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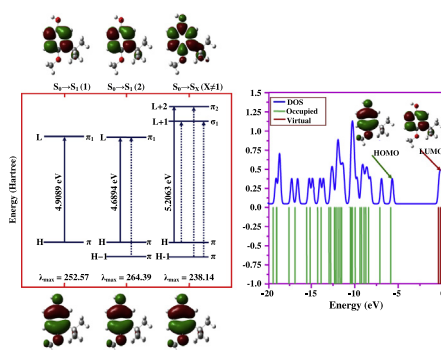
Quantum mechanical study and spectroscopic (FT-IR, FT-Raman, UV–Visible) study, potential energy surface scan, Fukui function analysis and HOMO–LUMO analysis of 3-tert-butyl-4-methoxyphenol by DFT methods

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HIGHLIGHTS

- FT-IR, FT-Raman, UV–Vis spectra of TBMP was examined.
- Potential energy surface has been carried.
- The NBO analysis explained the intra-molecular hydrogen bonding.
- First hyperpolarizability and HOMO, LUMO energy gap were theoretically predicted.

GRAPHICAL ABSTRACT



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ABSTRACT

This study represents an integral approach towards understanding the electronic and structural aspects of 3-tert-butyl-4-methoxyphenol (TBMP). Fourier-transform Infrared (FT-IR) and Fourier-transform Raman (FT-Raman) spectra of TBMP was recorded in the region 4000–400 cm⁻¹ and 3500–100 cm⁻¹, respectively. The molecular structures, vibrational wavenumbers, infrared intensities and Raman activities were calculated using DFT (B3LYP and LSDA) methods using 6-311++G (d,p) basis set. The most stable conformer of TBMP was identified from the computational results. The assignments of vibrational spectra have been carried out with the help of normal co-ordinate analysis (NCA) following the scaled quantum mechanical force field (SQMFF) methodology. The first order hyperpolarizability (β_0) and related properties (β , α_0 and $\Delta\alpha$) of TBMP have been discussed. The stability and charge delocalization of the molecule was studied by Natural Bond Orbital (NBO) analysis. UV–Visible spectrum and effects of solvents have been discussed and the electronic properties such as HOMO and LUMO energies were determined by time-dependent TD-DFT approach with B3LYP/6-311++G (d,p) level of theory. The molecule orbital contributions are studied by density of energy states (DOSs). The reactivity sites are identified by mapping the electron density into electrostatic potential surface (MEP). Mulliken analysis of atomic charges is also calculated. The thermodynamic properties at different temperatures were calculated, revealing the correlations between standard heat capacities, standard entropy and standard

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enthalpy changes with temperatures. Global hardness, global softness, global electrophilicity and ionization potential of the title compound are determined.

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Introduction

TBMP, $C_{11}H_{16}O_2$ is a yellowish waxy solid that is soluble in methanol, propylene glycol and ethanol and insoluble in water. Phenol and its derivatives is biologically and industrially useful compound. They are used in the manufacture of dyes, drugs, plastics, explosives and pesticides [1]. The properties of phenol and its derivatives are determined by their hydrogen and π -bonding system [2]. Antioxidant is a substance added in small quantities to hydrocarbons which are susceptible to oxidation, such as rubbers, plastics, foods and oils to inhibit or slow oxidative processes, while being itself oxidized. Antioxidative activity is implemented by the donation of an electron or hydrogen atom to a radical derivative. These antioxidants are usually hindered amines (p-phenylene diamine, trimethyl dihydroquinolines, alkylated diphenyl amines) or substituted phenolic compounds with one or more bulky functional groups such as a tertiary butyl [3]. In addition to this, phenol derivatives are biologically important compounds and are used in the manufacture of drugs [4].

Infrared and Raman spectroscopy is an efficient method to probe electronic and geometric structure of molecule, and has been widely used in studying the structural consequences. The vibrational spectroscopy is very important for investigation of inter- and intra-molecular interactions. The *ab initio* vibrational assignments of the infrared and Raman spectrum of molecules have been widely studied for structural investigation nowadays. In recent year's density functional theory (DFT) has become a powerful tool in the investigation of molecular structures and vibrational spectra, especially B3LYP method has been widely used [5–7]. Michalska et al. [8] reported a detailed study of the infrared spectrum of phenol using HF, MP2 and DFT methods with 6-31G (d,p) basis set. The BLYP functional method has been used in vibrational studies of some phenols [9,10]. The molecular structure and vibrational spectra and absorption spectra of butylated phenol and the best results obtained from B3LYP/6-311++G (d,p) computation [11].

In present study, the vibrational spectra of TBMP molecule have been thoroughly analyzed to identify the various normal modes with greater wavenumber accuracy. Density functional theory B3LYP/6-311++G (d,p) calculations have been performed to support our wavenumber assignments. The redistribution of electron density (ED) in various bonding, antibonding orbitals and $E(2)$ energies have been calculated by Natural Bond Orbital (NBO) analysis to provide evidence of stabilization originating from the hyper conjugation and various intra-molecular interactions. By analyzing the total density of states (DOS), the molecular orbital compositions and their contributions to the chemical bonding are studied. The UV spectroscopic studies along with HOMO–LUMO analysis have been used to elucidate information regarding charge transfer within the molecule. One key approach to understand solvent effect is the solvent-induced changes in the electronic transition of solutes generally referred to as solvatochromism. This present paper aims at reporting the effect of various solvents on the electronic spectra of compound. As a continuation of over recent studies on the dipole moment, nonlinear optical properties (NLO) and first order hyperpolarizability have also been studied. Moreover, Mulliken population analysis and the standard thermodynamic functions like heat capacity, entropy and enthalpy are reported on the basis of vibrational analysis and statistical thermodynamics, the calculated values of Fukui function employing the Mulliken charges, respectively.

Experimental details

The pure sample of TBMP in the light yellow waxy solid form was purchased from the Lancaster Chemical Company (UK), with a stated purity of greater than 98% and it was used as such without further purification. The FT-IR spectrum of this compound was recorded in the region $4000\text{--}400\text{ cm}^{-1}$ on IFS 66 V spectrometer equipped with an MCT detector using KBr beam splitter and global source. The FT-Raman spectrum of title molecule has been recorded using the 1064 nm line of a Nd:YAG laser as excitation wavelength in the region $3500\text{--}100\text{ cm}^{-1}$ on a BRUKER model RFS 66V spectrometer. The reported wavenumbers are expected to the accurate within $\pm 1\text{ cm}^{-1}$ resolution with 250 mW of power at the sample in both the techniques.

Computational details

The entire calculations was performed at DFT/B3LYP and LSDA levels with the standard basis set 6-311++G (d,p) on personal computer using GAUSSIAN 09W [12] program package, invoking gradient geometry optimization [13]. The global minimum energy conformer is used in the vibrational wavenumber calculation at the B3LYP and LSDA with using 6-311G++ (d,p) level. Subsequently, the vibrational in association with the molecule were derived along with their IR intensity and Raman activity. In order to fit the theoretical wavenumbers to the experimental, the scaling factors have been introduced by using a least square optimization method. The polarizability, hyperpolarizability and dipole moments of TBMP have been calculated using the same method. The HOMO–LUMO analysis has been carried out to explain the charge transfer within the molecule. The global hardness (η), global softness (ν), electronegativity (χ) and chemical potential (μ) have been calculated using the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The natural bonding orbital's (NBO) calculations [14] were performed using NBO 3.1 program as implemented in GAUSSIAN 09W package at DFT level in order to understand various second order interactions between the another subsystem, which is a measure of the intra-molecular delocalization or hyper-conjugation. To check whether the chosen set of symmetric coordinates contribute maximum to the potential energy associated with the molecule, the PED has been carried out. The transformation of force field, subsequent normal coordinate analysis and calculation of the PED were done on a PC with the MOLVIB program (Version 7.0-G77) written by Sundius [15]. The complete information's regarding population of electrons in sub-shells of atomic orbital's and electron densities of an atom in the title molecule.

Prediction of Raman intensity

The Raman activities (S_i) calculated with the GAUSSIAN 09W program were converted to Raman intensities (I_i) using the following relationship derived from the intensity theory of Raman scattering [16,17].

$$I_i = \frac{f(v_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i/kT)]}$$

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