

Inspecting the mechanism of nitration process in simple organic molecules through simulated ^1H NMR spectra using JSPEC View (Jmol)

N.Hemanth Reddy, S.Sreekar Reddy, N.Siddhartha Kumar Raju, D.L.Durga Prasad

School of Freshman engineering, Kalasalingam Academy of Research and Education, Anand nagar, Krishnankoil, Virudhunagar, Tamilnadu, India- 626 126

1. Introduction

Nitration is the class of chemical processes that introduces the nitro group into an organic chemical compound. The term nitration is also sometimes used incorrectly to represent different processes such as the formation of nitrate esters among nitric acid and alcohols which further take place in synthesizing nitro-glycerine. However, the main difference among the final structure of nitrates and nitro compounds is, the nitrogen atom forms a chemical bond with a non-oxygen atom such as the carbon or other nitrogen atoms. In the case of organic nitrates, the nitrogen is usually bonded with an oxygen atom which further has a bond to a carbon atom.

1.1 Nitration Mechanism

In Organic Chemistry, nitration is a process in which there is the replacement of a hydrogen atom (organic compound) with one or more nitro groups (single bond NO_2). The reaction usually occurs with high temperatures or we can say that the reaction is exothermic. Additionally, nitration reactions can be hazardous when performed on large scale in a batch. A large amount of heat is released and multiple nitrations can occur which can be really problematic. Therefore, nitration reaction is usually controlled by some sort of systematic cooling that is particularly designed to take away the excess generated energy. Besides, the ability to control isotherms in-flow allows improved selectivity and safety. As such, there have been many nitration reactions performed using continuous flow.

By-products are also usually formed where some products can also be highly explosive. Most of the nitration reactions are conducted at low temperatures mainly for safety reasons. Sometimes, nitration reactions are carried out with aliphatic compounds also. Nonetheless, nitration of aromatics is more commercially important.

1.2 Types of Nitration

Aromatic Nitration

This is a typical form of nitration syntheses wherein the “mixed acid”, a mixture of concentrated nitric acid and sulfuric acids is applied. The reaction between the mixture results in the formation of the nitronium ion (NO_2^+), which is the active species in aromatic nitration. Interestingly, this active ingredient also affects nitration without the need for mixed acid. On the other hand, during mixed-acid syntheses, sulfuric acid is not consumed. It rather acts as a catalyst and water absorbent. In the case of nitration of benzene which we will look at in detail below, the reaction is typically conducted at a warm temperature of 50 °C. The process is one example of electrophilic aromatic substitution,

Electrophilic aromatic substitution

Today there are several mechanisms that have been proposed such as the one involving single electron transfer (SET). But the above-mentioned is a common and popular reaction discussed in the syllabus.

1.3 Applications of Nitration

With the help of nitration reaction nitrogen is added to a benzene ring which can be used extensively in substitution reactions. The nitro group usually acts as a ring deactivator. As the ring consists of nitrogen it is very useful because it can be used as a directing group or a masked amino group. The products of aromatic nitrations are very important intermediates in industrial chemistry

2. Objectives:

- To perform the nitration of acetanilide to get p-nitroacetanilide.
- Exploring the mechanism of the nitration process.
- To create 3D structures for various organic molecules in Jmol interface.
- To evaluate the structural changes in the reactant and product with JSPEC view in Jmol.
- Analysing the nitration reaction in the compound.
- To analyze the nitration reaction in a few more molecules such as naphthalene, benzoic acid etc.

- Analysing the change in the structure of the reactant after the nitration process using ^1H NMR in Jmol.

3. EXPERIMENTAL PROCEDURES AND METHODS

Apparatus required:

- 100 ml beaker
- Water bath
- Measuring cylinder
- 250 ml beaker glass rod
- Buchner funnel
- 100 ml of conical flask
- Separating funnel
- RB-flask

Chemicals required:

- Acetanilide – 4g
- Glacial acid- 8 ml
- Nitric acid– 4 ml
- Conc. Sulphuric acid-10 ml

Procedure:

- 4 g of acetanilide is placed in a 100 ml beaker and 4 ml of glacial acetic acid was added to it.
- Gradually add conc. H_2SO_4 with stirring then the mixture becomes hot and the result is clear solution. Then the mixture was cooled on an ice bath.
- Meanwhile the nitrating mixture was prepared (4ml of conc.Nitric acid and 4 ml of conc.sulphuric acid).
- The nitrating mixture was added drop-by-drop to the obtained solution with stirring by measuring the temperature of the solution using thermometer.
- Then the mixture was allowed to stand at room temperature for half-an-hour.
- The mixture is cooled and poured into 100 ml of ice water with vigorous stirring in a beaker. Then the solution is filtered and dried.
- P-nitroacetanilide is obtained.

3.1. THE PROCESS OF NITRATION OF ACETANILIDE

Step 1: Adding 4 g of acetanilide to 4 ml of glacial acetic acid.



Step 2: 2.8 ml of conc. H_2SO_4 is gradually added with stirring when the mixture becomes hot and the result is clear solution.



Step 3: The mixture is cooled in the ice bath



Step 4: 4.4 ml of conc. Nitric acid and 4 ml of conc. H_2SO_4 are used to prepare nitration mixture



Step 5: Then mixture is taken out from the ice bath and allowed to stand at room temperature for half- an-hour.



Step 6: The mixture is cooled and poured and into 100 ml of ice water with vigorous stirring in a beaker



Step 7: p-nitro acetanilide precipitates and o-nitro acetanilide being soluble remains in the solution



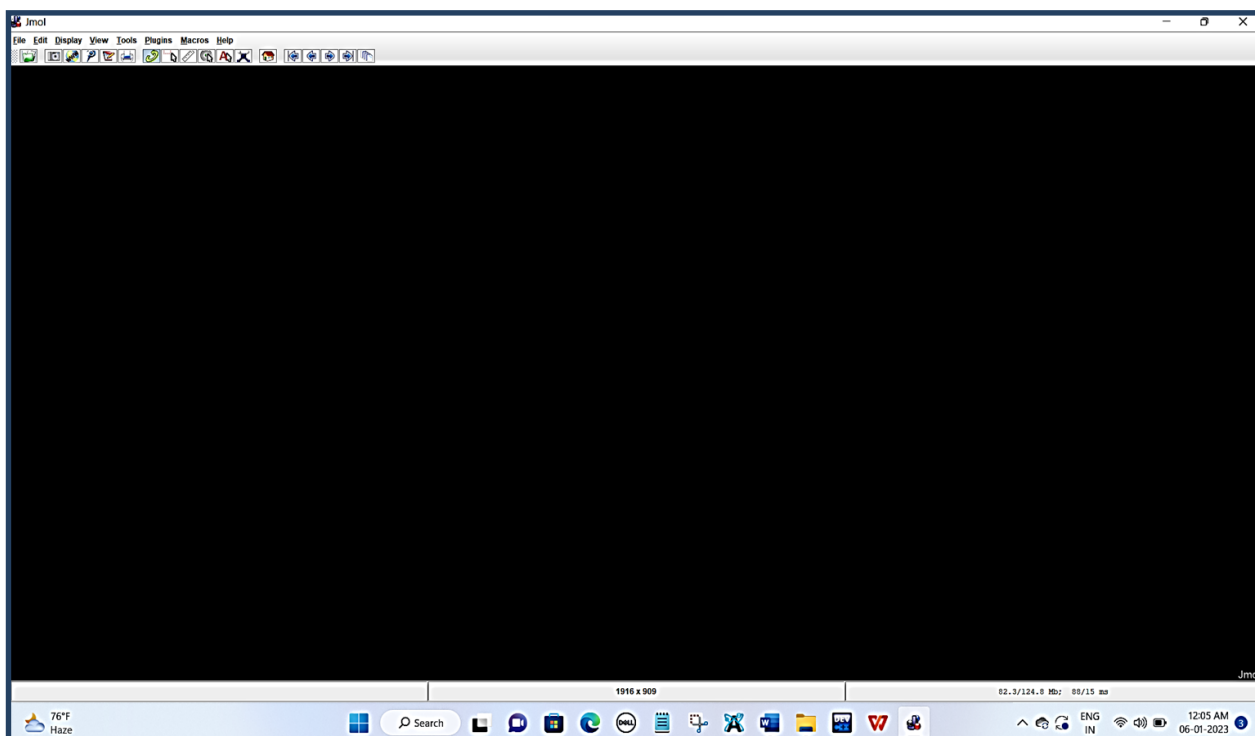
4. INSTALLATION OF Jmol

- Creating 3D molecular model
- Jmol is an open-source Java viewer for chemical structures and biomolecules in 3D
- It is free and open source software, written in Java, it runs on Windows, Mac OS X, Linux and Unix systems.



4.1. Procedure for installation of Jmol

- The open source Jmol software needs JAVA application installed in your computer. So better install the latest version.
- We can install JAVA application from www.java.com
- After installing JAVA go to <http://www.sourceforge.net> and search for Jmol and click on download.
- A zip file of Jmol will be installed.
- Now we need to extract Jmol.jar file from zip file and place it outside.
- Now to run Jmol we need to open the Jmol.jar file from the installed files.
- Now we can create and edit molecules using the Jmol.



3D STRUCTURE OF ACETANILIDE CREATED IN Jmol

About the compound

Compound name : Acetanilide

Chemical formula: $\text{C}_8\text{H}_9\text{NO}$

Molar mass: $135.166 \text{ g}\cdot\text{mol}^{-1}$

Melting point 114.3°C

Boiling point 304°C

4.2. Procedure for creating 3D structure of acetanilide in Jmol

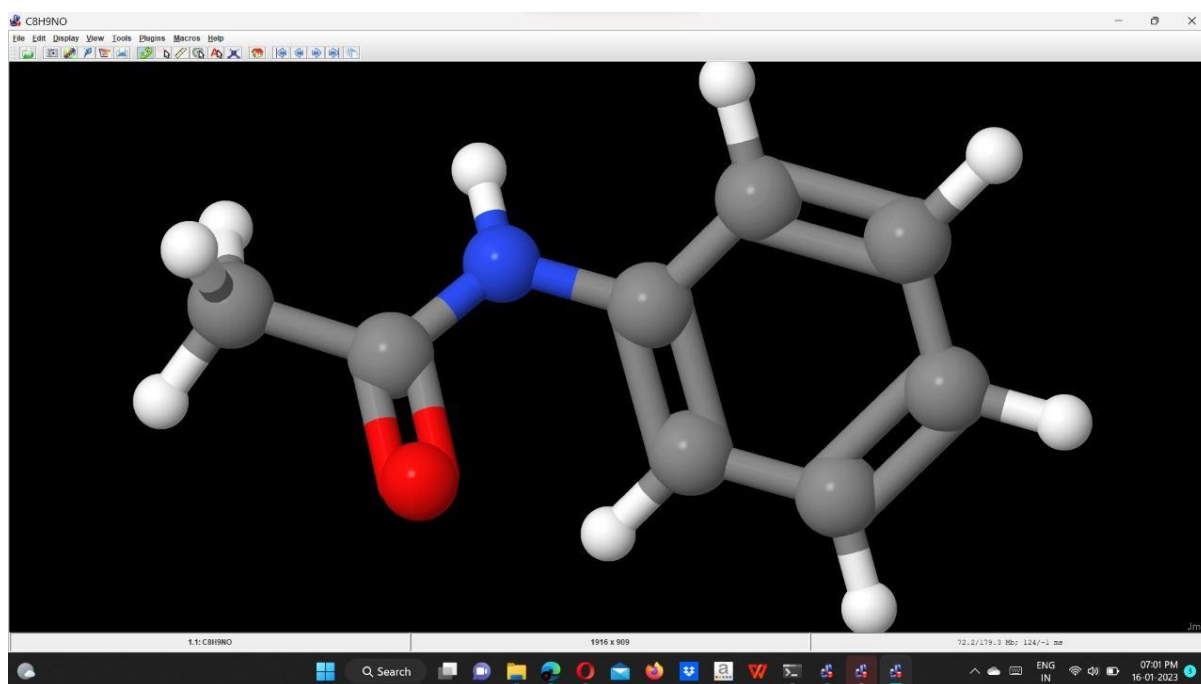
Step1: Open Jmol in your desktop or in your pc

Step2: Go to file and then click ‘Get MOL’

Step3: A dialogue box opens with the provision to type the molecule

Step 4: Type the name of the molecule as “Acetanilide” and click enter

Step 5: The 3D structure of acetanilide was imported from the database

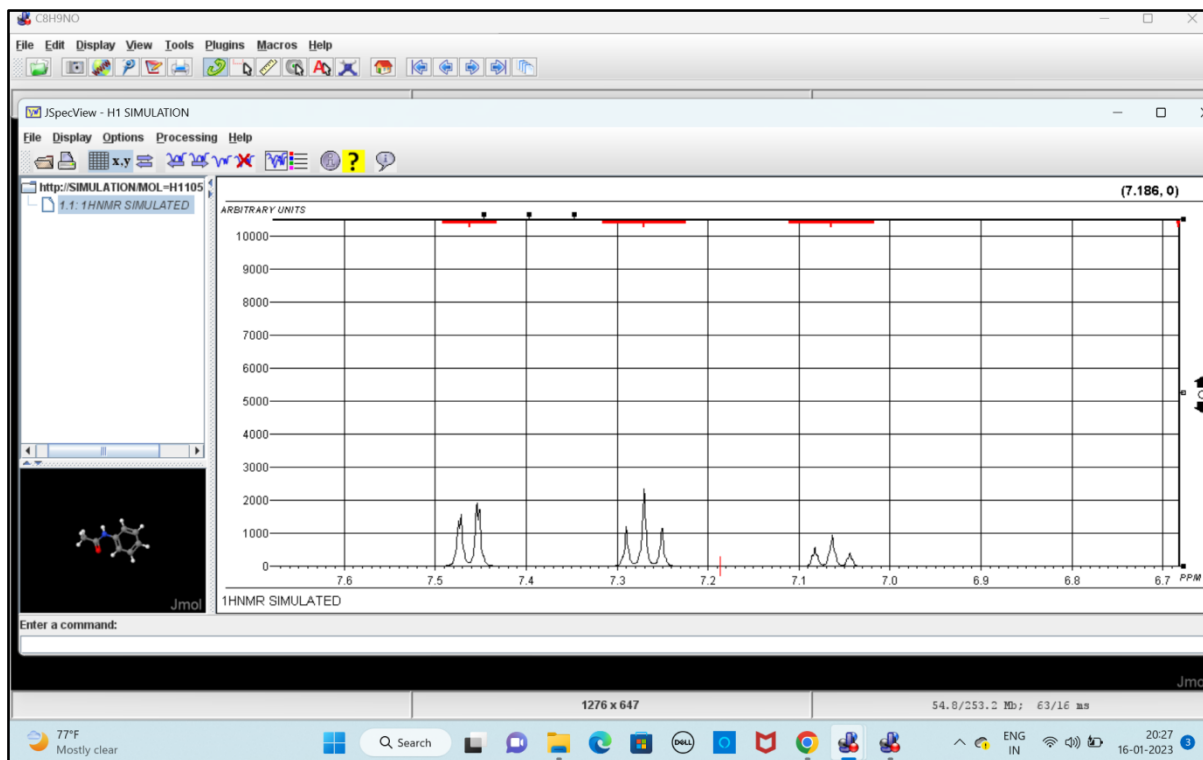


4.2.1. Procedure for obtaining ¹HNMR of Acetanilide in JSPEC view of Jmol

Step 1: Open the Jmol interface window with the 3D structure of acetanilide

Step 2: In the menu bar go to “tool” menu click the spectra inside that choose ¹HNMR

Step 3: New JSPEC view dialogue box opens with ¹HNMR spectra of acetanilide



About the compound:

Compound name:	p-nitroacetanilide
Chemical formula:	$\text{C}_8\text{H}_8\text{N}_2\text{O}_3$
Molar mass:	180.16 g/mol
Melting point	215°C
Boiling point	408.9°C

4.3. Procedure for creating 3D structure of p-nitroacetanilide in Jmol

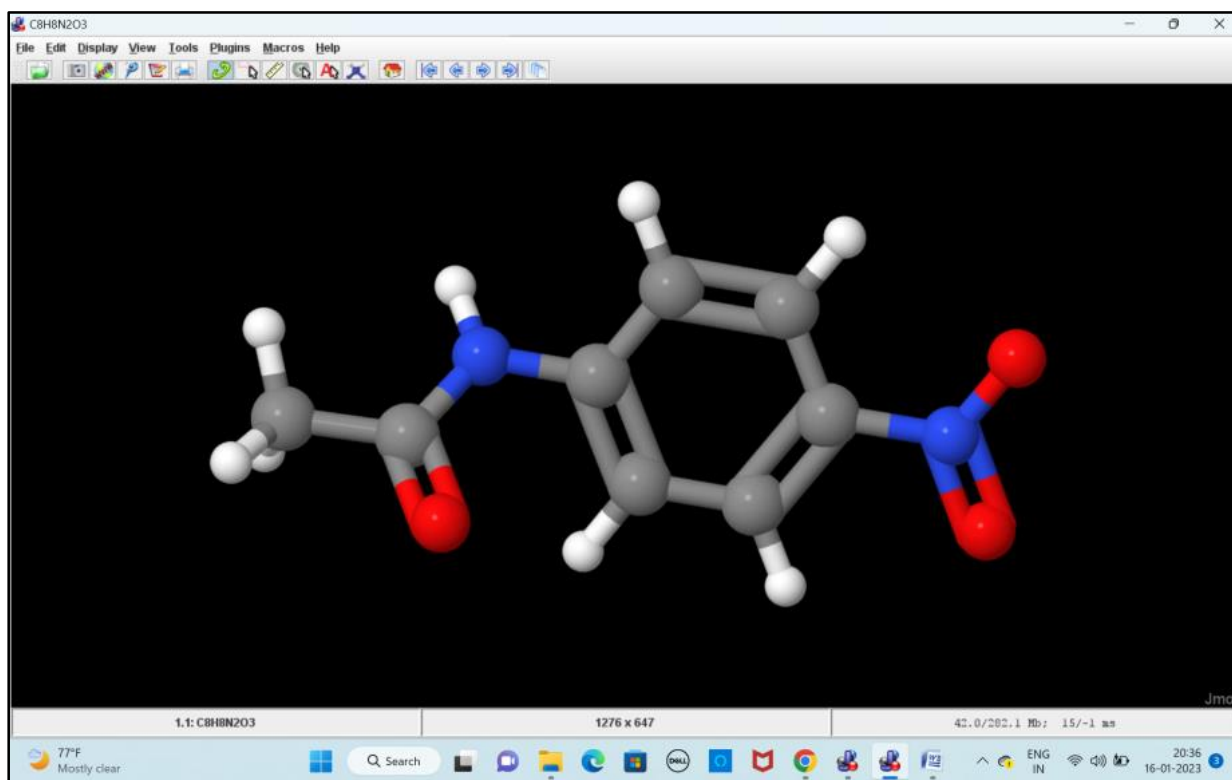
Step1: Open Jmol in your desktop or in your pc

Step2: Go to file and then click ‘**Get MOL**’

Step3: A dialogue box opens with the provision to type the molecule

Step 4: Type the name of the molecule as “p-nitroacetanilide” and click enter

Step 5: The 3D structure of p-nitroacetanilide was imported from the database

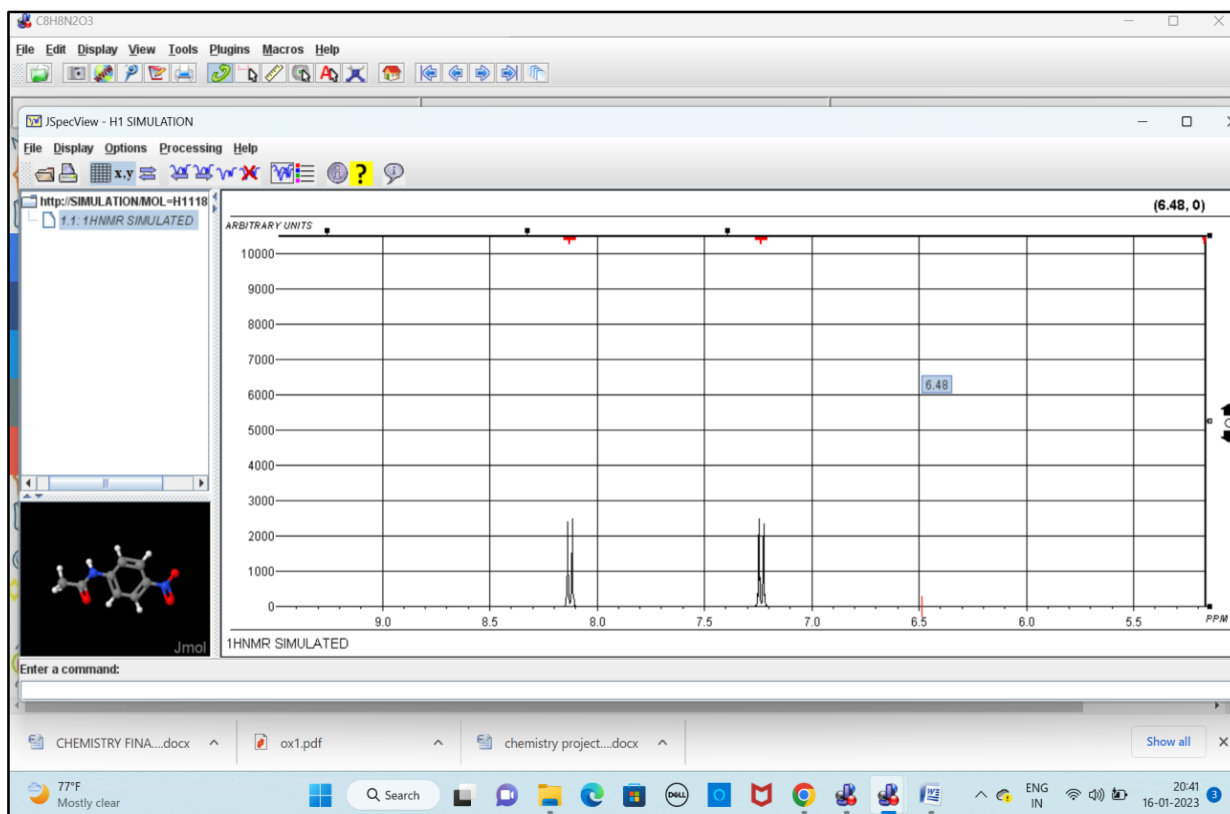


4.3.1. Procedure for obtaining ¹HNMR of p-Nitro acetanilide in JSPEC view of Jmol

Step 1: Open the Jmol interface window with the 3D structure of p-Nitro acetanilide

Step 2: In the menu bar go to “tool” menu click the spectra inside that choose ¹HNMR

Step 3: New JSPEC view dialogue box opens with ¹HNMR spectra of acetanilide



About the compound:

Compound name:	Naphthalene
Chemical formula:	$C_{10}H_8$
Molar mass:	128 g mol^{-1}
Melting point	74°C
Boiling point	218°C

4.4. Procedure for creating 3D structure of Naphthalene in Jmol

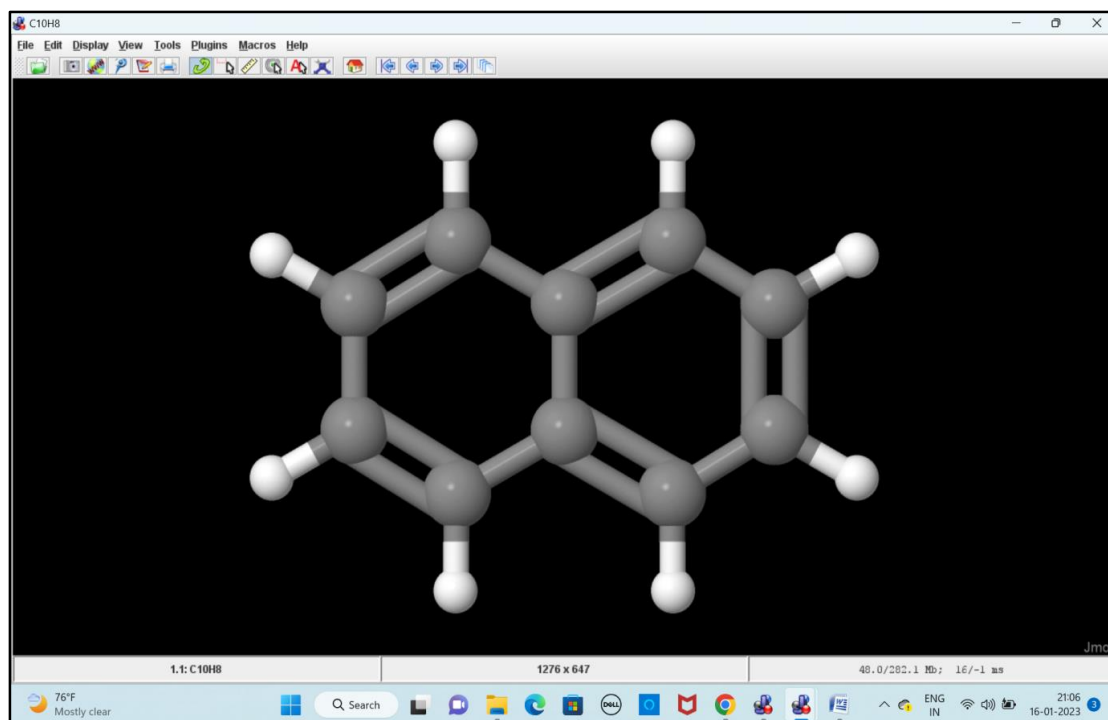
Step1: Open Jmol in your desktop or in your pc

Step2: Go to file and then click 'Get MOL'

Step3: A dialogue box opens with the provision to type the molecule

Step 4: Type the name of the molecule as Naphthalene and click enter

Step 5: The 3D structure of Naphthalene was imported from the database

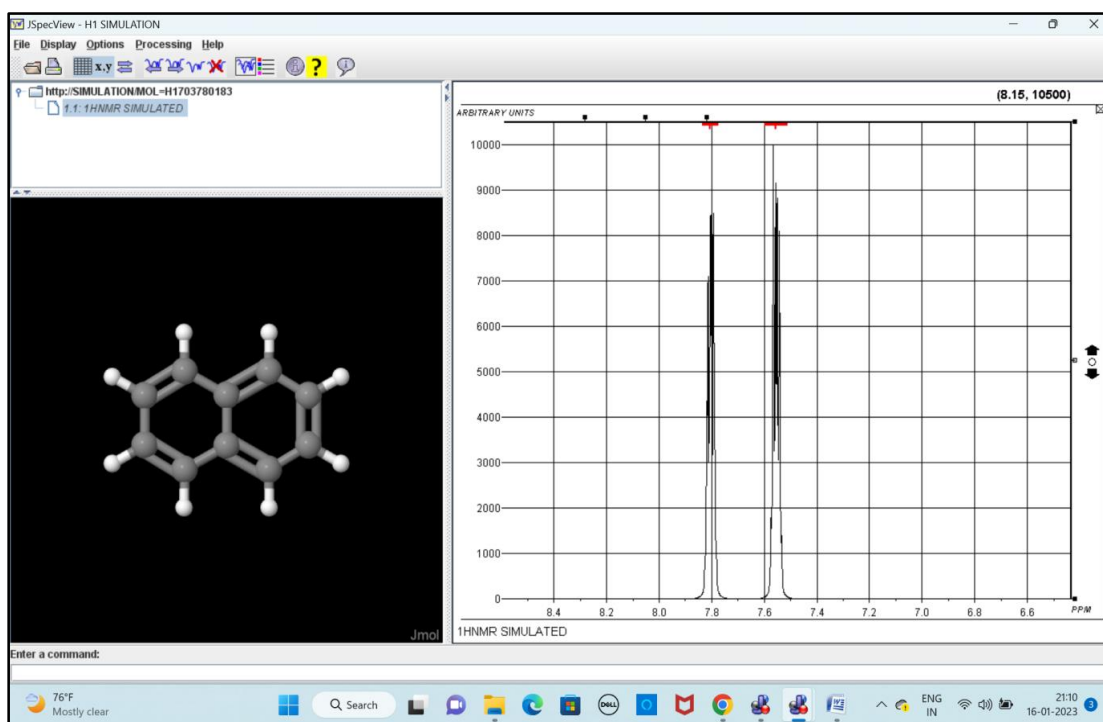


4.4.1. Procedure for obtaining ¹HNMR of Naphthalene in JSPEC view of Jmol

Step 1: Open the Jmol interface window with the 3D structure of Naphthalene

Step 2: In the menu bar go to “tool” menu click the spectra inside that choose ¹HNMR

Step 3: New JSPEC view dialogue box opens with ¹HNMR spectra of acetanilide



About the compound:

Compound name:	1-NITRONAPHTHALENE
Chemical formula:	C ₁₀ H ₇ NO
Molar mass:	173.1 g/mol
Melting point	304°C
Boiling point	304 °C

4.5. Procedure for creating 3D structure of 1-Nitronaphthalene in Jmol

Step 1: Open Jmol in your desktop or in your pc

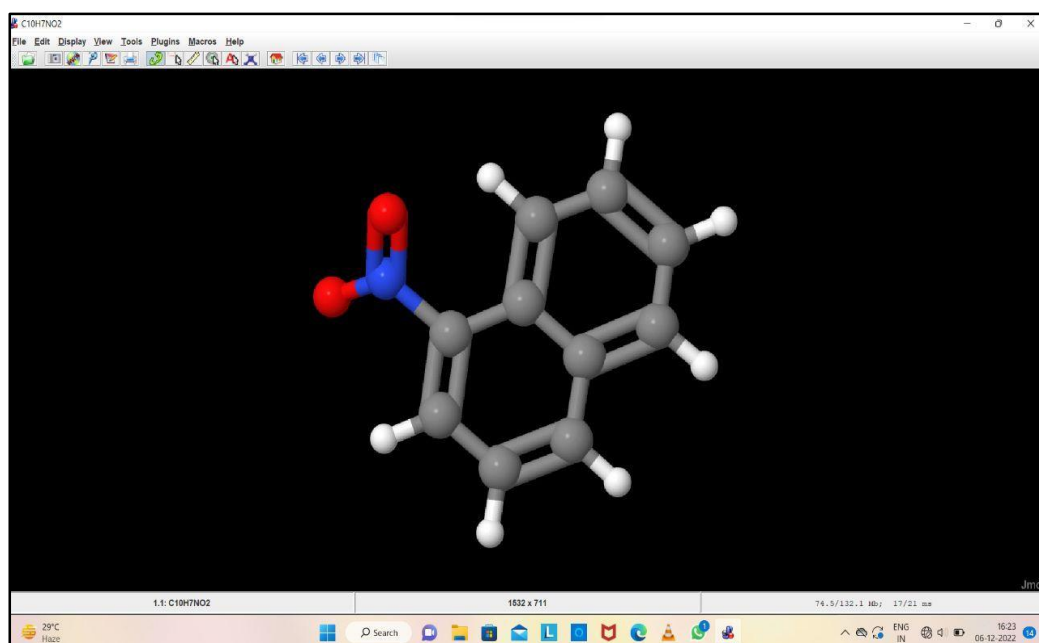
Step 2: Go to file and then click ‘Get MOL’

Step 3: A dialogue box opens with the provision to type the molecule

Step 4: Type the name of the molecule as “1-Nitronaphthalene” and click enter

Step 5: The 3D structure of 1-Nitronaphthalene was imported from the database

THE 3D STRUCTURE OF 1-NITRONAPHTHALENE IN Jmol



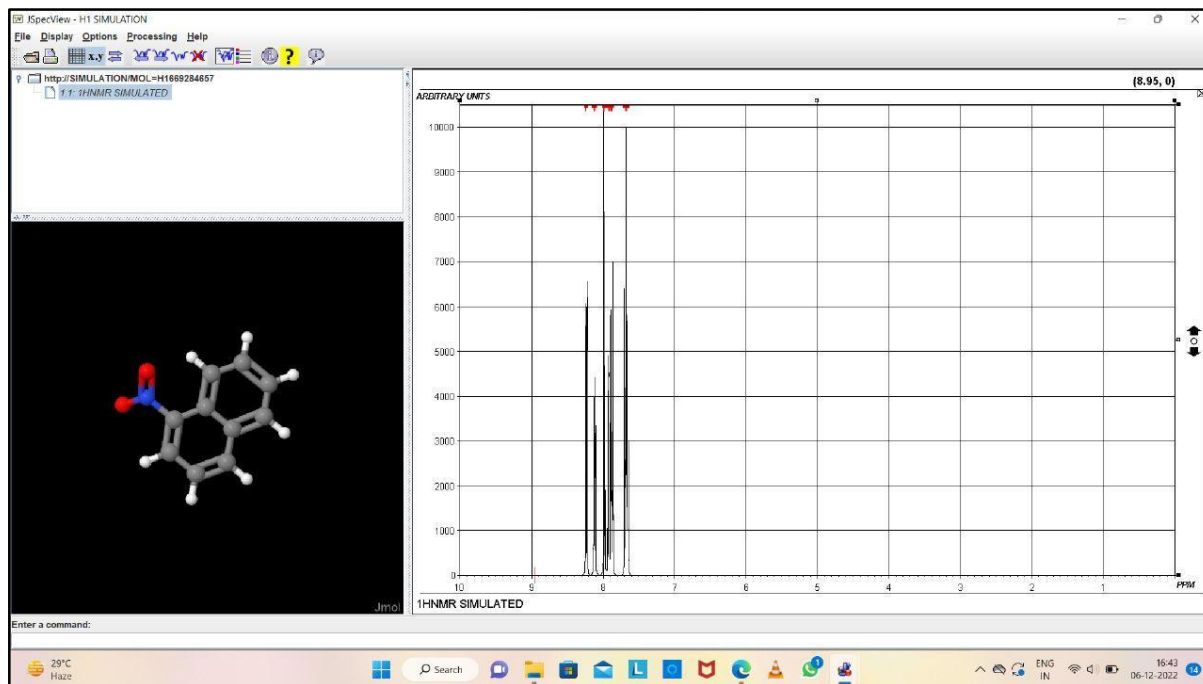
4.5.1. Procedure for obtaining ¹HNMR of 1-Nitronaphthalene in JSPEC view of Jmol

Step 1: Open the Jmol interface window with the 3D structure of 1-Nitronaphthalene

Step 2: In the menu bar go to “tool” menu click the spectra inside that choose ¹HNMR

Step 3: New JSPEC view dialogue box opens with ¹HNMR spectra of 1-Nitronaphthalene

1HNMR OF 1-NITRONAPHTHALANE IN JSPEC VIEW OF Jmol



About the compound:

Compound name:	BENZOICACID
Chemical formula:	C ₇ H ₆ O ₂
Molar mass:	122.123 g/mol
Melting point	122°C
Boiling point	249.2°C

4.6. Procedure for creating 3D structure of Benzoic acid in Jmol

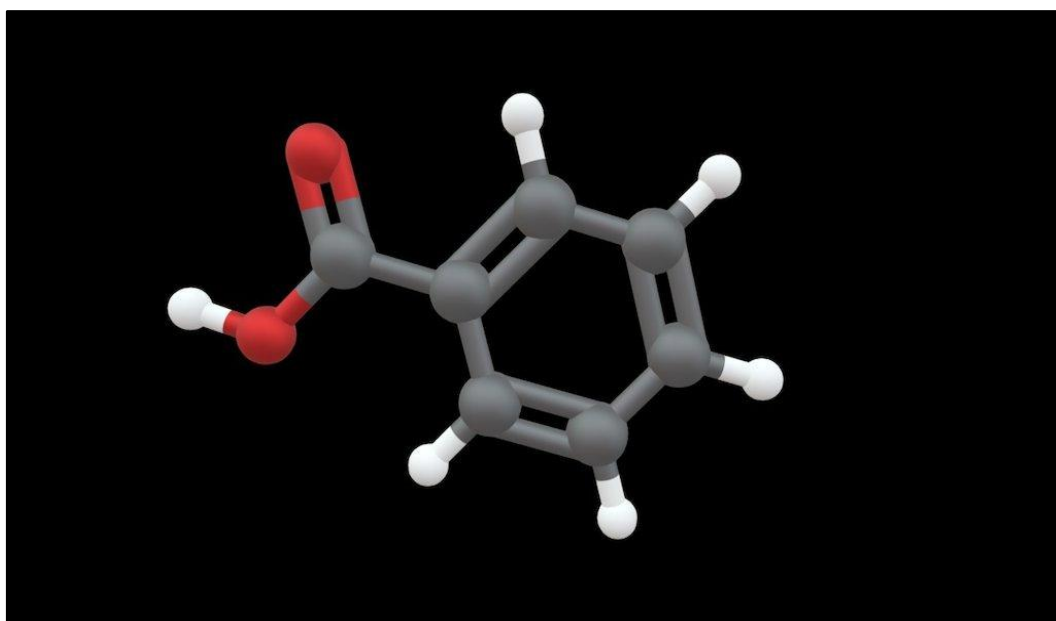
Step 1: Open Jmol in your desktop or in your pc

Step 2: Go to file and then click ‘**Get MOL**’

Step 3: A dialogue box opens with the provision to type the molecule

Step 4: Type the name of the molecule as “**Benzoic acid**” and click enter

Step 5: The 3D structure of benzoic acid was imported from the database

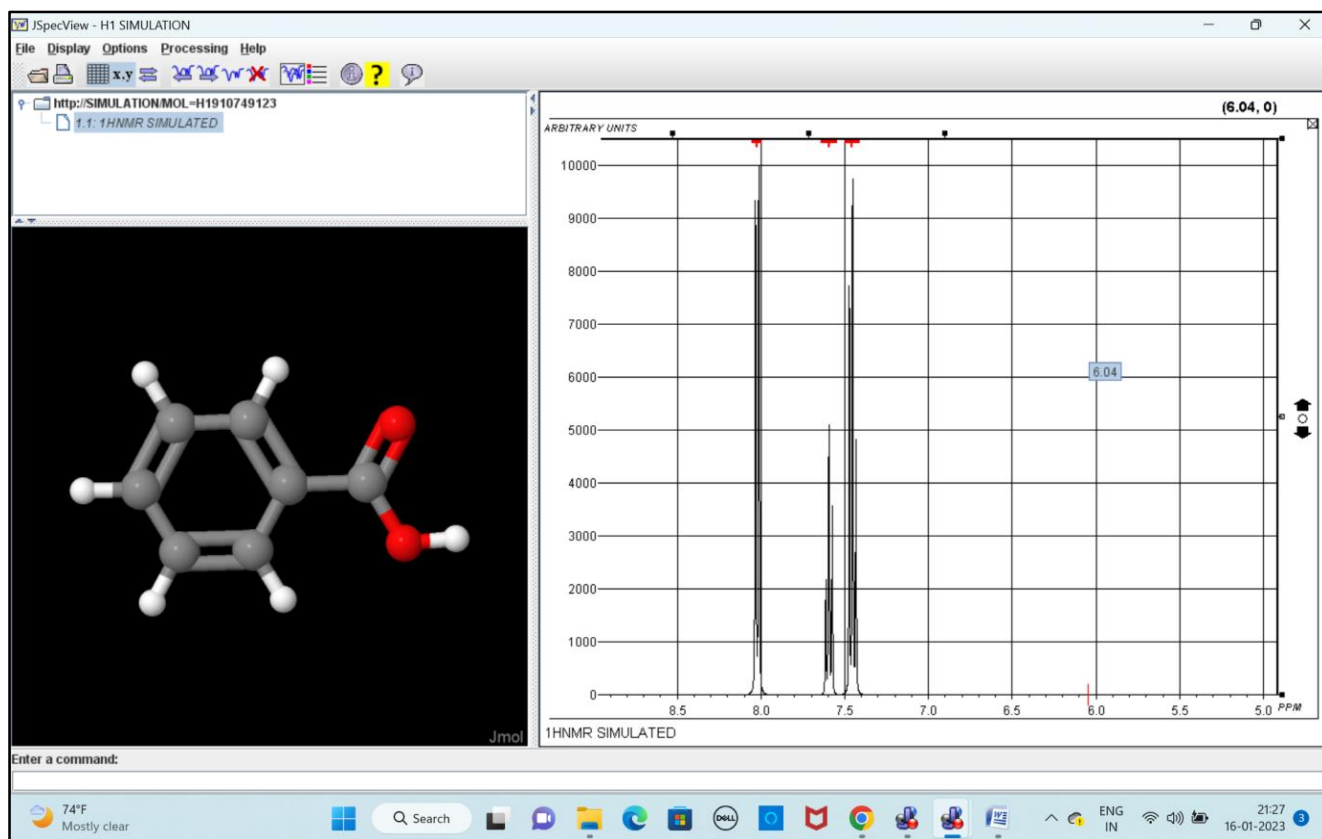


4.6.1. Procedure for obtaining 1HNMR of Benzoic acid in JSPEC view of Jmol

Step 1: Open the Jmol interface window with the 3D structure of benzoic acid

Step 2: In the menu bar go to “tool” menu click the spectra inside that choose 1HNMR

Step 3: New JSPEC view dialogue box opens with 1HNMR spectra of benzoic acid



About the compound:

Compound name:	3-NITROBENZOICACID
Chemical formula:	$C_7H_5NO_4$
Molar mass:	$167.12\text{g}\cdot\text{mol}^{-1}$
Melting point	139-141 °C
Boiling point	139-141°C

4.7. Procedure for creating 3D structure of 3-Nitrobenzoic acid in Jmol

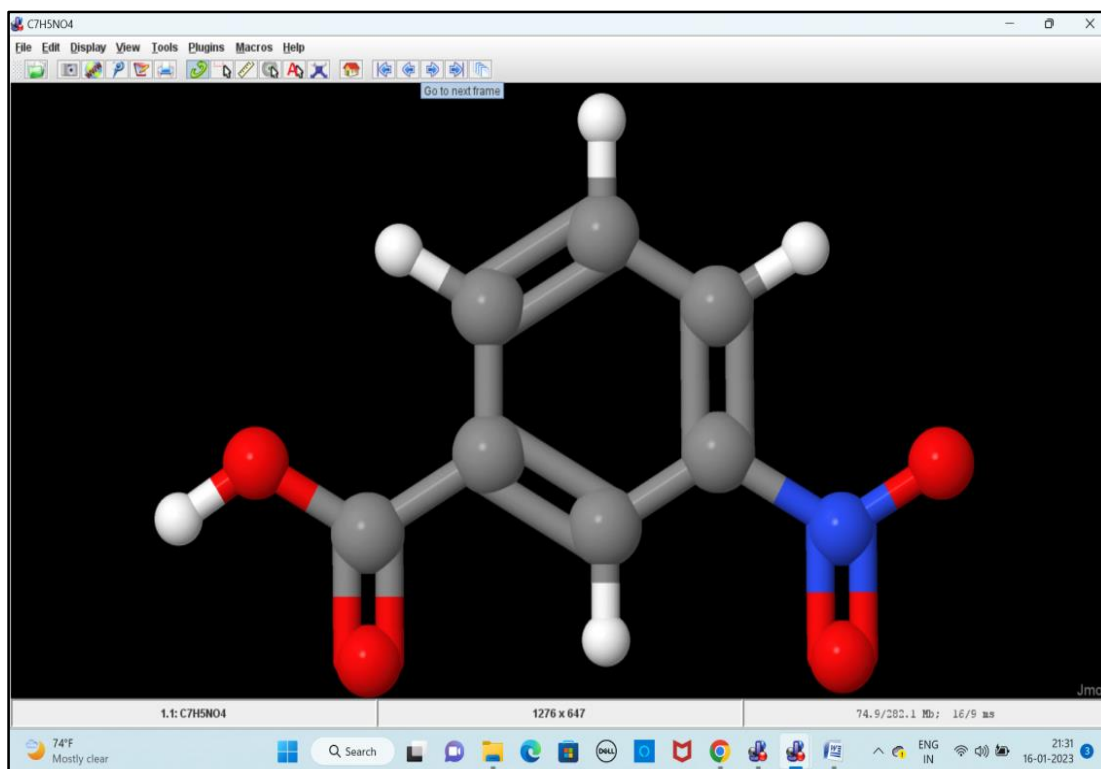
Step1: Open Jmol in your desktop or in your pc

Step2: Go to file and then click ‘Get MOL’

Step3: A dialogue box opens with the provision to type the molecule

Step 4: Type the name of the molecule as 3-Nitrobenzoic acid and click enter

Step 5: The 3D structure of 3-Nitrobenzoic acid was imported from the database

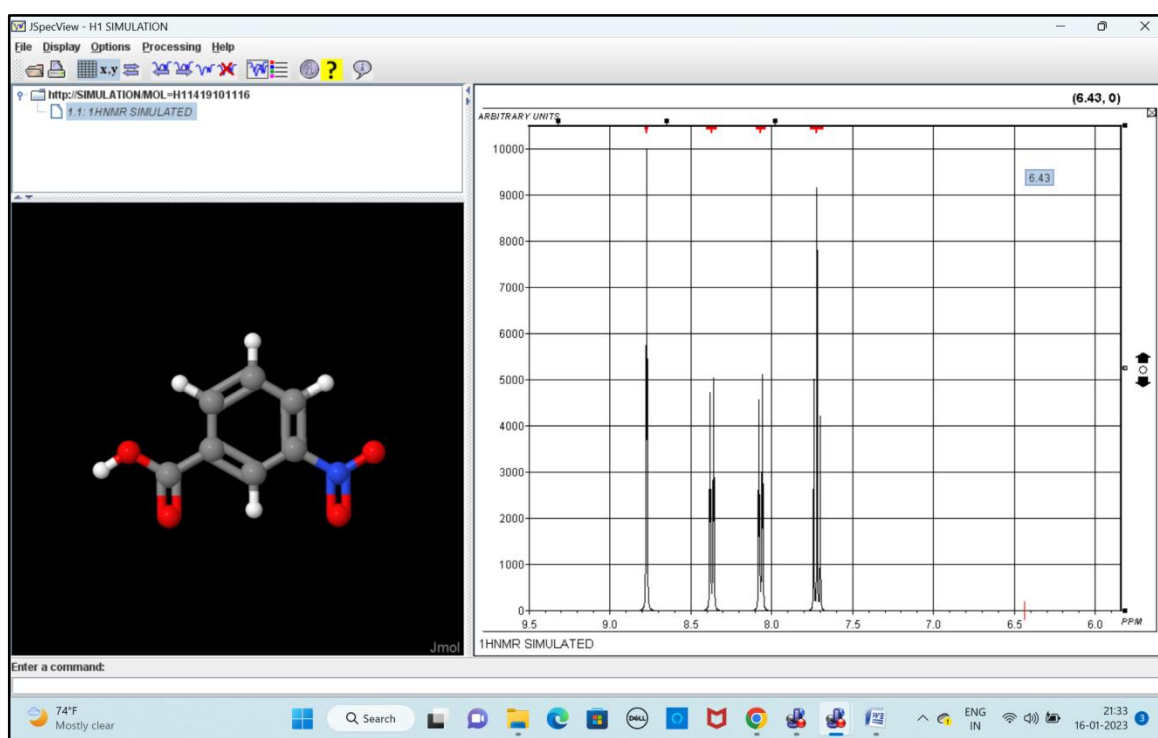


4.7.1. Procedure for obtaining ¹HNMR of 3-Nitrobenzoic acid in JSPEC view of Jmol

Step 1: Open the Jmol interface window with the 3D structure of 3-Nitrobenzoic acid

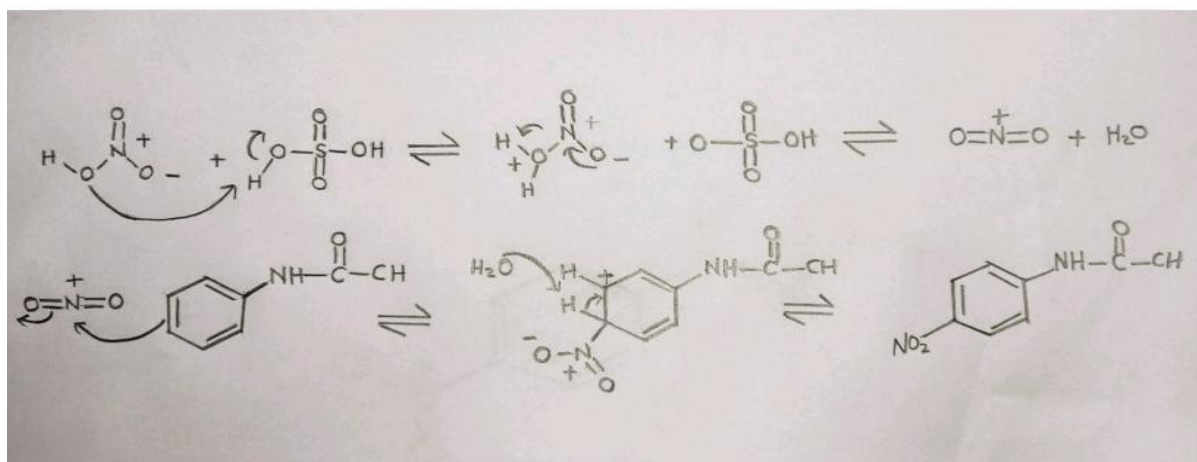
Step 2: In the menu bar go to “tool” menu click the spectra inside that choose ¹HNMR

Step 3: New JSPEC view dialogue box opens with ¹HNMR spectra of 3-Nitrobenzoic acid



5. Result and Discussion

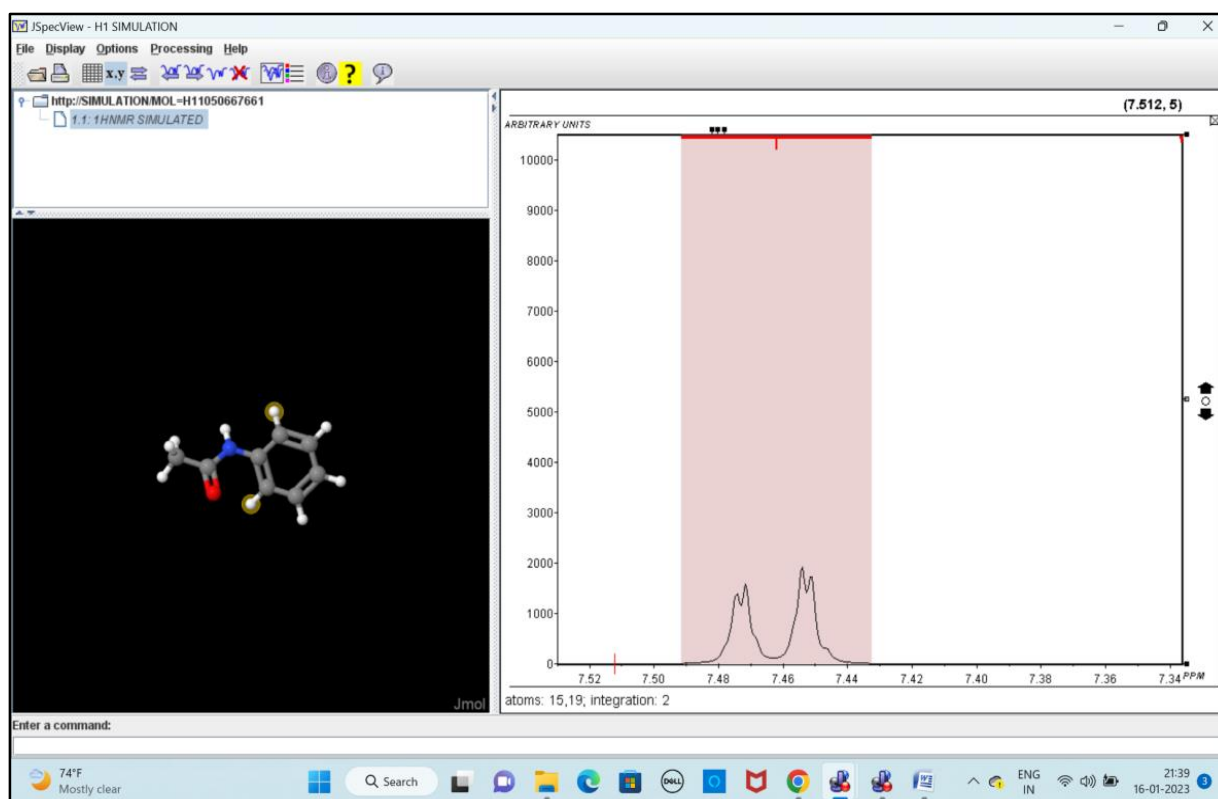
5.1. Mechanism of Nitration of acetanilide:



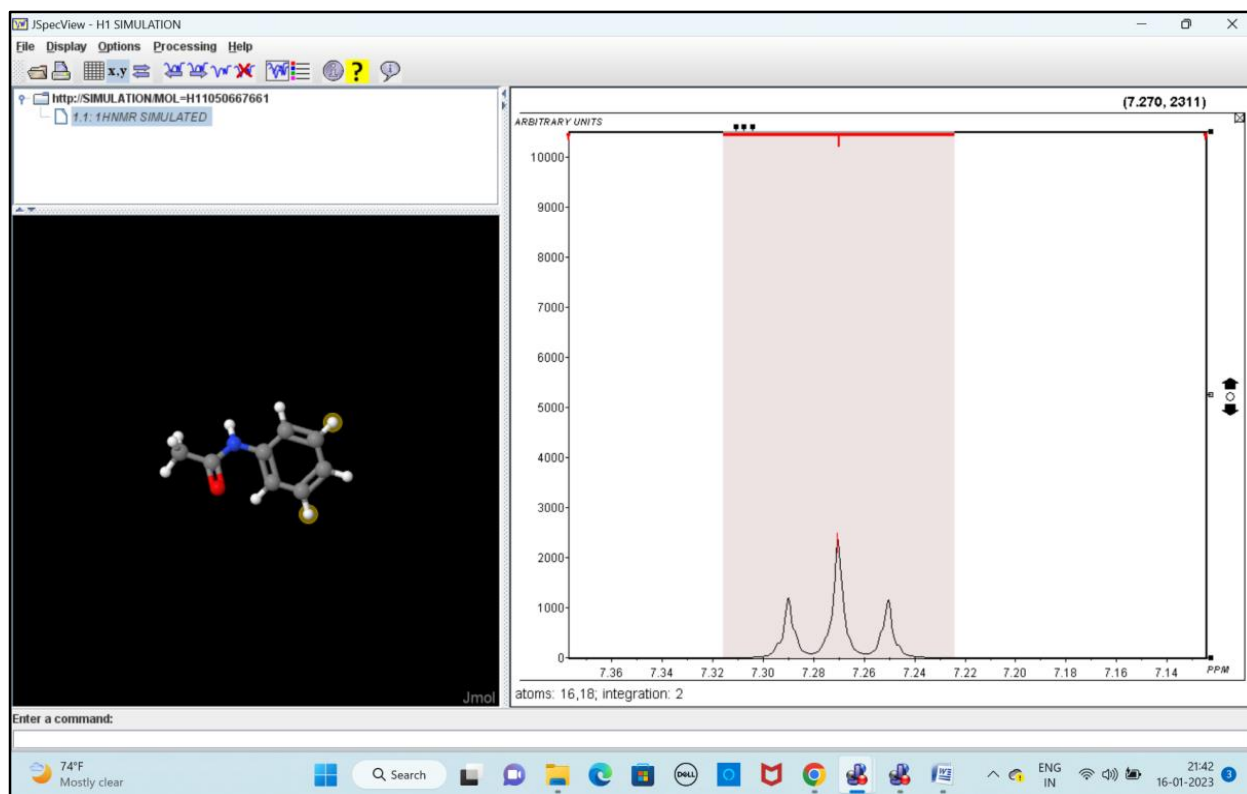
- The organic compound p-nitroacetanilide is prepared from acetanilide through nitration.
- The organic compound p-nitroacetanilide is prepared from acetanilide through nitration.
- When acetanilide is treated with nitrating mixture that is a mixture of nitric acid and sulphuric acid p-nitroacetanilide is formed.

- Along with p-nitroacetanilide, o-nitroacetanilide is also formed as a minor product.
- Since o-nitroacetanilide is very much soluble in alcohol it is very easy to isolate p-nitroacetanilide through crystallization.
- The electrophile -NO_2 will attach the para position because the -NHCOCH_3 is an electron releasing group.
- Nitro anilines can be prepared by this type of reactions because nitration of aniline is not possible, amino group gets oxidized with nitrating mixture.
- In order to protect the amino group from oxidation acetanilide is first nitrated to give p-nitroacetanilide and then on hydrolysis to give p-nitroaniline which is difficult to obtain by direct nitration.

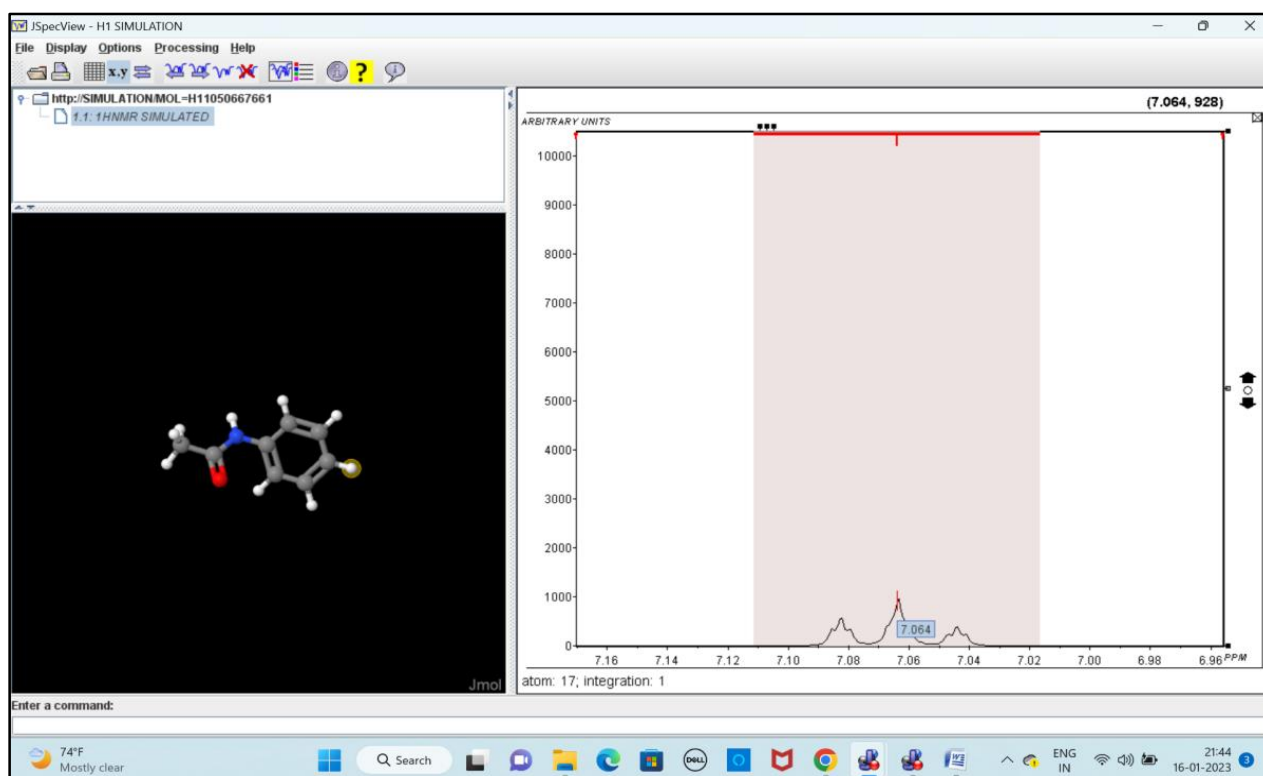
5.1.2. Interpretation of ^1H NMR of acetanilide molecule obtained from JSPEC view of Jmol



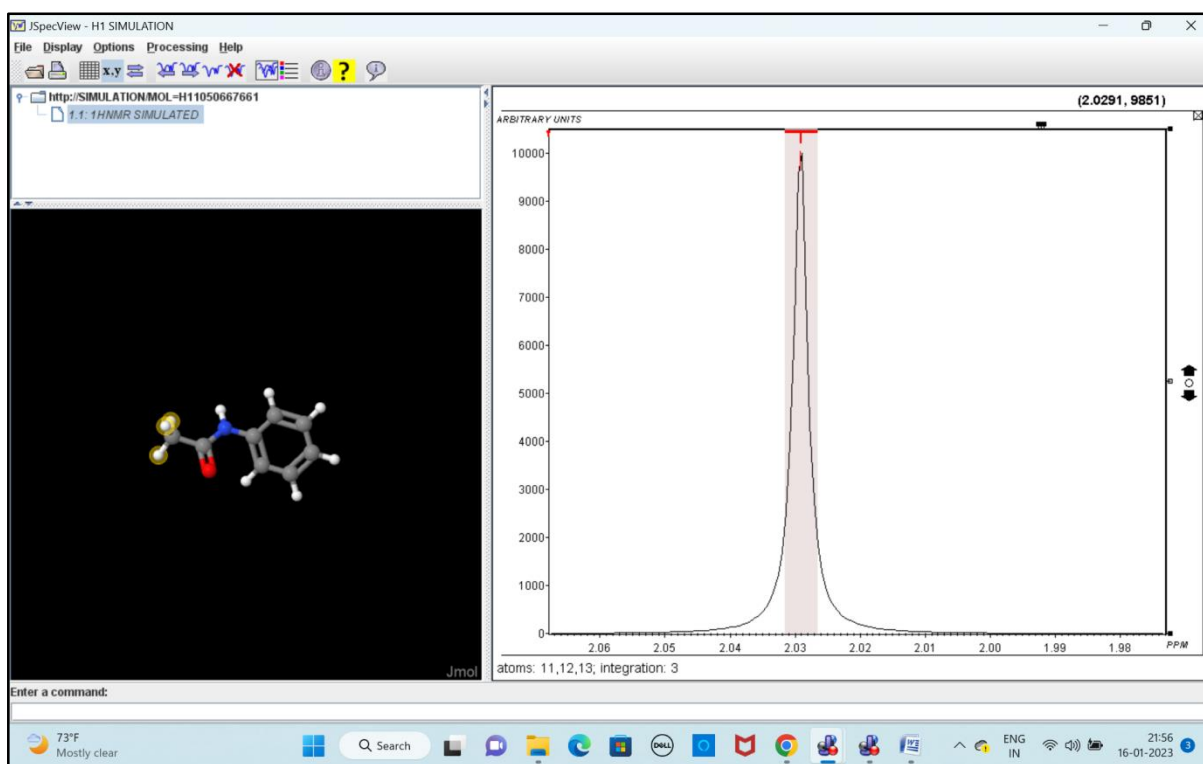
- Doublet peak was obtained for both the hydrogen's as they have only one equivalent hydrogen in their neighbouring position
- Position of the peaks were 7.47 and 7.45 PPM



- Triplet peak was obtained for the above highlighted hydrogen atom as they have two equivalent hydrogen in its neighbouring position
- The peak position was at 7.27 PPM

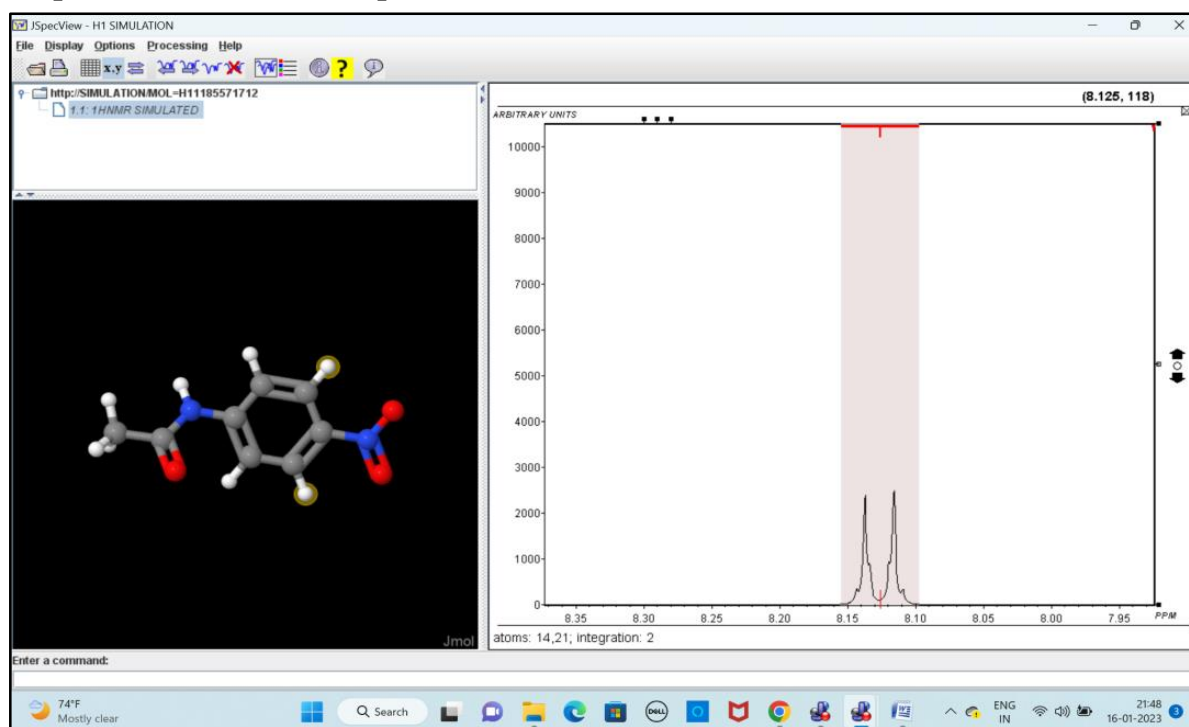


- Triplet peak was obtained for the above highlighted hydrogen atom as they have two equivalent hydrogen in its neighbouring position
- The peak position was at 7.06 PPM

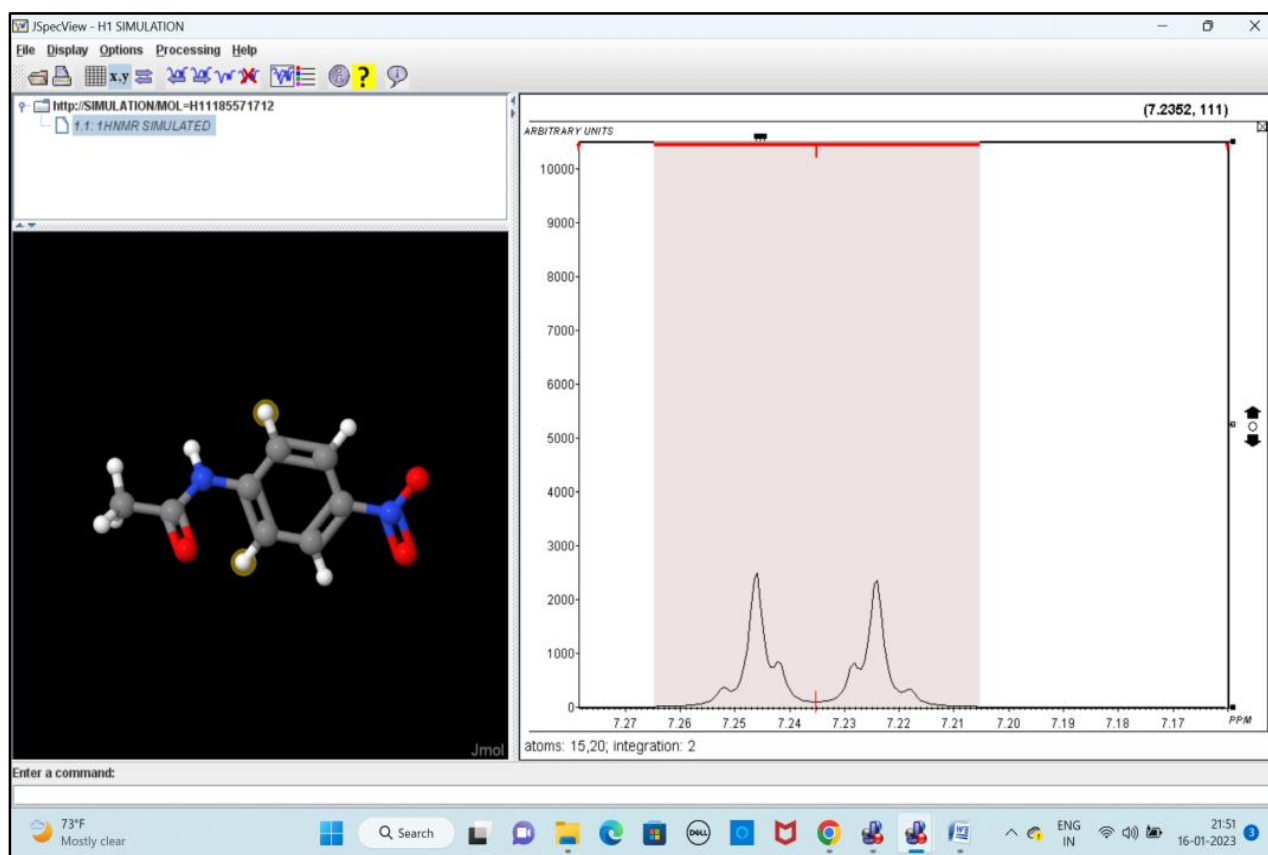


- Singlet peak was obtained for terminal methyl group
- Position of the peaks were 2.02 PPM

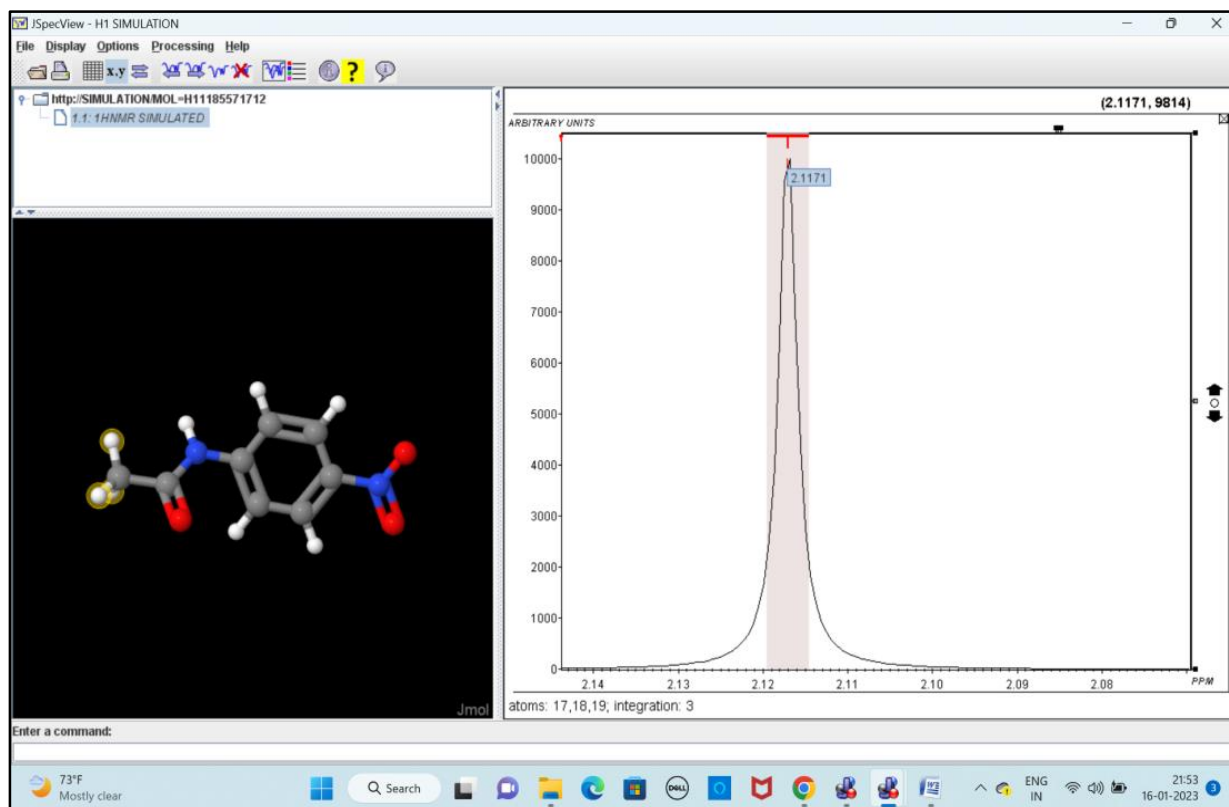
5.1.3. Interpretation of ^1H NMR of p-nitroacetanilide molecule obtained from JSPEC view of Jmol



- Doublet peak was obtained for both the hydrogen's as they have only one equivalent hydrogen in their neighbouring position
- Position of the peaks were 8.125 PPM



- Doublet peak was obtained for both the hydrogen's as they have only one equivalent hydrogen in their neighbouring position
- Position of the peaks were 7.23 PPM

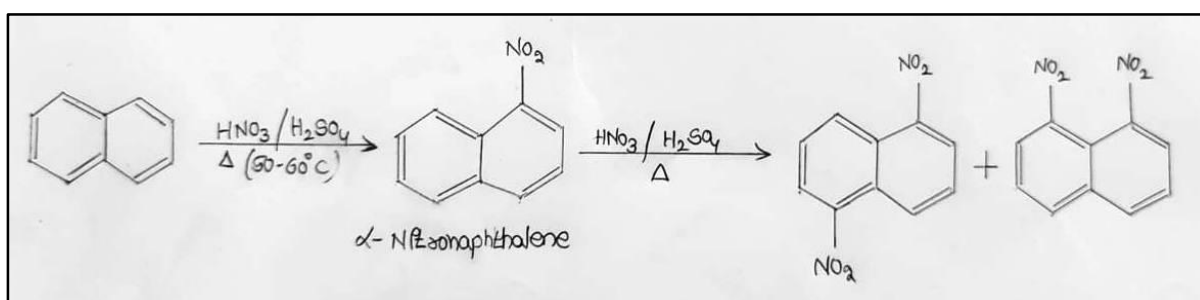


- Singlet peak was obtained for terminal methyl group
- Position of the peaks were 2.11 PPM

5.1.4. Comparison of ^1H NMR spectra of Acetanilide and p-Nitroacetanilide:

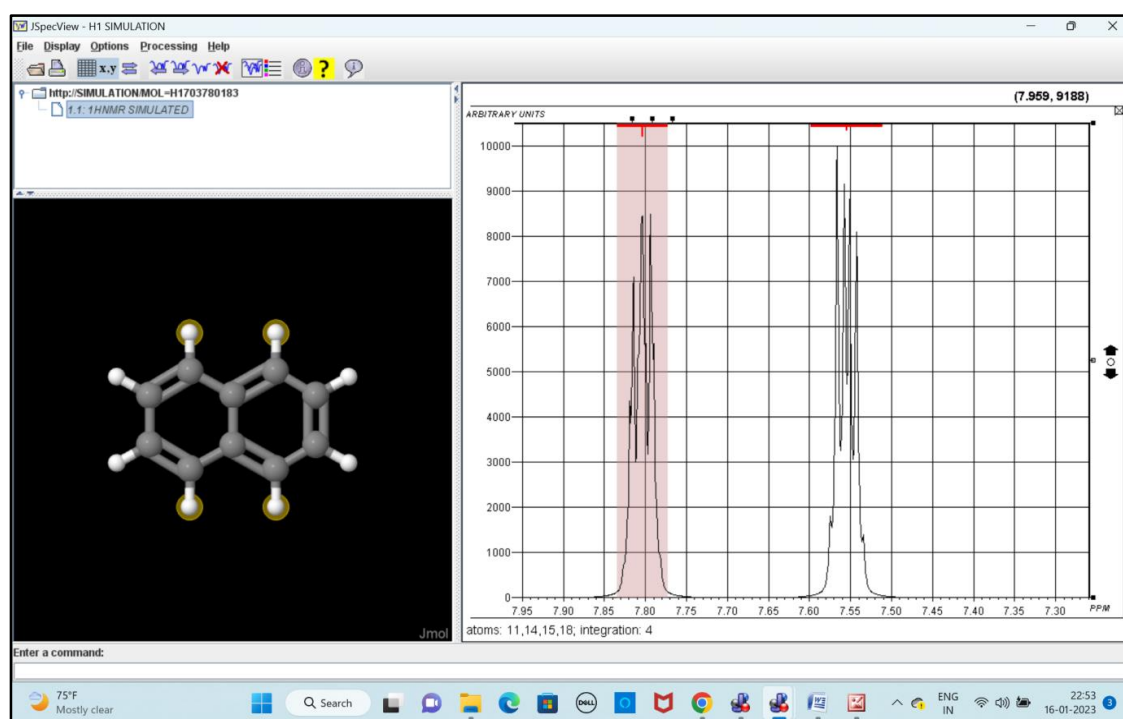
- The singlet peak for terminal methyl group is common in both acetanilide and p-Nitroacetanilide
- The doublet peaks for hydrogen's adjacent to $-\text{NH}$ group are common in both acetanilide and p-Nitroacetanilide
- The triplet peak for in acetanilide at 7.06 PPM was missing in the p-nitroacetanilide instead a doublet peak at 8.125 PPM was seen which means the Nitro group was substituted next to that hydrogen.
- The peak was also shifted to 8.125PPM due to the electron withdrawing nature of nitro group

5.2. Mechanism of Nitration of Naphthalene



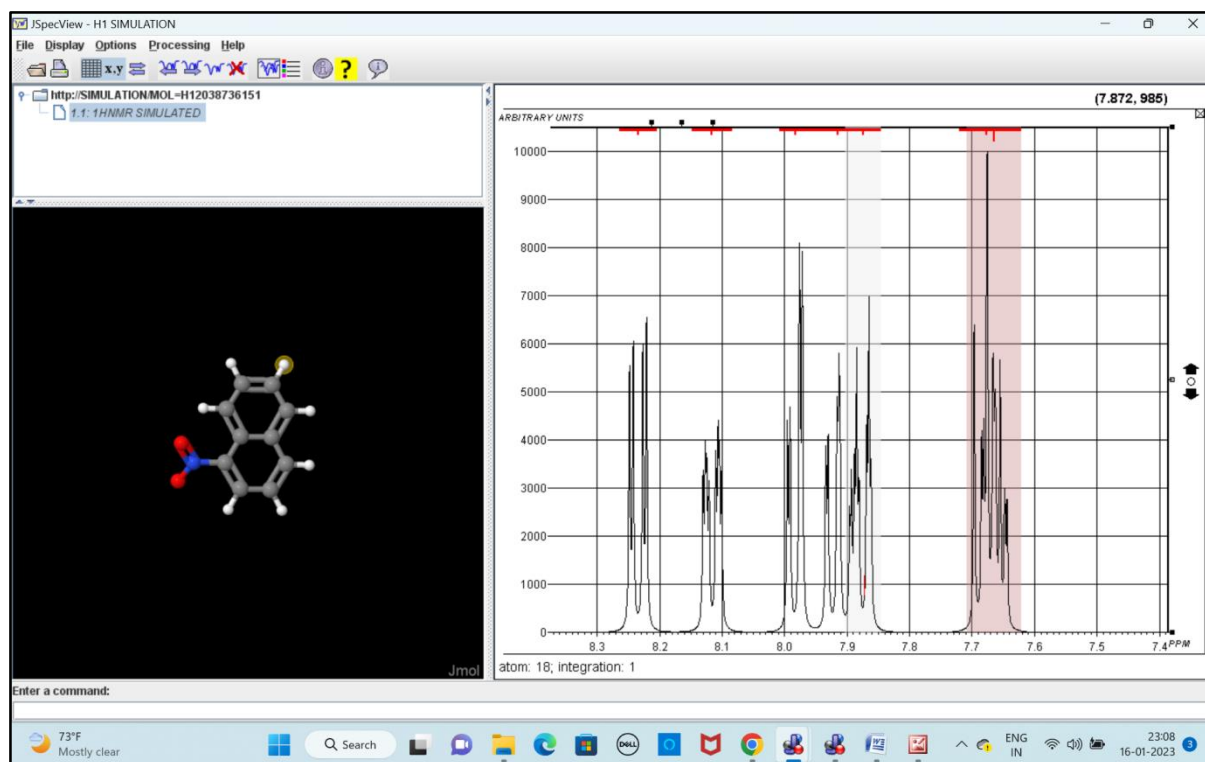
- The nitration of naphthalene is an electrophilic aromatic substitution.
- It involves the attack of nitronium ion, NO_2^+ , on the aromatic system.
- Nitration at C-1 produces a carbocation that has 7 resonance contributors.
- Four of these (1, 2, 6, and 7) preserve the aromaticity (six π electrons) of the second ring.
- Nitration at C-2 produces a carbocation that has 6 resonance contributors.
- Two of these (1 and 6) preserve the aromaticity of the second ring.
- So attack at C-1 is favoured, because it forms the most stable intermediate.
- The major product is 1-nitronaphthalene. The minor product is 2-nitronaphthalene.

5.2.1. Interpretation of ^1H NMR of Napthalene molecule obtained from JSPEC view of Jmol



- Two multiplet peaks were obtained with the integration of 4, which means numerous protons were there in the neighbouring environment
- The peak values were 7.8 and 7.5 PPM

5.2.2. Interpretation of ^1H NMR of 1-Nitronaphthalene molecule obtained from JSPEC view of Jmol

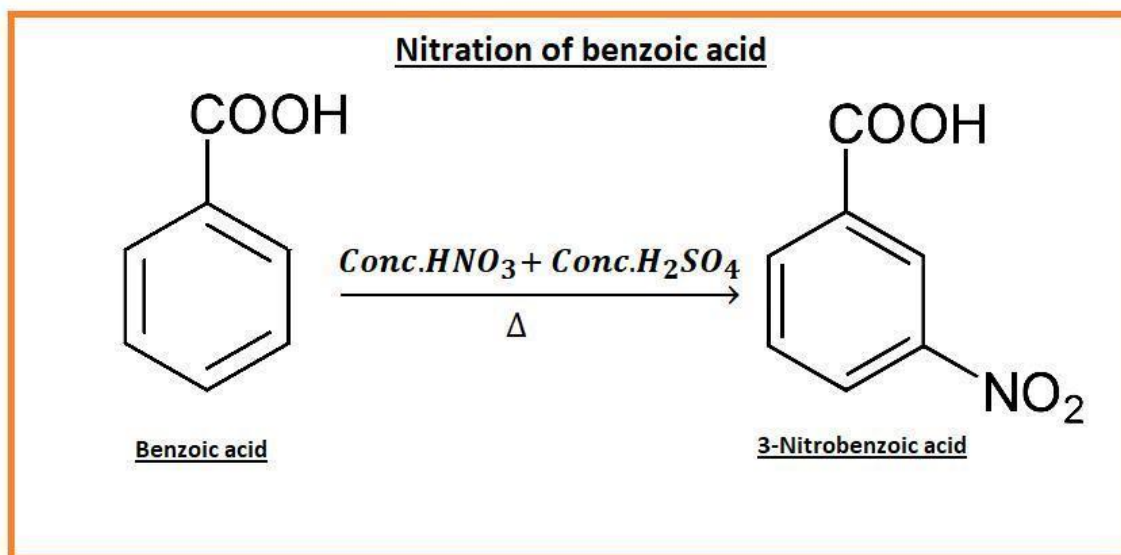


- The spectra of 1-Nitronaphthalene shows 7 sets of peaks corresponding to 7 types of hydrogen environment which means the substitution of nitro group have created 7 different types of hydrogen environments

5.2.3. Comparison of ^1H NMR spectra of Naphthalene and 1-Nitronaphthalene:

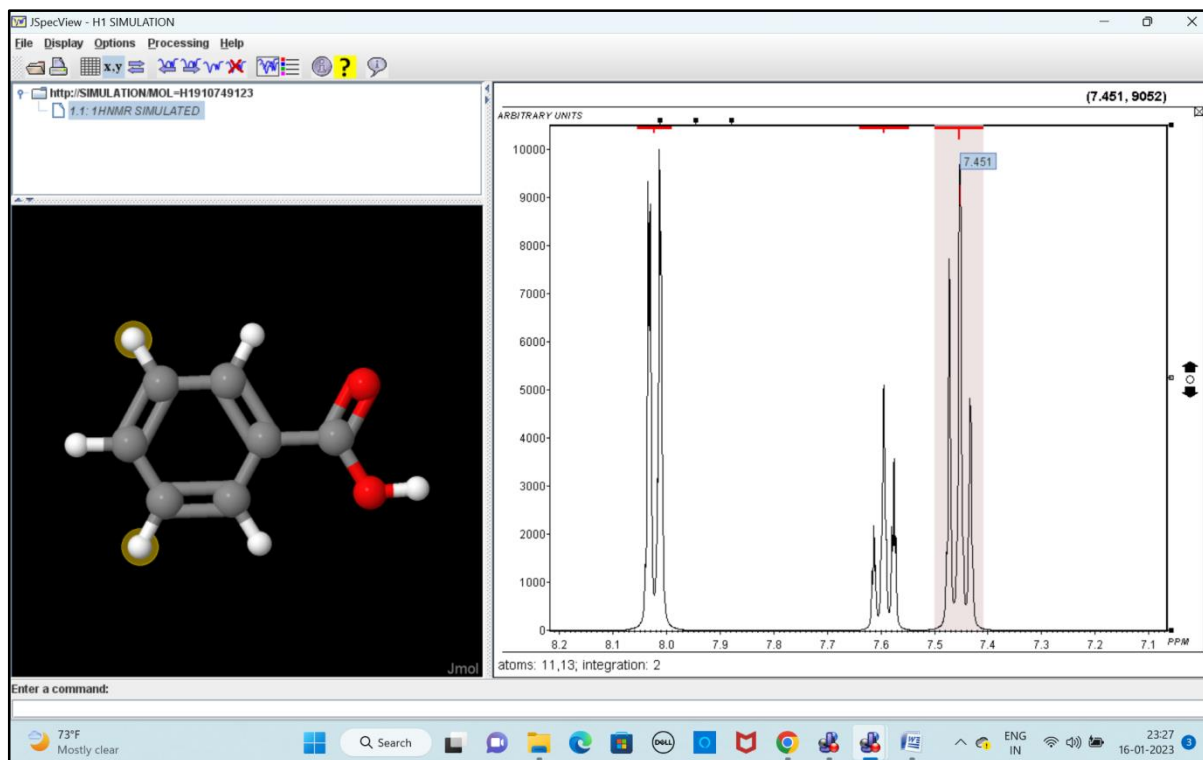
- The spectra of naphthalene shows only two sets of peaks whereas the 1- Nitro naphthalene shows 7 sets of peaks
- The hydrogen next to the nitro groups in the same ring shows the peaks at around 8.23 PPM
- The hydrogen in the para position to the nitro group in the same ring shows the peak at 8.11 PPM
- The hydrogen next to the nitro groups in the next ring shows the peaks at around 7.982 PPM and the adjacent hydrogens at 7.913 and 7.85 PPM
- The hydrogen in meta position to the nitro group in the same ring at 7.680 PPM and the next ring at 7.66 PPM

5.3. Mechanism of nitration of Benzoic acid to 3-Nitrobenzoic acid



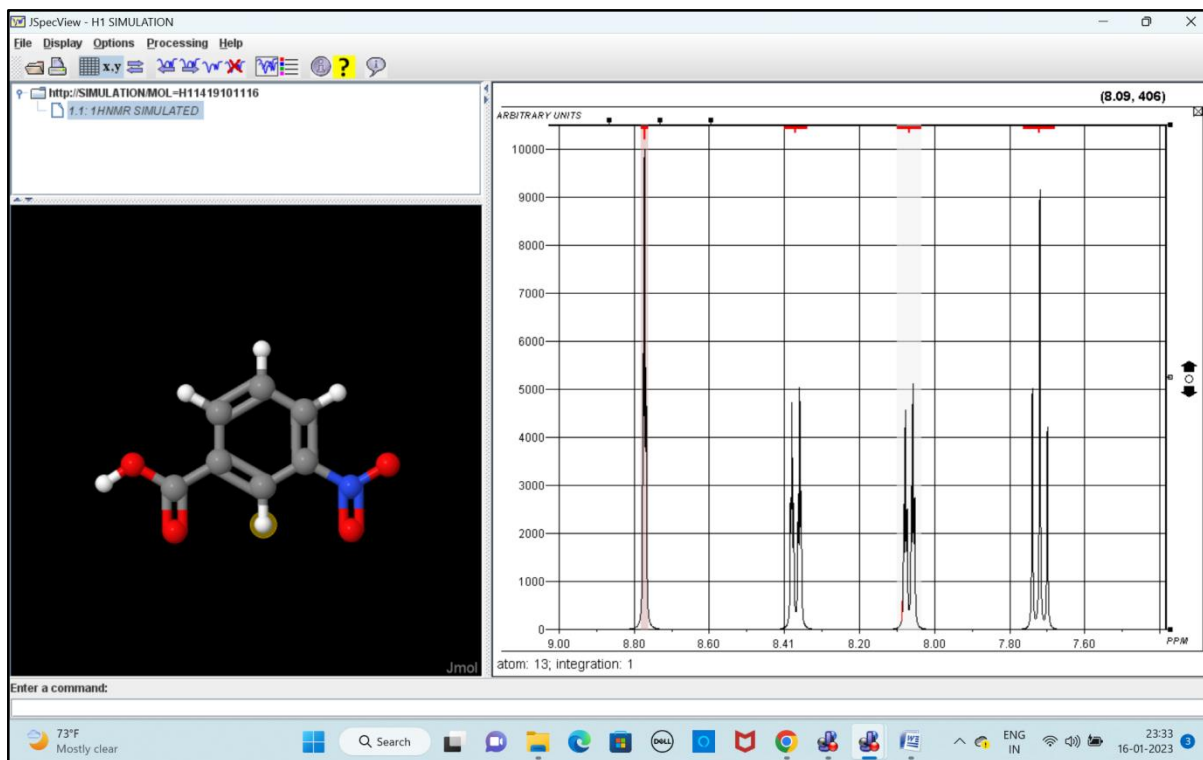
- 3-Nitrobenzoic acid is an organic compound with the formula $\text{C}_6\text{H}_4(\text{NO}_2)\text{COOH}$.
- It is an aromatic compound and under standard conditions, it is an off-white solid.
- m-Nitrobenzoic acid can be prepared by the nitration of benzoic acid by means of nitric acid
- a mixture of nitric and sulfuric acids or mixtures of nitrates and sulfuric acid; all these methods lead to the production of a mixture containing principally the m-nitrobenzoic acid
- m-nitrobenzoic acid with a smaller proportion of the ortho and 1–2 per cent of the para isomer.
- Nitration of benzotrichloride with subsequent hydrolysis also furnishes m-nitrobenzoic acid..
- The two substituents are in a meta position with respect to each other, giving the alternative name of m-nitrobenzoic acid.
- This compound can be useful as it is a precursor to 3-aminobenzoic acid

5.3.1 Interpretation of ^1H NMR of benzoic acid molecule obtained from JSPEC view of Jmol



- The spectra of benzoic acid shows three sets of peaks corresponding to three types of hydrogen environment
- The two hydrogens in the ortho position to the $-\text{COOH}$ group shows the peak at 8.026 PPM
- The hydrogen at the para position of the $-\text{COOH}$ group shows the peak at 7.59 PPM
- The two hydrogens at the meta position to the $-\text{COOH}$ group shows the peak at 7.45 PPM

5.3.2 Interpretation of ^1H NMR of benzoic acid molecule obtained from JSPEC view of Jmol



- The spectra of 3-nitrobenzoic acid shows four sets of peaks corresponding to four types of hydrogen environment
- The hydrogen in between the nitro group and $-\text{COOH}$ group shows at 8.77 PPM
- The hydrogen next to the nitro group – 8.37 PPM
- The hydrogen adjacent to the $-\text{COOH}$ group- 8.07 PPM
- The hydrogen meta to the both $-\text{COOH}$ and nitro group - 7.72 PPM

5.3.4. Comparison of ^1H NMR spectra of benzoic and 3-nitrobenzoic acid

- The spectra of benzoic acid show only three sets of peaks whereas the 1- Nitro naphthalene shows four sets of peaks.
- The hydrogen in meta position of benzoic acid at 7.45ppm and in 3-nitrobenzoic acid at 7.72ppm.

6. Conclusion

The structural changes in the reactant after the nitration reaction was analysed with the ¹HNMR from the Jmol. From the interpretation the position of the nitro group can be identified easily. The structural changes were accounted for with these NMR details. In conclusion, nitration sulphonation are chemical processes in which the nitro group is introduced into an organic chemical compound. The hydrogen atom of an organic compound is replaced with a sulfonic acid functional group, generally by a reaction with sulphuric acid at high temperatures.

Acknowledgement

We wish to express our gratitude to our KARE Management for providing the facilities for fabrication. We also wish to express our heartfelt thanks to Dr. Koteswara Rao Anne, Director Academics, Dr.N.Rajini, Dean Freshman Engineering and Dr. P. Sivaranjana project guide for their encouragement and support.