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Experimental and theoretical investigation of the molecular structure, conformational stability, hyperpolarizability, electrostatic potential, thermodynamic properties and NMR spectra of pharmaceutical important molecule: 4′-Methylpropiophenone

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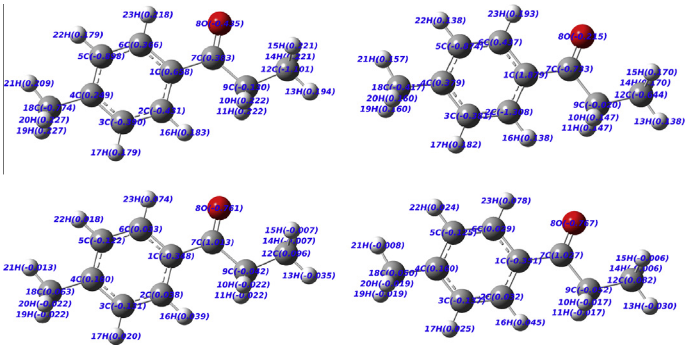
HIGHLIGHTS

- Propiophenone and their derivatives have great analytical and pharmaceutical applications.
- The FT-IR and FT-Raman spectra of MPP were studied.
- The calculations were carried out for MPP at HF and B3LYP methods.
- A comparison with the IR and Raman spectra of MPP have been constructed.

GRAPHICAL ABSTRACT



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ABSTRACT

Combined experimental and theoretical studies have been performed on the structure and vibrational spectra (IR and Raman spectra) of 4′-methylpropiophenone (MPP). The FT-IR and FT-Raman spectra of 4′-methylpropiophenone (MPP) have been recorded in the region 4000–400 cm^{-1} and 3500–100 cm^{-1}, respectively. The harmonic vibrational frequencies were calculated and the scaled values have been compared with experimental FT-IR and FT-Raman spectra. A detailed interpretation of the infrared and Raman spectra of MPP are also reported based on total energy distribution (TED). The observed and the calculated frequencies are found to be in good agreement. The ^{1}H and ^{13}C NMR chemical shifts have been calculated by Gauge-Independent Atomic Orbital (GIAO) method with B3LYP/6-311++G(d,p). The natural bond orbital (NBO), natural hybrid orbital (NHO) analysis and electronic properties, such as HOMO and LUMO energies, were performed by DFT approach. The calculated HOMO and LUMO energies show that charge transfer occurs within molecule. The first order hyperpolarizability (β_0) of the novel molecular system and related properties (β_{tot}, α_0 and $\Delta\alpha$) of MPP are calculated using DFT/6-311++G(d,p) method on the finite-field approach. The Mulliken charges, the values of electric dipole moment (μ) of the molecule were computed using DFT calculations. The thermodynamic functions of the title compound were also performed at the above method and basis set.

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Introduction

Aromatic ketones such as acetophenone, propiophenone and their derivatives have great analytical and pharmaceutical applications. Substituted propiophenones have tremendous pharmaceutical applications. A derivative, 3′-bromopropiophenone thiosemicarbazone, inhibited cruzain and could cure mammalian cell cultures infected with Trypanosoma cruzi [1]. 3-Bromoacetophenone is used as an intermediate product for the preparation of fenoprofen which is an anti-inflammatory, analgesic and antipyretic drug [2,3]. Chemically it is called as 1-(3-bromophenyl)-ethanone. Alzheimer's disease (progressive form of presenile dementia) is treated with the drug which was invented from 3-bromoacetophenonone [4]. It is used as a reaction initiator with organopolysiloxane, which is the base polymer to prepare silicone rubber [5]. It is also used as a coupling partner in microwave accelerated cross-coupling of a range of aryl boronic acids with aryl chlorides [6]. Substituted bromoacetophenone are used to synthesis dicationic diarylpyridines which are used as nucleic acid binding agents [7].

3-Chloropropiophenone is the major reactant for the preparation of Bupropion, which is a drug used to treat depression [8–10]. It increases the amount of norephineprine and dopamine in the brain, which develops certain neurological changes. Chemically it is called as 1-(3-chlorophenyl) propan-1-one. Similarly the other compound 3-nitropropiophenone is chemically called as 1-(3-nitrophenyl) propan-1-one, used as a pharmaceutical intermediate to manufacture antiviral compound. The antiviral compound is useful for managing HIV infection in human. This antiviral compound is an optically active compound. The antiviral activity is inhibited by the presence of other isomeric form of the compound. Thus the pharmacological activity of the antiviral compound is depending upon providing the compound in high optical purity [11]. The title compound is used as an antibacterial agent [12]. It is also used as a photo radical polymerization initiator to provide a cross linkable silyl group terminated vinyl polymer [13]. Density Functional Theory (DFT), accepted by the *ab initio* quantum chemistry community is a cost-effective general procedure for studying physical properties of the molecules. DFT calculations of vibrational spectra of many organic systems [14,15], have shown promising conformity with experimental results. Therefore, in this present investigation DFT technique is employed to study the complete vibrational spectra of the title compound and to identify the various normal modes with greater wavenumber accuracy. Several other investigations have been carried out on the title compound and its derivatives [16–20].

Literature survey reveals that to the best of our knowledge no *ab initio* HF/DFT frequency calculations of 4′-methylpropiophenone have been reported so far. Chemically 4′-methylpropiophenone is called 1-(4-methylphenyl) propan-1-one. It may be due to difficulty in interpreting the spectra of this molecule because of their complexity and low symmetry. Due to the absence of Raman spectra and vapour phase infrared spectra, a complete vibrational assignment is not available in the literature. Hence the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wavenumber accuracy. Assuming C_1 point group symmetry the band assignments have made. Density Functional Theory (DFT) calculation has been performed to support our wavenumber assignments. The theoretically predicted IR and Raman intensities are well in agreement with that of experimental spectral data.

Experimental details

4′-Methylpropiophenone (MPP) was provided by M/s Aldrich Chemicals, USA, which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The room temperature Fourier Transform infrared spectrum of MPP was measured in the 4000–400 cm^{-1} region at a resolution of ±1 cm^{-1} using a BRUKER IFS-66V FT-IR spectrometer equipped with a cooled MCT detector for the mid-IR range. KBr pellets were used in the spectral measurements. The FT-Raman was recorded on the same instrument with an FRA-106 FT-Raman accessory in the region 3500–100 cm^{-1}. The 1064 nm Nd:YAG laser was used as excitation source and the laser power was set to 200 mW. The reported wavenumbers are expected to be accurate within ±1 cm^{-1}. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) (400 MHz; CDCl3) spectra were recorded on a BRUKER HC400 instrument. Chemical shifts for protons are reported in parts per million scales downfield from tetramethylsilane.

Computational methods

The molecular structure of MPP and corresponding vibrational harmonic frequencies were calculated using Becke3–Lee–Yang–Parr (B3LYP) with 6-31+g(d) and 6-311++G(d,p) basis sets using GAUSSIAN 09 program package [21] without any constraint on the geometry. The harmonic vibrational frequencies have been analytically calculated by taking the second-order derivative of energy using the same level of theory. Transformation of force field from Cartesian to symmetry coordinate, scaling, subsequent normal coordinate analysis, and calculations of TED, IR and Raman intensities were made on a PC with the version V7.0-G77 of the MOLVIB program written by Sundius [22,23]. To achieve a close agreement between observed and calculated frequencies, the least-square fit refinement algorithm was used. By combining the results of the GAUSSVIEW [24] program with symmetry considerations, along with the available related molecules, vibrational frequency assignments were made with a high degree of accuracy. The calculated frequencies are scaled down to yield the coherent with the observed frequencies.

The electronic properties: HOMO–LUMO energies, absorption wavelengths and oscillator strengths are calculated using B3LYP method [25,26], based on the optimized structure in gas phase. Thermodynamic properties of the title compound at different temperatures have been calculated in gas phase using B3LYP/6-311++G(d,p) method. Moreover, the dipole moment, linear polarizabilities and first hyperpolarizabilities, chemical hardness and Mulliken atomic charge have also been studied.

Prediction of Raman intensities

The Raman intensities (I_i) were calculated from the Raman activities (S_i) obtained with the Gaussian 09 program, using the following relationship derived from the intensity theory of Raman scattering [27–29].

$$I_i = \frac{f(\upsilon_0 - \upsilon_i)^4 s_i}{\upsilon_i[1 - \exp(-hc\upsilon_i)]/kT}$$

where υ_0 is the exciting frequency (in cm^{-1} units), υ_i is the vibrational wavenumber if the *i*th normal mode, *h*, *c* and *k* are the universal constants and *f* is the suitably chosen common scaling factor for all the peak intensities. The simulated IR and Raman spectra have been plotted using Lorentzian band shapes with FWHM bandwidth of 10 cm^{-1}.

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