

Theoretical structural analysis of 3-CHLORO-4-FLUORO-ANILINE

Muhammad Aziz*^{1,2}, Sohail Nadeem¹ and Muhammad Anwar²

¹ School of science, University of Management and Technology, Lahore, Pakistan.

² Institute of Biochemistry University of Balochistan, Quetta, Pakistan

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ABSTRACT

This study was designed to compute the spectroscopic properties of aniline family, and educates the 3chloro-4-fluoro-aniline, which have unique pharmaceutical important. The structural and spectroscopic properties were investigated using a quantum calculation. The density functional theory approach at B3LYP/6-31G (d) data set is apply. IR and UV-Visible spectrophotometric estimated through GAMESS, Raman spectrogram was obtain through Gaussian and NMR C¹ and C¹³ spectrums were also predicted through computational methods. After obtaining the results, they were tabulated. The results of current computational analysis is in sense useful to predict even a complex aniline precursor and advantage of the current computational strategy is beneficial for other aniline molecules containing chlorine and fluorine atoms. The success of this Density function theoretical results opens a pathway to apply a correct algorithm and a force field for the assignments of aniline family spectroscopy property.

Keywords: Spectroscopy; Virtual calculation; amino benzene; DFT.

INTRODUCTION

The molecular formula of 3-chloro-4-fluoro aniline molecule is C₆H₅ClFN. Aniline consists of an amino group which is attached to phenyl group. Different halogen atoms are attached to it at various positions. In this way, the molecule would contain 14 atoms and 74 electrons. Aryl amines (aniline) belongs to aromatic amines, and is a broader family having prime importance in particular environmental assessment, pharmaceuticals, polymer [1], general industry and agrochemicals [2]. The under-consideration molecule, 3-choloro-4-flouro-aniline, is neither simple nor a complex member of the family. The attachment of chlorine at position 3 and

fluorine at position 4 with amino benzene, can alter their intrinsic properties to some extent. A famous fact for aniline is that it can act as a true metal. [3, 4]. It is in demand as a precursor for dye synthesis, and is used in synthesis of optically active molecules as well. The physiochemical properties' trends of the Aniline family have been measured by using density functional theory. It is a unique compound to test the DFT-method accuracy [5]. X-ray crystallography and microwave spectroscopy is reviewed in solid and gas phase. Substituted Aniline as Aniline hydrogen phthalate can be used as a spraying reagent in different chromatographic techniques like sugar

*Corresponding author: aziz1sh@hotmail.com

chromatography. Polyaniline (PANI) is easy to synthesize, as it possesses environmental stability and high specific pseudo capacitance [6]. It is excellent in rate and cycling stability improvement [6-10] and retains controllable chemical and physical properties which makes it a worthy and exclusive amongst conjugated polymers [11]. Anilines substituted with different chloro and nitro groups produce marker dyes which have vast application in fuel and gasoline [12]. Substituted aniline, as a reagent, functions to distinguish various sugars [13], and eradicate dyes from aqueous solution [14]. Chlorinated aniline acts as metabolites of the microbial degradation in various components [15]. Computational studies have been used to provide a framework for understanding the reaction pathway by Davies et al [16]. Many theoretical reviews have been done on non-planar geometries of aniline by HF/6-31G* [17]. Vaschetto et al. studied structural, electronic properties (IP, EA, first electronic excitation) and geometries of aniline; along its derivatives by using several DFT based methods like hybrid DFT methods (B3LYP, B3P86 and B3PW91) [18]. Computational softwares, as vibrational spectroscopy simulations, were used to assist in solving of chemical problems about half a century ago, but the field now a days is a product of the digital age. Through digital view it is possible to see actually issue in more comprehensible way, the industrial use of vibrational spectroscopy highlighted by many [19]. It is based on the methods of theoretical chemistry, consolidated into effective PC programs to figure the structural properties of a compound. With advancement in computational analytic chemistry based software, new paths have been opened to predict the results before performing real experimental analysis which bringing more perfection in analysis [20]. Various types of computational methods and models are

available. To select an appropriate model for the aforementioned aniline is a task. Spectroscopic study is an analytical tool for identifying organic compound. It is expected that experiments combined with computations will be powerful tool for determining absolute configurations. The new trend of Nano aniline particle is also rising, which indeed depends on the accuracy of the analysis. In the first step, the IR, UV-vis and Raman spectrograms of mentioned aniline compound should be stated. The International Academy of Quantum Molecular Science is embossing the results of theoretical calculation to almost near to real calculations. The key objective of current study is to show the vibration analytic results of 3-chloro-4-floro-aniline. Which is use by pharmaceutical manufacture for further necessary action.

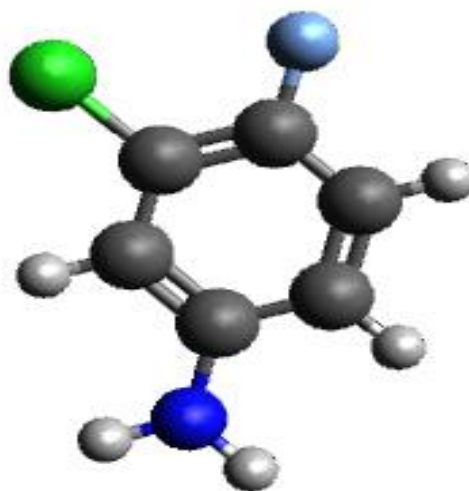


Fig. 1. Arrangement of atoms of 3-chloro-4-fluoro- aniline.

STEREOCHEMISTRY OF MOLECULE

The molecule contains an amino group with one simple aromatic ring with the attachment of halogen family. At Meta position, chlorine and at Para position, fluorine is attached. There are total five

hydrogen atoms. Three double bonds, no triple bond and ten single bonds are present, as shown in fig 1. Smile NC1=CC(=C(F)C=C1)Cl

COMPUTATIONAL METHODS

Avogadro 1.2 is used to draw the structure [21]. Universal force field is applied to optimize the geometry, and KnowItAll Informatics Systems is used for the comparison of theoretical results. Virtual calculation of molecule vibration and computation of Spectra is done by GAMESS[22] and Gaussian 9 [23] respectively. NMR prediction is done by Mestre Nova [24] .

Parameter Use

For IR spectra calculation, two modes are used. The single point and frequency in the basic set of B3LYP and to utilize full feature People basis 6-31G (d) is used. Although, it enhances the time of computation, however, giving better results. Parameter for Raman and UV-VIS calculations are same as above parameters.

COMPUTATIONAL RESULTS

IR Theoretical Value

The spectrogram for IR value for 3-chloro, 4-fluro aniline lies in 0-3500 cm^{-1} . It is clearly interpreted from fig. 1. The following attachments are bonded with aromatic ring:

- Amino group: 3357 -3471 cm^{-1} and NH_2 deforming is seen at 1697 cm^{-1} .
- Halogen group: The molecule contains two halogen members: Chlorine & Fluorine. Chlorine, which shows strong vibration at 900-800 cm^{-1} . However, in case of computational analysis, a minute peak appears at 34 cm^{-1} which is very difficult to distinguish. On the other hand, fluorine peak usually emerges at 1300-900 cm^{-1} . Therefore, in case of 3chloro-4-flouro-anline, the peak shifts towards 63.8 cm^{-1} which is barely highlighted.
- Aromatic ring: The aromatic ring contains tri-substitute attachments i.e. 1, 3 and 4 carbons as narrated in fig 1. The presence of ring is confirmed at 1650 - 1400 cm^{-1} . There are vivid and paramount peaks of aromatic ring.
 - From fig. 3, it has been clear that there is no difference and the spectrogram is completely overlapped. In computational analysis for determination of IR spectroscopy, there are two options available i.e. single point energy and frequency to highlight the difference in these two modes. From fig. 3, it is revealed that there is no difference. Ergo, for determination of IR frequency both options are applicable. It is hard to differentiate the results.



Fig. 2. I.R spectrogram of 3 chloro-4-fluoro-aniline.

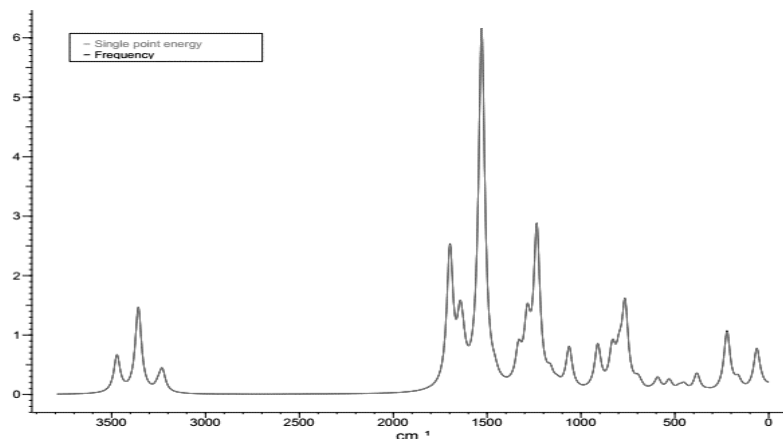


Fig. 3. Compression between single point IR spectra and frequency IR spectra.

UV-Vis theoretical value

As sketched in fig. 4, UV-Vis spectrogram shows excitation from 4.000-7.700eV.

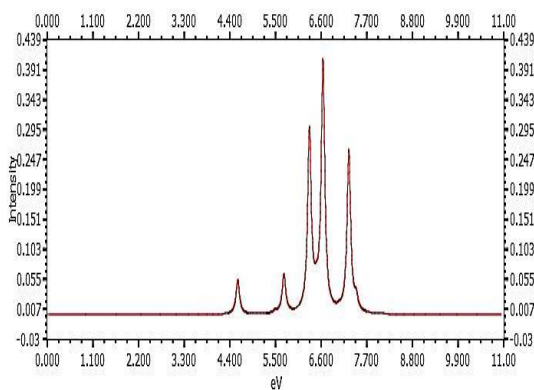


Fig. 4. UV-VIS spectrogram.

It is obvious from the graphical representation that the UV-V is spectrogram of 3-chloro-4-fluoro- aniline on Y-axis intensity, and the x-axis shows

the range in eV. Molecular formula tells us that there is amino axon chrome attached. The presence of aniline is observed at 210 -390 nm was previous available in literature the highest peak due to Deep UV range is at 6.600 eV =187.8nm. On the other hand, the smallest peak is observed at mid UV region that 4.56eV =271.8nm.

Raman Theoretical value

Fig. 5 depicts the Raman spectrogram of 3-chloro-4-fluoro-aniline. At 2915cm⁻¹ lay the broader peak of amino group which is due to anti symmetric stretching of hydrogen atoms attached with nitrogen. At point 1777cm⁻¹, amino group shows the scissoring of hydrogen atom. The small peak at 1692cm⁻¹ is caused by the aromatic ring vibration. The other paramount peak at 3233cm⁻¹ is because of the waging of hydrogen atoms attached with aromatic ring.

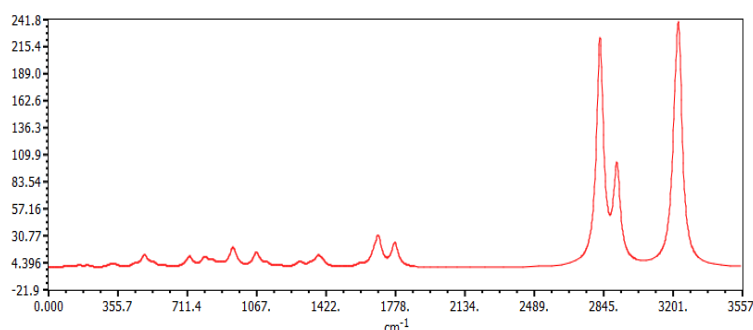


Fig. 5. Raman spectra of 3-chloro-4fluro-aniline.

NMR C¹³ Predication

Through C-NMR get information about the number of carbon atoms in a concern molecule, But also provide an information how those atoms are arranged. Fig 6 show that they do not all appear in the same place. The location of a particular peak is dependant on the chemical shift. Different types of factors affect chemical shift of a peak, mainly it can be explained by considering the electron density around the nuclei involved. The higher the electron density around the nucleus, the further downfield (shifted to the left) the peak will appear in the spectrum. The ¹³Carbon chemical shift is shown below. The concern molecule contains only carbon atoms which are present in benzene ring, only because the spectra C-13 NMR equals to benzene. The peak at pt. 1 at 143 pm is

due to amino group attached to carbon atom 1 as illustrated in fig. 1 which is profound in tabular form, as obvious in the fig.6.

NMR H¹ Predication

The under consideration molecule contains total five hydrogen atoms. The analysis of H¹ NMR is more important than C¹³ NMR in the current study to predict the structure. There are three Promont peaks as show in fig. 7. The peak at 7.05 ppm is due to (Hydrogen) Hydrogen atom 3 as stated in fig. 1, the next peak at 6.95 is caused by Hydrogen atom 4 and the last peak 6.48 is the result of hydrogen atom 5. On the other hand, the peaks of amino group, i.e. Hydrogen atom 1 and hydrogen atom 2 are minuscule.

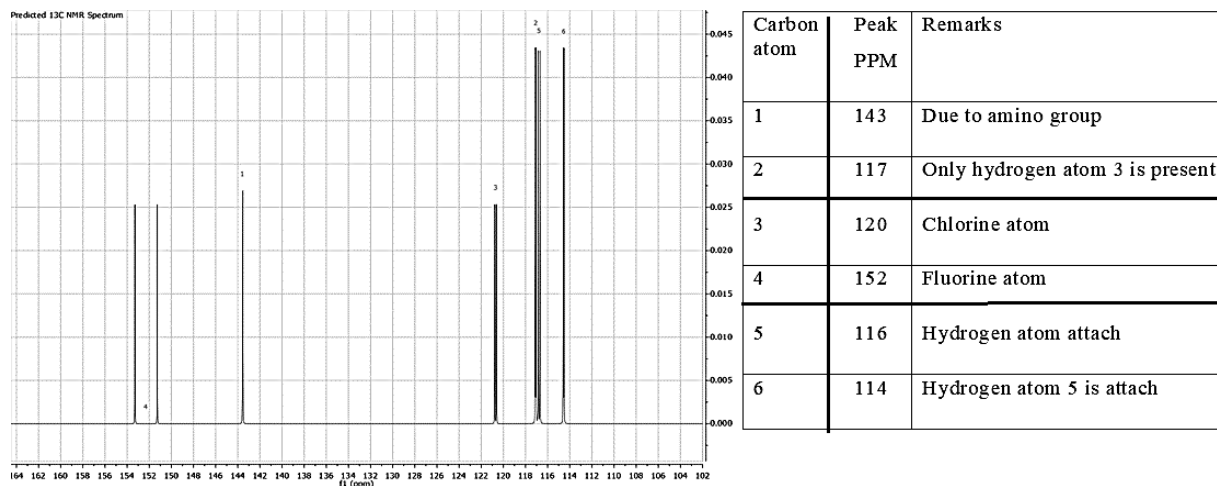


Fig. 6. NMR C-13 predication of the 3-chloro-4-fluro-aniline. On x-axis is in parts per million.

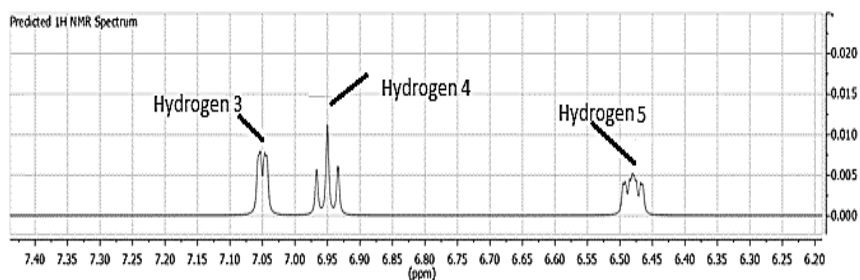


Fig. 7. NMR H¹ Spectrogram of 3-chloro-4-fluro-aniline. On x-axis is in parts per million.

CONCLUSION

The result of current computational analysis is in sense useful to predict even a complex aniline precursor and; success of the computational strategy is beneficial for other aniline molecules containing chlorine and fluorine atoms. The field of computational analysis calculation is still not fully developed to enlighten the vibrational property of organic molecules, which still needs to be reported. The success of these theoretical results opens a pathway to apply a correct algorithm and a force field for the assignments of aniline family spectroscopy. The key benefit of vibration analysis is to give an edge to keenly see the electron shift, donation and withdrawing effects more easily.

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SUPPLEMENTARY DATA

Meta data associated with the current study also obtain from corresponding author on request.

“The authors declare no conflicts of interest”

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