemical methods, namely density functional theory (DFT) and to find which of them would display better donor-acceptor properties suitable to make a solar cell.

Principle:

Following are the formulae to calculate the properties of the molecule:

For Hardness(η) and Softness(S),

$$\eta = -\frac{(E_{HOMO} - E_{LUMO})}{2} \qquad s = \frac{1}{2\eta}$$

For calculating band gap we can use the following formula with the energies of the HOMO and LUMO of the molecule.

$$Band\ gap = E_{HOMO} - E_{LUMO}$$

Files: q11.log, q12.log, q11opt.log, q12opt.log
Folder details: Main Folder/ch504_42/assignment2/q1/

‘

Observation:

For energy conversions, 1 hartree/particle or a.u = 27.211 eV.

Hence, **For M1**,

E_{HOMO} = -0.34661*27.211 = -9.431604 eV and E_{LUMO} = 0.03090*27.211= 0.84082 eV

Hardness(η) = -$\frac{(-9.43160-0.84082)}{2}$ = 5.13590 eV, Softness(S) = $\frac{1}{2*5.13590}$ = 0.09735

band gap(eV) = -9.43160 - 0.84082 = -10.27180 eV

For M2

E_{HOMO} = -0.33133*27.211 = -9.01582 eV and E_{LUMO} = 0.02958*27.211= 0.80490 eV

Hardness(η) = $-\frac{(-9.01582-0.80490)}{2}$ = 4.90136 eV, Softness(S) = $\frac{1}{2*4.90136}$ = 0.10182

band gap(eV) = -9.01582 - 0.80490 = -9.82072 eV

Compounds	E_{HOMO}(eV)	E_{LUMO}(eV)	Hardness(eV)	Softness(eV)	band gap (eV)
M1	-9.431604	0.84082	5.13590	0.09735	-10.27180
M2	-9.01582	0.80490	4.90136	0.10182	-9.82072

Relevant sections from output file:

M1

Observe that the HOMO energy turns out to be -0.34661 Hartee and LUMO energy is 0.03090 Hartee.

```
Alpha  occ. eigenvalues --  -15.53868 -15.51523 -11.29888 -11.27573 -11.26478
Alpha  occ. eigenvalues --  -11.23781 -11.23235 -11.22144 -11.21622 -11.21581
Alpha  occ. eigenvalues --  -11.21258 -11.21169  -1.28622  -1.26467  -1.19703
Alpha  occ. eigenvalues --   -1.14472  -1.04917  -1.04326  -0.92948  -0.86506
Alpha  occ. eigenvalues --   -0.84206  -0.78063  -0.72992  -0.70745  -0.66883
Alpha  occ. eigenvalues --   -0.64135  -0.62184  -0.61094  -0.58188  -0.57829
Alpha  occ. eigenvalues --   -0.55661  -0.54457  -0.53762  -0.52334  -0.50262
Alpha  occ. eigenvalues --   -0.49232  -0.48349  -0.43693  -0.36738  -0.34661
Alpha virt. eigenvalues --    0.03090   0.11630   0.15588   0.16433   0.21810
Alpha virt. eigenvalues --    0.23160   0.24366   0.25955   0.28865   0.30830
Alpha virt. eigenvalues --    0.31994   0.32717   0.34300   0.35919   0.39471
Alpha virt. eigenvalues --    0.41326   0.44094   0.46936   0.47719   0.50882
```

M2

Observe that the HOMO energy turns out to be -0.33133 Hartee and LUMO energy is 0.02958 Hartee.

```
Alpha  occ. eigenvalues --  -11.24153 -11.24011 -11.23413 -11.20044 -11.19509
Alpha  occ. eigenvalues --  -11.19439  -1.42341  -1.41850  -1.27704  -1.26634
Alpha  occ. eigenvalues --   -1.19903  -1.14922  -1.06354  -1.05204  -0.97355
Alpha  occ. eigenvalues --   -0.96741  -0.94297  -0.84868  -0.83818  -0.80052
Alpha  occ. eigenvalues --   -0.75252  -0.72544  -0.69406  -0.68877  -0.67321
Alpha  occ. eigenvalues --   -0.66667  -0.66345  -0.62949  -0.61809  -0.59140
Alpha  occ. eigenvalues --   -0.58914  -0.56972  -0.56839  -0.56362  -0.56349
Alpha  occ. eigenvalues --   -0.55362  -0.52054  -0.50889  -0.50105  -0.49914
Alpha  occ. eigenvalues --   -0.49255  -0.48452  -0.48239  -0.40985  -0.34031
Alpha  occ. eigenvalues --   -0.33133
Alpha virt. eigenvalues --    0.02958   0.14710   0.16831   0.17229   0.22523
Alpha virt. eigenvalues --    0.23112   0.25380   0.26242   0.27094   0.28349
Alpha virt. eigenvalues --    0.30709   0.31503   0.32206   0.32983   0.33236
```

Results/Conclusions:

- Energy Gap between HOMO and LUMO for M2 is 9.821eV which lower than energy gap in M1 which is 10.272eV. Therefore, M2 displays better donor-acceptor properties in comparison to M1. And because of small band gap M2 allows efficient transport of electrons from HOMO to LUMO upon absorption of light and due to this it is better for solar cells too.

Literature Comparison:

In this paper, our M2 is referred to as M5. While M1 is same for both. According to above mentioned paper, the λ_{abs} or the wavelength associated with the HOMO-LUMO transition has the order M2>M1, which means that the frequency if energy absorbed will have the reverse order (M2< M1). Therefore, our calculations that M2 will have smaller band gap is supported by this paper.

Extension of above concept to a new problem or situation:

Its size can be used to predict the strength and stability of transition metal complexes, as well as the colors they produce in solution. As a rule of thumb, the larger a compound's HOMO-LUMO gap, the more stable the compound, hence, it also tells us about the stability of a given compound. The energy of the HOMO-LUMO gap can also tell us about what wavelengths the compound can absorb. Or alternatively, measuring the wavelengths a compound absorbs in the lab can be used as a measure of the HOMO-LUMO gap.

Question: 2

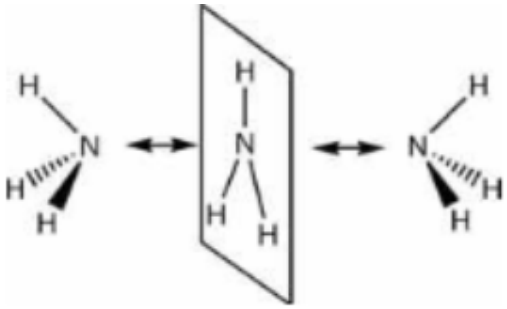
Aim:

To estimate the energy barriers for inversion of NH3 using the HF/3-21G*level of theory and find out the value of the imaginary frequency corresponding to the TS.

Principle:

In chemistry, a transition state(TS) is a very short-lived configuration of atoms at a local energy maximum in an energy profile diagram (aka reaction coordinate).A TS has partial bonds, an extremely short lifetime (measured in femtoseconds), and cannot be isolated. However, TS can be located on the potential energy surface using ab initio computations.

So when a molecule transitions from state to another, it has to cross energy barrier (local maxima or a transition state) to do so. When ammonia tries to invert itself, it achieves a planar configuration where all the four atoms are in the same plane (this is the transition state) as shown below.



1 **TS** **1'**

The energy difference between the transition state and the stable state is called the **energy barrier**. Inversion of ammonia is rapid at room temperature because of lower energy barrier.

Files: ammonia_pyra.log, ammonia_planar.log

Folder details: ethane Main Folder/ch504_42/assignment2/q2/

‘

Observation

E (1) (a.u.)	-55.8722033
E (TS) (a.u.)	-55.8696422
$E_{barrier}$ (Kcal/mol)	1.609709
Imaginary Frequency ($cm^{-}1$)	616.1000

Relevant sections from output file:

NH3 Pyramidal

```
N-N= 1.203626975416D+01 E-N=-1.552131572887D+02  KE= 5.575856366496D+01
1\1\GINC-ACADS\FOpt\RHF\3-21G*\H3N1\CH504_42\29-Jan-2023\0\\# HF/3-21G
* opt\\NH3\\0,1\N,0.0397087175,0.0414562163,0.0130930848\H,-0.02545126
29,0.0010041298,1.012739958\H,0.9864434486,-0.0221688675,-0.3113464011
\H,-0.442156922,0.8336435593,-0.3681217045\\Version=EM64L-G09RevA.02\S
tate=1-A\HF=-55.8722033\RMSD=1.292e-09\RMSF=8.990e-05\Dipole=0.3252664
,0.5593535,0.2390174\Quadrupole=0.2444423,-0.7136592,0.4692169,-0.8424
541,-0.3613582,-0.617449\PG=C01 [X(H3N1)]\\@
```

NH3 Planar

```
1\1\GINC-ACADS\Freq\RHF\3-21G*\H3N1\CH504_42\29-Jan-2023\0\\#N Geom=Al
lCheck Guess=TCheck SCRF=Check GenChk RHF/3-21G* Freq\\NH3planar\\0,1\
N,0.103974429,0.,-0.0313918369\H,-0.122272614,0.,0.9336541667\H,1.0528
633378,0.,-0.317878975\H,-0.6185207409,0.,-0.7099949925\\Version=EM64L
-G09RevA.02\State=1-A1\HF=-55.8696422\RMSD=4.604e-10\RMSF=1.873e-05\Ze
roPoint=0.0346878\Thermal=0.0375235\Dipole=0.0000452,0.,-0.0000137\Dip
oleDeriv=-0.395333,0.,-0.0000184,0.,-1.4493012,0.,-0.0000184,0.,-0.395
```

		1	2	3
		B1	A1	B2
Frequencies	--	-616.1000	1769.2763	1769.4243
Red. masses	--	1.2067	1.0941	1.0941
Frc consts	--	0.2699	2.0178	2.0181
IR Inten	--	823.5034	40.9281	40.9091

Results/Conclusions:

- As one can see above, the energy of the planar TS is more than the pyramidal structure. This is because of the lone pair of electrons associated with the central nitrogen atom. The non-bonding pair of electrons pushes away from the bonding pairs producing a trigonal pyramidal shape
- The energy barrier between the pyramidal and the planar state is close to 1.6kcal/mol which is very small. Hence, because of low energy barrier, at room temperature ammonia undergoes rapid inversion.
- The imaginary frequency of transitions turns out to be 616.1 cm^{-1}

Literature Comparison:

Energy barrier calculated by us using HF/3-21G level of theory is not same as one which we obtained experimentally in this paper. We calculated the energy barrier to be close to 1.6kcal/mol, while the value obtained experimentally is 5.8kcal/mol.

Extension of above concept to a new problem or situation:

The above concept can be used to find the transition state energy or the energy barrier of various compounds and this can be extremely useful in understanding the rate or conditions at which a reaction will take place. Hvaing the knowledge of transition state energy can help us to understand the effect of a specific catalyst during the reaction. It may therefore, help us find new and better catalyst for the reactions.