FT-IR and FT-Raman spectroscopic and computed vibrational frequency analysis on 2-Oxindole using HF and DFT calculations

R.K. SANGEEETHA

Department of Physics, Sri Eshwar College of Engineering, Coimbatore-641202, Tamil Nadu India

Email:sangeetha@sece.ac.in

P.VIDHYA

Department of Physics, Nehru Institute of Engineering and Technology,Coimbatore,Tamil Nadu,India

ABSTRACT

Quantum mechanical solvation analysis was carried out for the industrially significant oxindoles derivatives using the solvents at 298 K with varied dielectric constants. The electrostatic, dispersion and repulsive interaction components of Gibb’s free energy of solution along with cavitation energies for these systems are computed by the B3LYP method with 6-311++G(d,p) basis set. The FT-IR and FT-Raman were verified. The influences of substituent on the solubility of oxindoles derivatives were investigated.

Keywords— Density Functional Theory, FT IR,FT Raman,Vibrational assignments,HF method

# INTRODUCTION

Hetero cyclic compounds containing 5-or 6-membered ring are important for their diverse biological activities [1]. For example, indole – 2,3-diones, which represent a large family of heterocyclic compounds, have been extensively explored for developing pharmaceutically important molecule-substituted isatins [2] especially are reported to show a wide range of biological activities such as antibacterial [3], anti-fungal [4,5], antiviral [6] and anti-HIV, [7,8], antileukemia [9]. These compounds were also reported to have effects on central nervous system [10,11]. The chemistry of oxazolidione ant its derivatives has received considerable attention owing to their synthetic and biological importance [12]. The oxazolidione moiety has been incorporated into a wide variety of therapeutically interesting compounds that have antibacterial, anti-fungal [13,14]. Oxindoles containing an oxazolidione nucleus have been shown to have antibacterial activity and Inhibitor property. The naturally occurring oxindole derivatives convolutamydine has been found to exhibit potent activity in the differentiation of HL-60 human plomyelocytic leukemic cells. The varied biological activities of oxindole derivatives have attracted the synthetic chemists to a number of synthetic strategies. [15-19] Plant hormone, indole 3- acetic acid and the animal hormone, melatonin, a potent antioxidant are the most important indole derivatives.[20] Some of oxindole derivatives found in marine fish and shellfish are reported to exhibit radical scavenging activity comparable to known powerful antioxidants like uric acid and indole in humans [21] Tuberculosis (TB) is a chronic necrotizing bacterial infection with wide variety of manifestations cause by mycobacterium tuberculosis, which has been a scourge of humanity for thousands of years and remains one of the prevalent health tribulations in the world [22]. In this paper we report the spectral studies of a series of 2-Oxinole derivatives.

# EXPERIMENTAL METHOD

The spectroscopic grade 2-oxindole was purchased from sigma Aldrich chemicals U.S.A and used as such for recording spectra without further purification. The FT-IR Spectrum of the title compound was recorded using Bruker IFS 66V spectrometer in the range of 4000-100cm-1. The spectral resolution is ±2 cm-1. The FT-Raman spectrum of 2-Oxindole was also recorded in the same instrument with FRA 106 Raman molecule equipped with Nd: YAG laser source operating at 1.064µm with 200Mw power. Both the spectra were recorded in the range of 4000-100cm-1 with scanning speed of 30cm-1min-1 of spectral width 2 cm-1. The frequencies of all sharp bands are accurate to ±1 cm-1. 2-Oxindole with GAUSSIAN 09W software package [23] HF functional [24,25] standard 6-311G (d,p) and 6-311++G(,p) basis set (referred to as “large” basis) and the density functional method used is B3LYP, that is Becke’s three – Parameter hybrid functional with the LEE-Yang-Parr correlation functional method with 6-311++G(d,p). The harmonic vibrational frequencies calculate for 2-Oxindole at HF and B3LYP levels using the triple split valence basis set along with the diffuse and polarization functions. It may be point out that compute wave number corresponds to the isolated molecular state in the gaseous phase whereas the experimental wave numbers correspond to the solid state spectra. In order to evaluate the energetic behavior of the title compound, we carried out calculations in vacuum and inorganic solvent (ethanol). The energies of important molecular orbitals of 2-Oxindole, the highest occupied Molecular orbitals (HOMO), and the lowest unoccupied Molecular orbitals (LUMO), were calculated using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) level in order to elucidate the intramolecular, hybridization, and delocalization of electron density within the molecule. The result of interaction is a loss of occupancy from the density of electron in NBO of the idealized Lewis structure, into an empty non-Lewis Orbital. For each donor (i) and acceptor (j), the stabilization energy E(2) associated with delocalization ij is estimated as

E (2) = -nσ <σ/F/ σ>2

\_\_\_\_\_\_\_\_\_\_

Eσ\* - Eσ

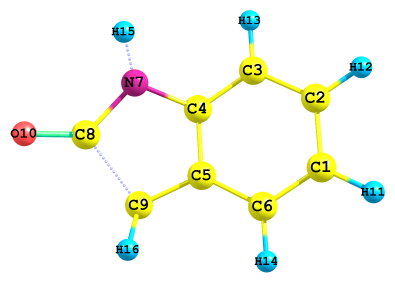
= - nσ Fij2/ E (1)

Where <σ/F/ σ>2 or Fij2 is the fockmatrix element I and j NBOs orbitals, Eσ\* and Eσ are the energies σ and σ\* NBOs and nσ is the population of the donor σ orbital. Zero-point vibrational energy, internal energy ant its translational, rotational, and vibrational contributions, entropy and heat capacity of 2-Oxindole are computed through the calculation of partition functions [26-28].

# RESULT AND DISCUSSION

## **Molecular Geometry**

The most Optimized geometry performed by HF and DFT of 2-Oxindole molecule with atoms numbering is shown in fig.1. The molecule consists NH and O2 connected to a benzene ring. The zero point vibrational energy of the molecule is 85.76,85.68 & 80.211kcal/mol as predicted by HF/6-311G(d,p) & HF/6-311++G(d,p) B3LYP/6-311G(d,p) & B3LYP/6-311++G(d,p) respectively. In comparison with the experimental values, it is observed that most of the calculated bond length values are slightly larger than the experimental values. This may be due to the fact that the calculations are performed for the isolated molecules (gaseous Phase) while the experimental spectra are recorded in solid phase. This is in accordance with earlier work [29]. The benzene ring appears to be a little distorted from its regular symmetry as the computed bond lengths. In accordance with the basis set ;B3LYP/6-311++G(d,p) the order of the bond length lie as C5-C9>C4-C5>C2-C3>C1-C6>C1-C2>C3-C4 the irregular symmetry of the benzene ring is also evident from the decrease in value of the bond lengths, the bond angle order lie as C6-C5-C9>C3-C4-C5>C1-C2-C3>C2-C1-C6>C4-C5-C6>C1-C6-C5>C2-C3-C4>C4-C5-C9. The comparative graphs, for different basis sets, of bond lengths, bond angles are presented in the fig 2,3 respectively, which show that all of them are slightly larger in HF when compared to that in other methods.



**Fig.1 Optimized structure of 2-Oxindole**

## 

**Fig 2 . Bond length differences between theoretical (HF and DFT) approaches**



**Fig 3: Bond angle differences between theoretical (HF and DFT) approaches**

**B. Vibrational Assignments**

The 2-Oxindole molecule consists of 17 atoms, so it has 45 normal vibrational modes. The observed vibrational assignments and analysis of 2-oxindole are discussed in terms of fundamental bands. The harmonic vibrational frequencies calculated for 2-oxindole at HF and B3LYP along with the observed FT-IR and FT-Raman frequencies for various modes of vibration. While comparative values of IR and Raman intensities are determined. The recorded FT-IR and FT-Raman spectra of 2-Oxindole are given in fig 4 and fig 5,6.

**Frequency Assessment Analysis**

The frequencies calculated by B3LYP perfectly coincide with the experimentally observed values of IR and Raman without scaling. While comparing the assessment of frequencies by the DFT method, the B3LYP/6-311++G(d,p) basis set. Computed frequency values coincide accurately than other sets. The evaluated frequencies belong to both fingerprint and functional group regions. HF set gives the frequencies accurately for C-H, N-H, C=C, C=O, C-N stretching vibrations where as B3LYP/6-311++G(d,p) set yields. The frequencies accurately for C-H, N-H in plane bending C-H, N-H, C-C-C out of plane bending and ring stretching vibrations.

**C-H Vibrations**

The presence of C-H Vibration in the 3000-3100cm-1 confirms the molecule to be hetero aromatic [30-32]. In this case, the bands have been observed at IR and Raman spectra at and 3066cm-1.C-H stretching vibrations and all the bands in the symmetric region. The aromatic C-H in plane bending vibration normally occurs in the region 1300-1000cm-1[33]. In this present case, the C-H in plane bending vibrations are found at and 1280, 1234, 1156,1100,1017cm-1. The aromatic C-H out of plane bending vibrations normally occurs in the region 900-660 cm-1. In this present case, the C-H out of plane bending vibrations are found at and 671cm-1. Strong band in the range between 700,300,494,540,600,671.

**C-C Vibrations**

The ring C-C stretching vibrations known as semicircle stretching usually occur in the region 1400-1625 cm-1[34-35] In this present case C-C vibrations are found at 1432 & 1385cm-1. The bands between 1590-1650 cm-1 in benzene derivatives usually assigned to C=C stretching vibrations of the present compound are observed with very strong intensity at 1624,1599,1667 cm-1. The C=C stretching vibration normally occurs in the weak region 2260-2190cm-1. In this present case the C=C stretching vibrations are found at 2949, 2920cm-1. The C-C-C in plane bending vibrations are observed with medium intensity at 740 and 690cm-1 in IR and the out of plane bending vibrations are appeared with very strong intensity at 460 and 390 cm-1. These assignments are in good agreement with the literatures [36]. In this present case C-C-C out of plane bending vibrations are found at 321,307.

**C=O vibrations**

Generally, C=O stretching vibrations in aromatic compound form a band in the region of 1790-1720 cm-1.

**N-H vibrations**

N-H stretching vibrations occur in the region 3500-3300 cm-1. N-H in plane bending vibrations occur in the region 1570-1630 cm-1. In this present case N-H in plane bending vibrations are found at 1479cm-1. N-H out of plane bending vibrations occur in the region 909-666cm-1. In this present case is 909,860,810.









**Fig 4 . Theoretical FT-IR Spectrum of 2- Oxindole**



****





**Fig 5: Theoretical FT-Raman Spectrum of 2-Oxindole**



**Fig 6: Experimentel FT-IR and Raman spectrum of 2-Oxindole**

**C. Mulliken atomic Charges**

Mulliken atomic charge calculation is an important tool in the application of quantum chemical calculation to molecular system because atomic charges influence dipole moment, molecular polarizability, and electronic structure, other physical properties of molecular systems. The calculated mulliken charge values are determined. The atomic charge depends on the basis set presumably occur due to polarization. For example, the change of N(7) atom is -1.001376 for HF/6-311G(d,p) -0.846853 for HF/6-311++G(d,p) -0.811848 for B3LYP/6-311++G(d,p) -0.553572 for B3LYP/6-311++G(d,p). The charge distribution of carbon group is increasing trend in HF and B3LYP methods. The charge of H11, H12, H13, H14, H15, H16, H17 is positive in both HF and DFT diffused functions [37]. Considering all methods and basis sets used in the atomic chares calculation, the carbon atoms exhibit substantial negative charges which are donor atoms. Hydrogen atom exhibits a positive charge, which is an acceptor atom the mulliken charge distributions of 2-Oxindole is increasing trend in B3LYP as compared by HF methods. A comparison of Mullikan’s atomic charge obtained by the theoretical (HF and DFT) approaches is illustrated in fig 7. It may be seen that the two methods give comparable atomic charges.



**Fig.8.Variation of atomic charges for different basis sets.**

**Conclusion**

A detailed vibrational assignment and analysis is carried out for the molecule 2-Oxindole.The equilibrium geometries, harmonic vibrational frequencies, bond length, bond angle. IR and Raman spectra of 2-Oxindole are also determined and analyzed theoretically by abinitio- HF and DFT (B3LYP) methods with 6-311G(d,p) and 6-311++G(d,p) basis sets. The vibrational frequencies were calculated and scaled values are compared with the recorded FT-IR and FT-Raman spectra of the compound. The observed and the calculated frequencies are found to be agreement. Furthermore, the thermodynamic and total dipole moment properties of the compound have been calculated in order to get insight in to molecular structure of the compound. These computations are carried out with the main aim that the results will be assistance in the quest of experimental and theoretical evidence for the title molecule in biological activity and coordination chemistry.

##### REFERENCES

* 1. S. Aruna, M. Vimalan, P.C. Thomas, K. Tamizharasan, K. Ambujam, J. Madhavan, P. Sagayaraj, Growth and characterization of semi organic nonlinear optical LHPCL crystals. Cryst Res Technol. 2007;42:180-85.
  2. J. Chandrasekaran, B. Babu, S. Balaprabhakaran, P. Ilayabarathi, P. Maadeswaran, K. Sathishkumar, Growth optical and mechanical studies of 3,5-dinitrobenzoic acid single crystals. Optik. 2013;124:1250-53.
  3. L. Guru Prasad, V. Krishnakumar, R. Nagalakshmi, Investigations on the physicochemical properties of 2,4-dinitrophenol:Efﬁcient organic nonlinear optical crystal for frequency doubling. Physica B. 2010;405:1652-57.
  4. J. Chandrasekaran, B. Babu, S. Balaprabhakaran, Growth, structural, spectral and optical studies on 2,4-dinitrophenol organic single crystals. Optik. 2013;124:4296-99.
  5. S. Dhanuskodi, S. Manivannan, K. Kirschbacum, J. Philip, S. Selladurai, Structural, thermal and dielectric studies on new solution grown 4-dimethylaminopyridinium dihydrogen phosphate crystal. J Cryst growth. 2006;290:548-53.
  6. L. Guru Prasad, V. Krishnakumar, R. Nagalakshmi, Growth and characterization of semi- organic nonlinear optical crystal: sodium 2,4-dinitrophenolate monohydrate. Spectrochim Acta Part A. 2013;110:377-82.
  7. R. Uthrakumar, C. Vesta, R. Robert, G. Mangalam, S. Jerome Das, Optical mechanical studies on unidirectional grown tri-nitrophenol methyl p-hydroxybenzoate bulk single crystal. Physica B. 2010;405:4274-78.
  8. B. Milton Boaz, S. Jerome Das, Studies on the growth and characterization of a NLO active sodium substituted lithium p-nitrophenolate single crystal. J Cryst Growth. 2005;279:383- 89.
  9. Tianliang Chen, Zhihua Sun, Cheng Song, Yan Ge, Junhua Luo, Wenxiong Lin, Maochun Hong. Bulk crystal growth and optical and thermal properties of the nonlinear optical crystal L-Histidinium-4-nitrophenolate 4-nitrophenol (LHPP). Cryst Growth Des. 2012;12:2673- 78.
  10. P. Srinivasan, T. Kanagasekaran, N. Vijayan, G. Bhagavannarayana, R. Gopalakrishnan, P. Ramasamy, Studies on the growth, optical, thermal and dielectric aspects of a proton transfer complex – Dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol (DMAPNP) crystals for nonlinear optical applications. Opt Mater. 2007;30:553-64.
  11. V. Krishnakumar, M. Rajaboopathi, R. Nagalakshmi, Studies on vibrational, dielectric, mechanical and thermal properties of organic nonlinear optical co-crystal:2,6- diaminopyridinium-4-nitrophenolate-4-nitrophenol. Physica B. 2012;407:1119-23.
  12. G. Anandha babu, R. Perumal Ramasamy, P. Ramasamy, Synthesis, crystal growth and characterization of an efficient nonlinear optical D-π-A type single crystal:2- Aminopyridinium 4-nitrophenolate 4-nitrophenol. Mater Chem Phys. 2009;117:326-30.
  13. M. Jose, B. Sridhar, G. Bhagavannarayana, K. Sugandhi, R. Uthrakumar, C. Justin Raj, D. Tamilvendhan, S. Jerome Das, Growth, structural, optical, thermal and mechanical studies of novel semi-organic NLO active single crystal:Heptaaqua-p-nitrophenoato strontium (I) nitrophenol. J Cryst Growth. 2010;312:793-99.
  14. L.N. Wang, X.Q. Wang, G.H. Zhang, X.T. Liu, Z.H. Sun, G.H. Sun, L. Wang, W.T. Yu, D. Xu, Single crystal growth, crystal structure and characterization of a novel crystal:L-arginine 4-nitrophenolate 4-nitrophenol dehydrate (LAPP). J Cryst Growth. 2011;327:133-39.
  15. M. Prakash, M. Lydia Caroline, D. Geetha, Growth, structural, spectral, optical and thermal studies on amino acid based new NLO single crystal: L-phenylalanine-4-nitrophenol. Spectrochim Acta Part A. 2013;108:32-37.
  16. M. Senthil Pandian, N. Pattanaboonmee, P. Ramasamy, P. Manyum, Studies on conventional and Sankaranarayanan-Ramasamy method (SR) grown ferroelectric glycine phosphite (GPI) single crystals, J Cryst Growth. 2011;314:207-12.
  17. M. Senthil Pandian, K. Boopathi, P. Ramasamy, G. Bhagavannarayana, The growth of benzophenone crystals by Sankaranarayanan–Ramasamy (SR) method and slow evaporation solution technique (SEST): A comparative investigation, Mater Res Bull. 2012;47:826-35
  18. M. Senthil Pandian, P. Ramasamy, P. Binay Kumar, A comparative study of ferroelectric triglycine sulfate (TGS) crystals grown by conventional slow evaporation and unidirectional method, Mater Res Bull. 2012;47:1587-97.
  19. M. Senthil Pandian, P. Ramasamy, Sodium sulfanilate dihydrate (SSDH) single crystals grown by conventional slow evaporation and Sankaranarayanan-Ramasamy (SR) method and its comparative characterization analysis, Mater Chem Phys. 2012;132:1019-28.
  20. G. Shanmugam, K. Ravi Kumar, B. Sridhar, S. Brahadeeswaran, Synthesis, structure, growth and characterization of a novel organic NLO single crystal: Morpholin-4-ium p-aminobenzoate. Mater Res Bull. 2012;47:2315-23.
  21. J. Mary Linet, S. Jerome Das, Optical, mechanical and transport properties of unidirectional grown L-tartaric acid bulk single crystal for non-linear application. Mater Chem Phys. 2011;126:886-90.
  22. G. Ganesh, A. Ramadoss, P.S. Kannan, A. SubbiahPandi, Crystal growth, structural, thermal, and dielectric characterization of Tutton salt (NH4)2Fe(SO4)2.6H2O crystals. J Therm Anal Calorim. 2013;112:547-54
  23. Neeti Goel, Nidhi Sinha, Binay Kumar. Enhanced optical, NLO, Dielectric and thermal properties of novel sodium hydrogen phthalate single crystals doped with zinc, Opt Mater. 2013;35:479-86.
  24. B. Babu, J. Chandrasekaran, S. Balaprabhakaran, P. Ilayabarathi, Optical, structural and electrical properties of pure and urea doped KDP crystals, Mater-Sci Poland. 2013;31:151- 57.S. Arjunan, A. Bhaskaran, R. Mohan Kumar, R. Mohan and R. Jayavel, Effect of Iodic Acid Dopant on the Growth and Structural, Optical, and Electrical Properties of L-Arginine Phosphate Single Crystals, Mater. Manuf. Process. 2012;27:49-52.
  25. G. Shanmugam, K. Thirupugalmani, R. Rakhikrishna, J. Philip, S. Brahadeeswaran, Thermophysical, mechanical and dielectric studies on piperidinium p-hydroxybenzoate, J Therm Anal Calorim. 2013;114:1245-54.
  26. U. Von Hundelshausen, Electrooptic effect and dielectric properties of cadmium- mercury-thiocyanate crystals, Phys Lett A. 1971;34:405-06.
  27. B. Milton Boaz, S. Mary Navis Priya, J. Mary Linet, P. Martin Deva Prasath, S. Jerome Das, Photoconductivity and dielectric studies on NLO active NPNa and NPLi single crystals. Opt Mater. 2007;29:827-32.
  28. M. Jose, R. Uthrakumar, A. Jeya Rajendran, S. Jerome Das, Optical and spectroscopic studies of potassium p-nitrophenolate dihydrate crystal for frequency doubling applications. Spectrochimica Acta part A. 2012;86:495-99.
  29. S.K. Kurtz, T.T. Perry, A powder technique for the evaluation of nonlinear optical materials. J Appl Phys. 1968;39:3798-13.
  30. I. Fleming, Frontier Orbitals and Organic Chemical Reactions, Wiley, London, 1976.
  31. T.A. Koopmans, *Physica*1 (1993) 104
  32. H. Chermette, *J. Comput. Chem.* 20 (1999) 129–154.
  33. R.G. Parr, L.V. Szentpaly and S. Liu, *J. Am. Chem. Soc.,*121(1999) 1922.
  34. B. Mohanbabu, R. Bharathikannan, G. Siva, Journal of Materials Science: Materials in Electronics, 28, 2017, 13740.
  35. B. Dhanalakshmi, S. Ponnusamy, C. Muthamizhchelvan, Growth and characterization of a solution grown, new organic crystal:L-histidine-4-nitrophenolate 4-nitrophenol (LHPP). J Crystal Growth. 2010;313:30-36.
  36. B.Yogeswari, R.[Kanakaraju](https://www.tandfonline.com/author/Kanakaraju%2C+Ramasamy), [S.Boopathi](https://www.tandfonline.com/author/Boopathi%2C+Subramaniam) & [P.Kolandaivel](https://www.tandfonline.com/author/Kolandaivel%2C+Ponmalai),[Molecular Simulation](https://www.tandfonline.com/journals/gmos20), [Volume **40**, 2014 - Issue 12](https://www.tandfonline.com/toc/gmos20/40/12)
  37. S Ponnuswamy, A Akila, D Deepa Rajakumari, V Shreevidhyaa Suressh, G Usha, Journal of Chemical Sciences, Volume **127,** 2051-2061 (2015)