INVESTIGATE THE SPECTROSCOPY, THERMODYNAMICS PROPERTIES AND FUKUI FUNCTIONAL ANALYSIS OF PHOSPHONATE DERIVATIVE

YASSAR PARVEZ ROUNYAL[1], FARHANA KOWSER[2]

ABSTRACT

This study investigates the spectroscopic, thermodynamic properties, and Fukui function analysis of a newly synthesized phosphonate derivative. Using Nuclear Magnetic Resonance (NMR), Infrared (IR) spectroscopy, and Ultraviolet-Visible (UV-Vis) spectroscopy, we elucidate the structural and electronic characteristics of the compound. Computational methods, including Density Functional Theory (DFT), were employed to calculate thermodynamic properties such as enthalpy, entropy, and Gibbs free energy. Additionally, Fukui function analysis was performed to assess the reactivity and selectivity of the molecule. The combined experimental and theoretical approaches provide a comprehensive understanding of the phosphonate derivative, highlighting its potential applications in material science and pharmaceutical.

1. INTRODUCTION TO SPECTROSCOPY

The word Spectroscopy appears to mean the watching of images but the modern subject covers the interaction of electromagnetic radiations with matter. Spectroscopy is the branch of physics and chemistry which deals with the observation and interpretation of radiation emitted and absorbed by atoms and molecules and throws light on their structure. It provides information not only about the arrangement and motion of the outer electron (optical spectroscopy), but also about the inner electrons (X-rays) and about the angular momentum, magnetic moment, distribution of charge and magnetism of the nucleus. These radiations when interact with matter give different types of spectroscopy. For example, electromagnetic radiation when absorbed with matter in the region of radio frequency gives rise to Electron Spin (ESR) or Nuclear Magnetic Resonance spectroscopy (NMR). In the UV-Visible region, Ultraviolet and visible light brings about movement of valence shell electrons, typically from a filled bonding molecular orbital to an unfilled anti bonding orbital. So, it is known as electronic spectroscopy. The vibrational excitation of molecular frame work of a compound of infrared radiation in infrared region is known as vibrational spectroscopy. Quanta of microwave radiation effect rotation around bonds gives rise to rotational spectroscopy. The different types of spectroscopy techniques and quantum chemical methods can provide the valuable information about the molecular structure. The transition between the electronic energy levels in the visible or UV regions results in electronic spectra. Information regarding molecular orbitals and bonding are provided. Vibrational transitions occur in infrared regions of electromagnetic spectrum and provide the information about the functional groups and bonds of organic compounds. Spectroscopy also plays an important role to study the biological activities of the molecules which is the need of present day. Spectroscopic methods are generally used to measure the energy difference between the various molecular energy levels and to determine molecular and atomic structures.

The importance of spectroscopy in the physical and processes going on in planets, stars, comets and their interstellar medium has continued to grow as a result of the use of satellites and the building of radio telescopes for the microwave and millimetre wave region. Nowadays, spectroscopy is one of the most powerful tools available for the study of atomic and molecular structures of wide range of samples.

The total energy of molecule which is the most important parameter for spectroscopic studies discussed above consists of contributions due to the electronic configuration, vibration, rotation, translation with various inter-electron, inter-nuclear and electron-nuclear interactions is expressed as

$$E_{Total} = E_{elec} + E_{vib} + E_{rot} + E_{trans} + E_{en} + E_{nn} + E_{ee}.$$

Where E Total-total energy, E elec-electronic energy, E vib-vibrational energy, E rot-rotational energy, E trans-translational energy, E en -electron -nuclear interaction, E nn- nuclear- nuclear interaction, E ee.-electron -electron interaction.

2. ABSORPTION SPECTROSCOPY

Absorption spectroscopy involves the use of spectroscopic techniques that measure the absorption of radiation in matter. Absorption spectroscopy is generally used as an analytical chemistry tool with wide applications ranging from remote sensing, astronomy and most importantly to atomic and molecular physics. Moreover, theoretical models allow for the absorption spectra of atoms and molecules to be related to other physical properties such as electronic structure, atomic or molecular mass and molecular geometry. There is a wide range of experimental approaches for measuring absorption spectra. The most common arrangement is to direct a generated beam of radiation that passes through it. The transmitted energy can be used to calculate the absorption, the type of interactions and applications.

3. ELECTROMAGNETIC SPECTRUM

The electromagnetic spectrum has a range of different types of electromagnetic waves. These waves include radio waves, microwaves, infrared, visible light, ultraviolet, X-rays, and gamma rays. Each type of wave has a different wavelength and frequency. Radio waves have the longest wavelength and lowest frequency, while gamma rays have the shortest wavelength and highest frequency. Ultra violet waves have even shorter wavelengths than visible light.

S.no.	Electromagnetic radiation	Type of transitions	*Applications*
1.	**X-Ray**	**Core level electrons**	*Used for determining the geometric and electronic structure of molecules, major applications include study of amorphous solid, ions in solutions, and detection of bone fracture*
2.	**UV-Vis**	**Valence electrons**	*Used for the of organic compounds, biological macromolecules*
3.	**Microwave**	**Molecular rotation, electron's**	*Used for studying molecular structure, internal motions and molecular interactions.*
4.	**Radiowave**	**Nuclear spin**	*Used to study chemical kinetics, the mechanism of chemical reactions, the energy spectrum and properties of semiconductors and metals*

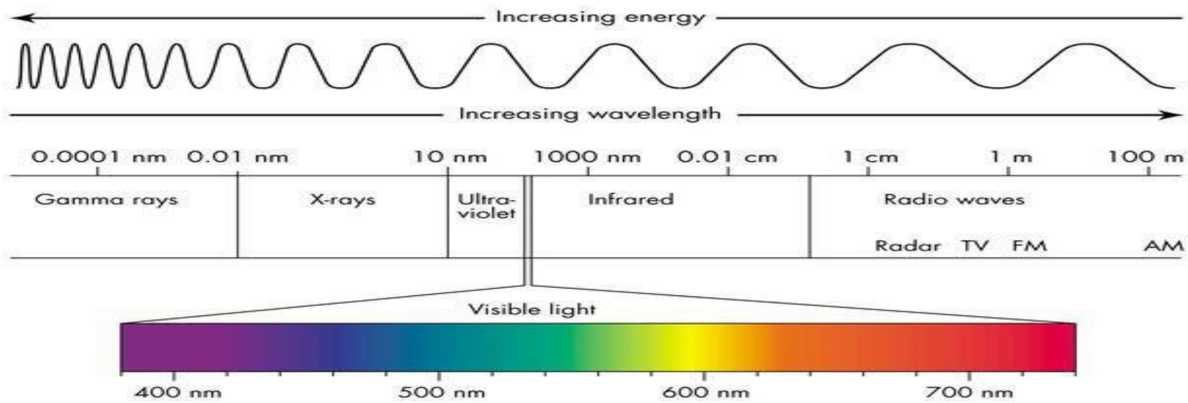


Fig.1.1 Range of various radiation

4. VIBRATIONAL SPECTROSCOPY

Vibrational spectroscopy is a method of characterizing and identifying compounds that works bmeasuring the vibrations of compound. Each compound has a unique measurement of vibrations, allowing compounds to be identified. Vibrational spectroscopy includes several techniques, but the most important are mid- infrared (MIR), near-IR (NIR), and Raman spectroscopy. Raman spectroscopy calculates relative frequencies in which the sample absorbs radiation. It is based on periodic changes of dipole moments (InfraRed) or polarizabilities (Raman) caused by molecular vibrations of molecules or groups of atoms and the combined discrete energy transitions and changes of frequency during absorption(InfraRed) or polarizabilities (Raman) caused by molecular vibrations of molar molecules or groups of atoms and the combined discrete energy transitions and changes of frequencies during absorption(InfraRed) or scattering (Raman) of electromagnetic radiations. It is perhaps the most commonly used spectroscopic technique due to its wide-ranging applications from differentiating chemical structures to studying mineralization process. It also gives information about the functional groups present in molecules and hence is used in forensic analysis which is used to settle many civil and criminal cases.

5. IR SPECTRASCOPY:

The most frequent spectroscopic technique used by organic and inorganic chemists is Infrared Spectroscopy (IR). It deals with the absorption of radiation in the infrared region of the electromagnetic spectrum. The studies of infrared absorption spectra gained importance in the year 1935 when IR absorption of certain organic molecules containing – OH groups was reported. IR spectrum gives sufficient information about the structure of a compound and also can be used as analytic tool to access the purity of a compound. Even though IR spectroscopy is a much better, more useful, and faster method than any other analytic method, there are certain limitations to it. Molecules that have higher molecular weights and are more complex are difficult to be studied in this technique. The absorption of infrared radiation by a molecule causes change in their vibrational and rotational energy levels and hence IR – spectroscopy is also known as vibrational – rotational spectroscopy. Unlike UV – spectroscopy which has fewer peaks in their spectrum, IR spectroscopy provides spectrum with a large number of absorption bands and hence provide a plenty of information about the structure of a compound.

Principle:

As with other types of energy absorption, molecules are excited to a higher energy state when they absorb infrared radiation. The absorption of infrared radiation is, like other absorption processes, a quantized process. A molecule absorbs only selected frequencies (energies) of infrared radiation. The absorption of infrared radiation corresponds to the energy changes from 8 to 40 KJ/mole. Radiations energy range corresponds to the range encompassing the stretching and bending vibrational frequencies of the bonds in most covalent molecules. In the absorption process, those frequencies of infrared radiation that match the natural vibrational frequencies of the molecule in question are absorbed, and the energy absorbed serves to increase the amplitude of the vibrational motions of the bonds in the molecule. Note, however, that not all bonds in a molecule are capable of absorbing infrared energy, even if the frequency of the radiation exactly matches that of the bond motion. Only those bonds that have a dipole moment that changes as a function of time are capable of absorbing infrared radiation. Symmetric bonds, such as those of H_2 or Cl_2 do not absorb infrared radiation. A bond must present an electrical dipole that is changing at the same frequency as the incoming radiation for energy to be transferred. The changing electrical dipole of the bond can then couple with the sinusoidal changing electromagnetic field of the incoming radiation. Thus, a symmetric bond that has identical or nearly identical groups on each end will not absorb in the infrared. For the purpose of an organic chemist, the bonds most likely to be affected by this restraint are those of symmetric or pseudo symmetric alkenes and alkynes.

Infrared Region:

The infrared spectrum can be divided into three main regions; the far infrared (<400cm^{-1}), the mid – infrared (4000 – 400cm^{-1}) and the near infrared (13000 – 4000cm^{-1}). The mid IR region is of greatest practical use to the organic chemist, but the near and the far infrared regions also provide important information about certain materials.

- **Near – infrared Region (13000 – 4000cm^{-1}):** The absorptions observed in the near – infrared region are overtones or combinations of the fundamental stretching bands. Bands in the near infrared are usually weak in intensity. They are often overlapped and hence are less useful than the bands in mid – infrared region. NIR show some similarities to UV – visible spectrophotometry and some to mid-IR spectroscopy. Indeed, the spectrometers used in this region are often combined UV - visible – NIR ones.

- **Mid IR Region:** The mid – infrared spectrum extends from 4000 to 400cm^{-1} and results from vibrational and rotational transitions. This region is most useful in the organic chemist since most of the organic molecules absorb in this region. The mid – infrared can be divided into two regions; functional group region (4000 – 1300) and fingerprint region (1300 – 600).

1. **Functional Group Region (4000 – 1300):** Most of the functional groups present in organic molecules exhibits absorption bands in the region 4000 – 1300cm^{-1}, hence this is known as functional group region. In this region each band can be assigned to a particular deformation of the molecule, the movement of a group of atoms, or the bending or stretching of a particular bond.
2. **Fingerprint Region (1300 – 600):** The region from 1300 – 600cm^{-1} usually contains complicated series of absorption. These are mainly due to molecular vibrations, usually bending motions that are characteristic of the entire molecule or large fragments of the molecule. Except enantiomers, any two different compounds cannot have precisely the same absorption pattern in this region. Thus, absorption pattern in this region are unique for any particular compound that is why this is known as fingerprint region.To understand the importance of fingerprint region to identify a compound, we can take the example of propan-1-ol and propan-2-ol. Both the compounds are alcohol and contain exactly the same bond. Now, if you compare infrared spectra of these compounds, the functional group region is very similar for both the compounds but the fingerprint region is totally different. Therefore, fingerprint region could be crucial to find.

- **Far – infrared Region (600 – 100cm^{-1}):** The far – infrared spectrum extends from 600 – 100cm^{-1}. Organometallic and inorganic molecules contain heavy atoms and have weak bonds, therefore the fundamental vibrations of the molecule fall in this region. Lattice vibrations of crystalline materials occur in this region.

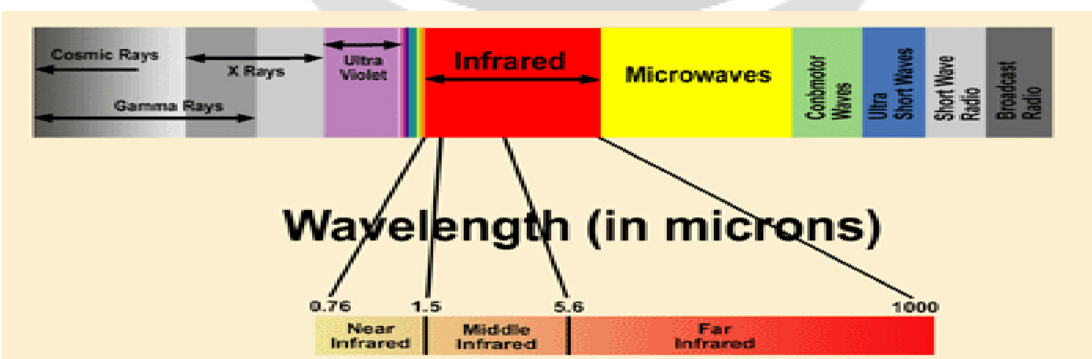


Fig.1.2 Region of IR

Synthesis, structural, vibrational, electronic, thermal and Fukui analysis of phosphonate derivative:
Organophosphonates are versatile substrates that constitute core unit of several natural products [1] and bioactive compounds [2]. Due to the diverse applications of phosphonates in industrial, medicinal and agricultural purposes, their synthesis has been a focus of interest for organic and medicinal chemists [3].

In particular, α- hydroxyphosphonates represents an elite class of organic compounds due to their broad range of pharmacological properties such as antifungal [4], antiviral [5], anticancer [6], rennin inhibitory [7], and HIV protease [8]. These medicinally privileged scaffolds are also applied as enzyme inhibitors [9], metabolic probes [10], peptide mimetics [11], as flame retardants [12] and additives. Furthermore biphosphonates are popular drugs which are for the treatment of bone related disorders.
Additionally, they act as pioneer materials for the synthesis of 1,2-diketones , and also applied as ligands in asymmetric synthesis . Organophosphonates also find utility as key intermediates in construction of numerous natural and synthetic products including un-natural aminoacids. Because of diverse applications of α-hydroxyphosphonates, the compound was synthesized for its detailed experimental and theoretical studies.

Phosphonate Derivatives

Phosphonate derivatives are compounds containing the phosphonate group (P(=O)(OH)2), which are of significant interest due to their diverse applications in agriculture as herbicides, in medicine as antiviral and anticancer agents, and in material science for the development of flame retardants and corrosion inhibitors . Their unique chemical properties, such as stability and the ability to form strong bonds with metals, make them valuable in various industrial and pharmaceutical applications

Thermodynamic Properties

Thermodynamic properties such as enthalpy, entropy, and Gibbs free energy are critical for understanding the stability and reactivity of phosphonate derivatives. Computational methods, particularly Density Functional Theory (DFT), have been extensively used to predict these properties. DFT calculations provide a detailed understanding of the thermodynamic stability and can be correlated with experimental data to validate theoretical models . Studies have shown that the phosphonate group can significantly influence the thermodynamic behavior of the molecule, impacting its potential applications.

Fukui Function Analysis

Fukui function analysis, derived from conceptual DFT, is a valuable method for predicting the reactivity and selectivity of molecules. It helps identify regions within a molecule that are more likely to participate in chemical reactions. Previous research has demonstrated that Fukui functions can effectively predict reactive sites in phosphonate derivatives, aiding in the design of more efficient and selective compounds for various applications.

RESULTS AND DISCUSSION:

GEOMETRIC STRUCTURE

The optimized structure of the diethyl (hydroxy(4-methoxyphenyl) methyl)phosphonate is shown in Fig. 4.2(a) and corresponding bond lengths and bond angles calculated by DFT method using 6-311G(d,p) basis set for the optimized structure.

The minimum energies of the optimized structure of diethyl (hydroxy(4-methoxyphenyl) methyl) Phosphonate calculated by the HF/6-311G(d,p) and B3LYP/6-311G(d,p) are -1180.80289381 a.u. and-1186.49677314 a.u. The energy difference is about -5.69 a.u.

The minimum energy calculated for the phosphonate derivative shows that the DFT calculated optimized structural energy is less as compared with HF calculated minimum energy. Hence, the DFT calculated optimized structures for the derivative is more stable than HF ones

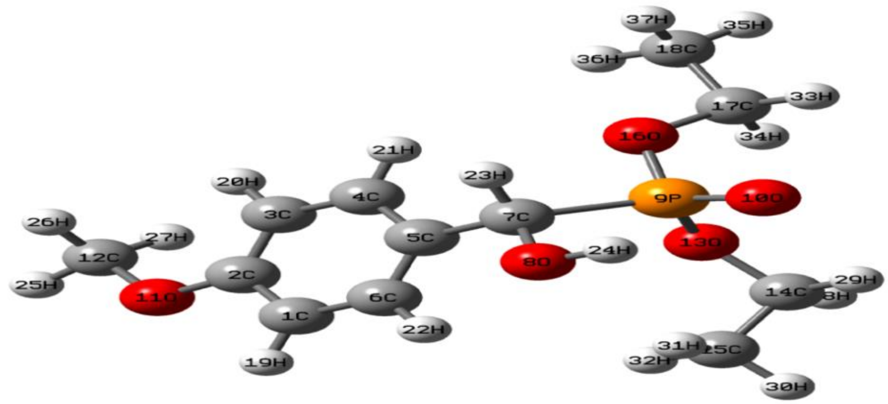


Fig.1.3 optimized structure of the diethyl (hydroxy(4-methoxyphenyl) methyl) phosphonate

FTIR SPECTROSCOPY AND VIBRATIONAL ANALYSIS

The vibrational analysis of the compound diethyl (hydroxy(4-methoxyphenyl) methyl) phosphonate(C12H19O5P) was carried out with DFT (B3LYP) level. DFT (B3LYP) is an efficient method to carry the vibrational analysis of the compound [34]. Diethyl (hydroxy(4-methoxyphenyl) methyl) phosphonate(C12H19O5P) consists of 37 atoms so they have (3N-6) 105 normal vibrational modes. Positive values of all the 105 modes of vibrations of the compound confirmed that geometries are located at true local minima of potential energy surface.

The calculated wavenumbers are usually higher than the corresponding experimental ones, due to the combination of electron correlation effects and insufficient basis set deficiencies. Therefore, in order to improve the calculated values, the discrepancy between experimental and theory is removed by computing anharmonic corrections explicitly, by introducing scalar field, by direct scaling of the calculated wavenumbers with a proper scaling factor. It is well known that different scaling factors reproduce theoretical wavenumbers in good agreement with the experimental wavenumbers. In the present study, the computed wavenumbers have been scaled by 0.967 for the derivative. The assignments of the wavenumbers have been done with the help of VEDA by using PED (potential energy distribution).

1. C-H vibrations

Normally above 3250-2950 cm-1, the aromatic C-H stretching vibrations occurs. Substituent's nature does not affect the bands in this region. In this compound, the experimental (IR) C-H stretching vibration of compound were observed in the range 3109-2973 cm-1 and the computed scaled wavenumbers in the range 3107-2982 cm-1.

2. C-O vibrations

The C-O stretching vibration occurs as a strongest band in the region 1300-1000 cm-1. For the compound (C12H19O5P), C-O stretching vibrations observed in the FTIR spectrum at 1222, 1058 and 1020 cm-1 corresponds to the calculated bands at 1235, 1034 and 1024 cm-1 with 51, 72 and 82% contribution.

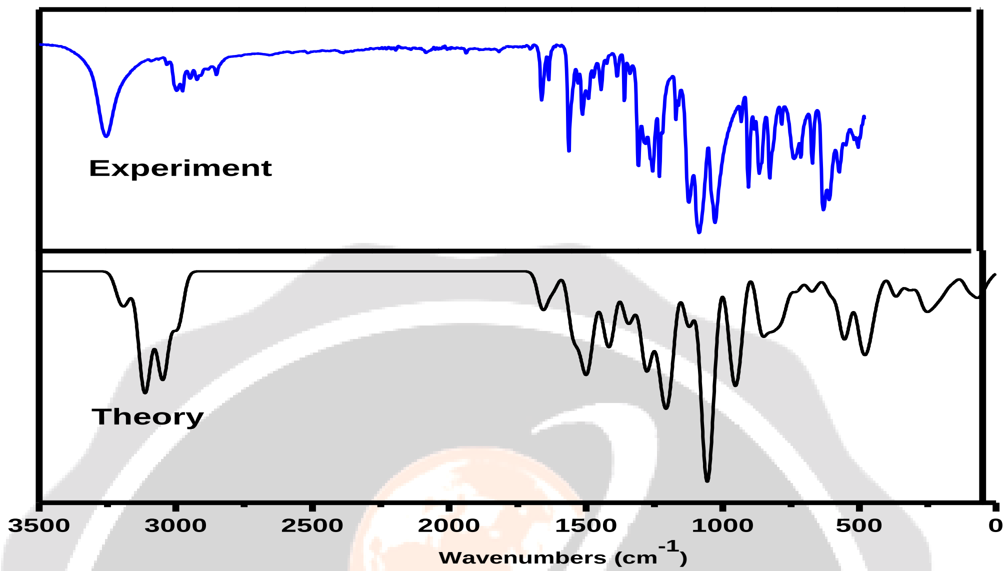
3. C-C vibrations

The C-C stretching modes of the phenyl group are expected in the range from 1650-1200 cm-1 [39]. Therefore, the strong vibrational frequency bands at 1611, 1541, 1300 and 1194 cm-1 are assigned to C-C stretching vibrations in FTIR spectrum and the strong vibrational frequency bands at 1606, 1585 and 1198 cm-1 which coincides well with the calculated vibrational bands at 1603, 1565, 1308 and 1206 cm-1 with significant contribution of TED. The medium intensity band experimentally at 834 and 837 cm-1 are also attributed to C-C stretching and matches well with the calculated frequency value at 832 cm-1.

4.P-C vibrations

The P-C stretching modes appear in the region of 754-634 cm-1 medium-weak in IR. In FTIR spectrum frequency bands at 754 and 662 cm-1. The computed theoretical wavenumber of P-C stretching vibrations at 759 and

654 cm-1 by 6-311G(d,p) coincides very well with the experimental value and the PED corresponds is 59% and 38% is shown . A close agreement between observed and calculated spectra cabe seen from the figure



CONCLUSIONS

Diethyl (hydroxy(4-methoxyphenyl) methyl) phosphonate has been synthesized and the derivative is characterized by FTIR and UV-Vis. The structural geometrical parameters, vibrational, electronic, HOMO-LUMO, Fukui analysis, and the thermodynamic properties of the derivative are performed on the basis of DFT calculations at B3LYP/6-311G(d,p) basis set. A good agreement between observed and calculated wavenumbers and all observed wavenumbers have been assigned. The compound diethyl (hydroxy(4-methoxyphenyl) methyl) phosphonate is chemically stable up to 1720C. Using NBO analysis, the stability of the molecule arising from the hyper-conjugative interaction and charge delocalization has been studied for the derivative. Fukui function analysis helps in identifying the nucleophilic and electrophilic behaviour of a specific site within a molecule of the derivative. The correlations between the statistical thermodynamics and temperature are obtained and show that increase in temperature causes the increase in heat capacities, entropies and enthalpies. The present chapter gave a comprehensive complete structural informations, vibrational assignments, NBO analysis and electronic properties and thermal properties of the phosphonate derivative.

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