

THEORETICAL INVESTIGATION OF COUMALIC ACID

Sundas Jamil¹, Sohail Nadeem¹, Muhammad Aziz².

¹Department of Chemistry, University of Management and Technology, Lahore

²Institute of Biochemistry, University of Baluchistan, Quetta, Pakistan

KEYWORDS	ABSTRACT
Spectrum, Computational Study, DFT	Current study was designed to evaluate Coumalic Acid theoretically, which is a Bio-organic molecule. The structural, spectroscopic like the Infrared and UV-Visible properties were investigated using a quantum calculation approach under the density functional theory at B3LYP/6-31G(d) data set. The Infrared spectrogram lies between 400-3800 cm ⁻¹ with a few coercion and minute peaks. Thermochemistry calculations show that molecule is exothermic in nature, NMR H ¹ and C ¹³ prediction results are tabulated. Today's Challenges in Computational Chemistry is use of the appropriate tool and method to highlight the chemical property of mention molecule which is also highlight in the current research. The main advantage of virtual analysis provides an edge to easily view the electron shift, donation and withdrawing effect easily. The computational evaluation approach used here could also be useful for investigation of other bio-organic compounds.

INTRODUCTION

The discovery of bio-organic molecule Coumalic acid begins in the middle of the nineteen century. The scientific name of compound is "2-oxo 2-H pyran-5-carboxylic acid" having empirical formula C₃H₂O₂ and molecular formula is C₆H₄O₄. It is the polar molecule (Imagawa, Sueda & Kawanisi, 1974). Generally, it can be prepared in the situ by self-condensation of the malic acid, concentrated and fuming Sulphuric acid (Wiley & Smith, 1951). Biologically investigated that toxicity level of Coumalic acid depends on the number of alkyl groups attached to it. As length of chain increases the toxicity and can give high cardio-activity (Campbell & Hunt, 1947). A study of Gharib, Khatib, Nassr and Dief (2017) was limited to kinetic parameters of the Coumalic acids (Wiley & Knabeschuh, 1955). The derivatives of compounds are daily used synthetic chemicals and are associated with our everyday life in the forms of the nourishment ingredients, acidulates, cosmetic products, cleansers items, germination, biodegradable polymers, record films, garment fibers, rubbers and pharmaceuticals (Ohi, Kitamura & Hata, 2003).

Coumalate can undergo Diels Alder reaction with dienes to give different good products. Its thermal reactions with different dienes like Buta and Penta diene gives synthetically tricyclic products (Imagawa, Nakagawa, Kawanisi & Sisido, 1979). However, Ohi et al. (2003) explained coumalic acid as a stimulating agent in germination of plasmodiphora spores and preventor for clubroots in Chinese cabbage (Sato, Nishio, & Hirai, 1989). If methyl or ethyl groups are attached to the Coumalic acid, it can give wide variety of the functionalized β,γ-unsaturated carboxylic acids (Plevová, Chang, Martin, Llopis, Dechoux & Thorimbert, 2016). With development of computational software there is lot of chance to enlighten the perfection in analysis Finally, future directions through computational chemistry (Jensen, 2017) are discussed. The different types of the Quantum methods and computational models are accessible but to choose the correct one for aforementioned compound is key task of computational chemistry (Cramer, 2013).

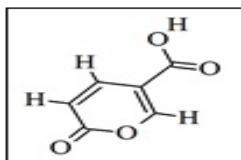
The vibrational spectroscopic study is an analytical tool for identifying organic compound (Siesler, 2016) with recent developments in computational techniques, it is hoped that experiments combined with computations will be a powerful tool for determining absolute

configuration. Nowadays, a plethora of computational software are used to enlighten the theoretical analytical calculations. For the first time, IR spectra of mentioned compound has been reported. Computational software are spectroscopic simulations which assist in solving chemical problems dates back to half a century (Cowan, 1968). It is depending on the methodological techniques of theoretical chemistry, consolidated effective into desk top computers programs, to calculate the basic structural properties of the compound. The international academy of quantum molecular science is decorating consequences results of theoretical calculation which is almost near to experimental calculation. Key objective of current study is to show the vibrational study of Coumalic acid.

Stereo-Chemistry

The concern compound contains a total of 14 atoms/ bonds. There are 10 non-Hydrogen bond(s), four multiple bonds, one rotatable bond, four double bonds, one aromatic ring, four hydrogen atoms, six carbon atoms and four oxygen atoms and at the tip there is a hydroxyl group as shown in figure 1.

Figure 1 Coumalic Acid Arrangements of Atoms



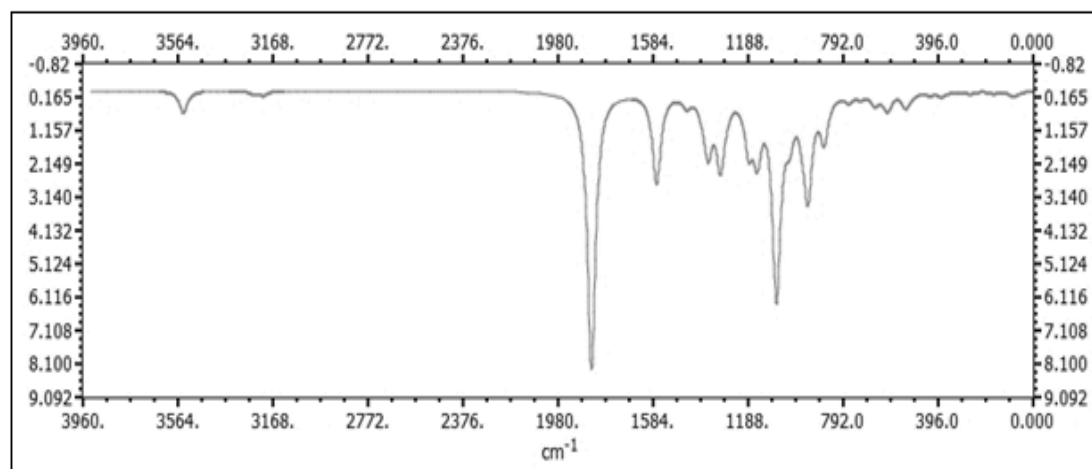
METHOD AND MATERIAL

Computational Methods

3D molecular structure was drawn with the aid of Avogadro 1.2 (Hanwell, Curtis, Lonie, Vandermeersch, Zurek & Hutchison, 2012). In this regard, for the calculation of IR, UV-Vis and Thermochemistry Gamess (Computational software) is used. For prediction of NMR C and H Mestrenova (Stimulation software) is used. To view the results Gabedit 2.50 was used (Allouche, 2011). Density Functional Theory (DFT) technique is the most commonly used approach (Chaban & Gerber, 2008) when it comes to the computation geometry of the compound universal force field is applied under the Steepest Descent algorithm.

Infrared Photometric

Figure 2 IR Spectrogram of Coumalic Acid



On X-axis show the cm-1 and Y-axis show the intensity.

Figure 3 NMR Hydrogen

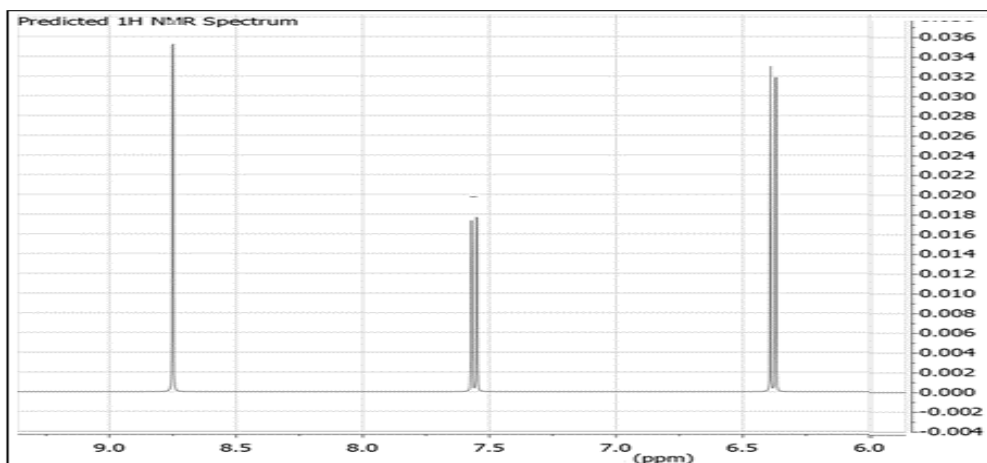


Figure 3 show the predicting NMR H¹ of Coumalic Acid. On X-axis value in PPM.

Figure 4 NMR Carbon 13

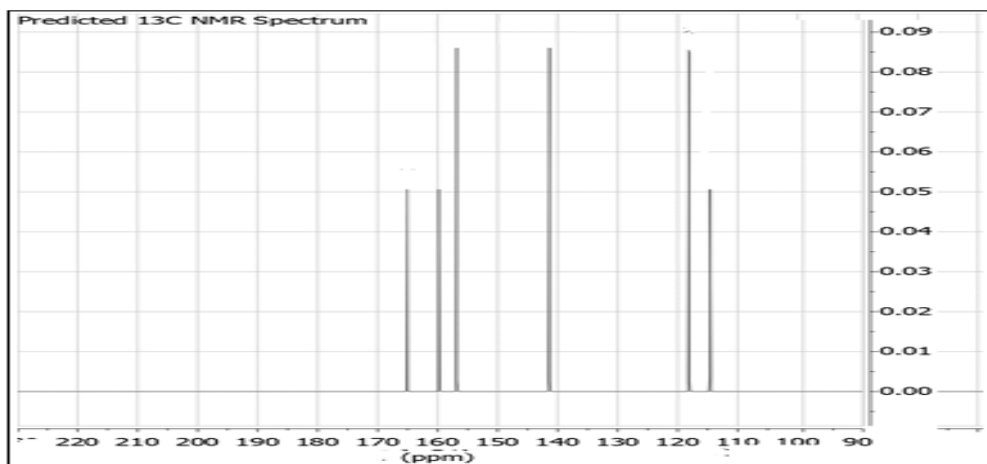


Figure 4 show the predicting NMR C¹³ of Coumalic Acid. On X-axis value in PPM.

Figure 5 UV-Vis Spectra

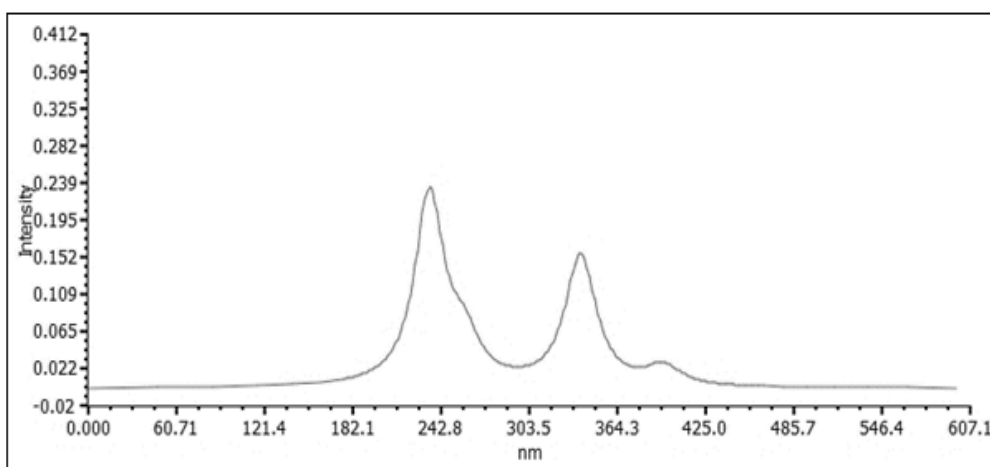


Figure 5 show the UV-V is spectrogram of the Coumalic Acid. On X-axis value is in the nanometer.

RESULT AND DISCUSSION

Computational chemistry that uses simulation software to solving the chemical problems. It uses methods of theoretical chemistry, incorporated into efficient computer programs, to calculate the chemical properties of concern molecule. This field is used to describe the computational techniques and understanding the chemical properties of the molecule. The computational analysis become an integral part of chemical analysis processes. These types of studies provide vital layer for the chemists, after this their intellectual pursuits, inquiries and concerned research becomes more cognized.

Thermochemistry

The sum of enthalpy (thermal) of the molecule is theoretically calculated at 25° applying pressure 1 atm on molecule is -331720.6kcal/mol. The result implies that the molecule is exothermic in nature

IR Frequency

Alcohol: The absorption band for the alcohol is the glimpsed at 3535cm/1 medium OH stretching. Another identification band of alcohol due to medium deforming 1467cm/1.

Ester: C=O strong starching is at 1857cm/1, C-O medium stretching 1160cm/1. 873.4 is due to rocking of carbon 2 and carbon 3. The peak at 1072cm/1 carbon 6 and oxygen 1 which also put an impact of terminal hydrogen as shown in figure 1. At 1568 cm/1 is movement of single ring carbons atoms. The dominate peak 1843.6 cm/1 is due to anti symmetric stretching, vibration between Carbon atom 1 and oxygen atom 3. The minute peak at 3544.4 cm/1 is due to bouncing of hydrogen no. 4 which is attached to oxygen no. 1 is radical symmetric also called symmetric stretching.

NMR: NMR (Nuclear Magnetic Resonance) is widely used to exploit magnetic properties of atomic nuclei and detailed information about the structure, dynamics and reaction state. NMR also confirm the 3D structure and limited the use of X-ray crystallography. To display the result NMR spectra is divided in to two figures, is used to reduce the number of variables for pattern recognition techniques and to mitigate effects from variations in peak positions however, shifts in peaks near boundaries can cause dramatic quantitative changes and difficult to understand.

NMR summary of carbon atoms are as follows in table 1. The NMR of carbon is more important to predict structure of Coumalic Acid. As shown in figure 1 there are six carbon atoms. The six non-neglect peaks of carbon NMR is shown in figure 4.

Table 1 Peaks PPM (C-Atom), Where C= Carbon

Peaks PPM	C-Atom
165	1
114	2
156	3
159	4
118	5
141	6

Table 2 Peaks (ppm) H-Atom, Where H=Hydrogen, *= N.A

Peaks (ppm)	H-Atom
8.75	1
7.56	2
6.38	3
*	4

NMR summary of Hydrogen atoms are as follows in table 2. There are total four hydrogen atoms in Coumalic Acid as shown in figure 1. The NMR H¹ spectrogram shows three paramount peaks. The UV-Vis Spectrogram shows there are two paramount peaks starting from 220nm to 400nm. The dominant peak of carbon-oxygen double bond easily seen in spectrograph.

CONCLUSION

The result of computational evaluation is in sense of useful tool to predict even complex atoms. Through computational chemistry the vibrational property of title molecules is reported. The success of these theoretical results opens a pathway to apply a correct algorithm and a force field for the assignments of spectroscopy. Spectrophotometry is used to elaborate the structural information as already mention structure role in any scientific query is the initial key to understand. The main advantage of virtual analysis provides an edge to easily view the electron shift, donation and withdrawing effect easily. The results of current study also be used as a library to predict the results for future analysis. With the increasing demand of new candidates in pharmaceutical sector and find out the toxicity level of any molecule computational modeling at 3D level resolve these complexities.

REFERENCES

- Allouche, A. R. (2011). Gabedit: A graphical user interface for the computational chemistry softwares. *Journal of computational chemistry*, 32 (1), 174-82.
- Campbell, N., & Hunt, J. (1947). Unsaturated lactones. Some esters of aconic and coumalic acids. *Journal of the Chemical Society*, 1176-1179.
- Chaban, G. M., & Gerber, R. B. (2008). Anharmonic vibrational spectroscopy calculations with electronic structure potentials: comparison of MP2 and DFT for organic molecules. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)*, 120(1), 273-279.
- Comprehensive Biotechnology (Third Edition), Pages 172-187, <https://doi.org/10.1016/B978-0-444-64046-8.00159-2>.
- Cowan, R. D. (1968). Theoretical calculation of atomic spectra using digital computers. *JOSA*, 58(6), 808-818.
- Cramer, C. J. (2013). *Essentials of computational chemistry: theories and models*: John Wiley & Sons.
- Gharib, E. A., Khatib, R. M., Nassr, L. A. E., & Dief, A. M. (2017). Kinetics, reactivity, initial-transition state analysis and thermodynamic parameters of base-catalyzed hydrolysis of coumalic acid in solvents with different polarities. *Arabian Journal of Chemistry*, 10(1), S988-S995.
- Hanwell, M. D., Curtis, D. E., Lonie, D. C., Vandermeersch, T., Zurek, E., Hutchison, G. R. (2012). Avogadro an advanced semantic chemical editor, visualization, and analysis platform. *Journal of Cheminformatics*, 4 (1), 17.
- Imagawa, T., Nakagawa, T., Kawanisi, M., & Sisido, K. (1979). Double Diels-Alder Reactions of Coumalic Acid with 1, 3-Dienes. *Bulletin of the Chemical Society of Japan*, 52(5), 1506-1510.
- Imagawa, T., Sueda, N., & Kawanisi, M. (1974). Diels-Alder reaction of methyl coumalate with 1, 3-dienes. *Tetrahedron*, 30(14), 2227-2231.
- Jensen, F. (2017). *Introduction to computational chemistry*: John wiley & sons.

Ohi, M., Kitamura, T., & Hata, S. (2003). Stimulation by caffeic acid, coumalic acid, and corilagin of the germination of resting spores of the clubroot pathogen *Plasmodiophora brassicae*. *Bioscience, biotechnology, and biochemistry*, 67(1), 170-173.

Plevová, K., Chang, L., Martin, E., Llopis, Q., Dechoux, L., & Thorimbert, S. (2016). Regio- and Stereoselective Preparation of β , γ -Unsaturated Carboxylic Acids by One-Pot Sequential Double 1, 6-Addition of Grignard Reagents to Methyl Coumalate. *Advanced Synthesis & Catalysis*, 358(20), 3293-3297.

Sato, T., Nishio, T., & Hirai, M. (1989). Plant regeneration from isolated microspore cultures of Chinese cabbage (*Brassica campestris* spp. *pekinensis*). *Plant Cell Reports*, 8(8), 486-488.

Siesler, H. W. (2016). *Vibrational Spectroscopy Reference Module in Materials Science and Materials Engineering*: Elsevier.

Wiley, R. H., & Knabeschuh, L. H. (1955). 2-Pyrones. XIII.1 The Chemistry of Coumalic Acid and its Derivatives. *Journal of the American Chemical Society*, 77(6), 1615-1617.

Wiley, R., & Smith, N. (1951). The Coumalic acid. *The Organic Syntheses*, 31, 23-24.