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Comparative vibrational spectroscopic studies, HOMO–LUMO, NBO analyses and thermodynamic functions of *p*-cresol and 2-methyl-*p*-cresol based on DFT calculations

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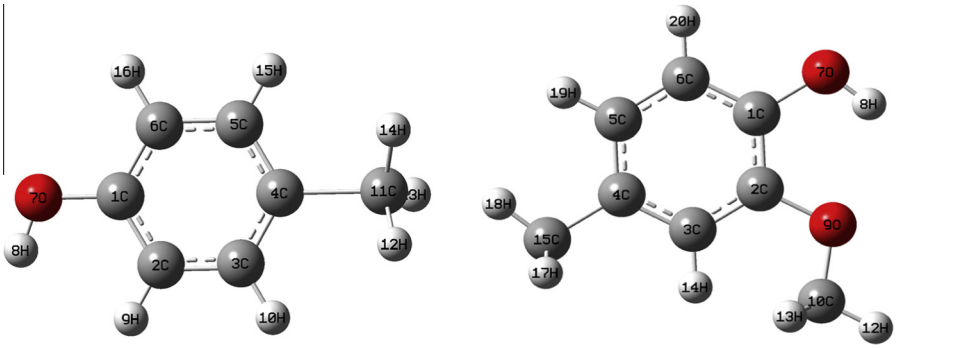
HIGHLIGHTS

- The FT-IR and FT-Raman spectra of *p*-cresol and 2-methyl-*p*-cresol were analyzed.
- The calculations were carried out at B3LYP/cc-pvdz and B3PW91/cc-pvdz.
- HOMO–LUMO, NPA and chemical reactivity were performed.
- Molecular electrostatic potential of *p*-cresol and 2-methyl-*p*-cresol was calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study structural properties of p-cresol, and 2-methoxy-p-cresol have been studied by using B3LYP/cc-pvdz and B3PW91/cc-pvdz of Density Functional Theory (DFT) utilizing Becke three exchange functional and Lee Yang Paar correlation functional. The Fourier transform infrared and Fourier transform Raman spectra of title molecules were recorded (solid phase). Optimized geometry, harmonic vibrational frequencies and various thermodynamic parameters of the title compounds were calculated with B3LYP/cc-pvdz, and B3PW91/cc-pvdz basis sets. Non-linear optical (NLO) behavior of the p-cresol and 2-methoxy-p-cresol were investigated by determining of electric dipole moment, polarizability α, and hyperpolarizability β using the above mentioned basis sets. The molecular properties such as ionization potential, electronegativity, chemical potential, electrophilicity have been deduced from HOMO–LUMO analysis employing the same basis sets. A detailed interpretation of the infrared and Raman spectra of title molecules were reported. UV spectrum was measured in different solvent. The energy and oscillator strength are calculated by Time Dependant Density Functional Theory (TD-DFT) results. The calculated HOMO and LUMO energies also confirm that charge transfer occurs within the molecule. The complete assignments were performed on the basis of the potential energy distribution (PED) of vibrational modes, calculated with scaled quantum mechanics (SQM) method. Finally the theoretical FT-IR, FT-Raman, and UV spectra of the title molecules have also been constructed.

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Introduction

p-Cresol is an organic compound with the formula $CH_3C_6H_4(OH)$. It is a colorless solid that is widely used intermediate in the production of other chemicals. It is a derivative of phenol, an isomer of *o*-cresol and *m*-cresol [1]. Together with many other compounds, *p*-cresol is traditionally extracted from coal tar, the volatilized materials obtained in the roasting of coal to produce coke. This residue contains a few percent of phenol and cresol. The *p*-cresol is mainly consumed in the production of antioxidants, e.g., butylated hydroxytoluene (BHT). Methoxy phenol are used in manufacturing photoconductive and novolac resins for electronics industry, UV protectors, and stabilizers and antioxidants for plastics and rubbers. They are also used in analgesics, food additives, fragrances, biocides, fungicides, dye for pharmaceuticals and food additive industry. Another use is as an intermediate to manufacture other stabilizers, dyes, pharmaceuticals and plasticizers. In our previous work we have analyzed inter and intra-molecular interaction, vibrational assignments, and HOMO, LUMO analysis of phenol derivatives and are 2-hydroxy-5-bromobenzaldehyde, 2-hydroxy-p-toluic acid and 4-methoxy-5-nitrobenzaldehyde reported in the literature [2–4].

In the present work, harmonic-vibrational frequencies calculated for minimum energy conformer of p-cresol (PC) and 2-methoxy-p-cresol (MPC) using B3LYP/cc-pvdz and B3PW91/cc-pvdz methods. The calculated spectra of these molecule are compared to that of experimentally observed FT-IR and FT-Raman spectra. The HOMO and LUMO analysis have been used to elucidate information regarding ionization potential (IP), electron affinity (EA), electronegativity (χ), electrophilicity index (ω), hardness (η), and chemical potential (μ) are all correlated. These are confirming the charge transfer within the molecules and also molecular electrostatic potential (MESP) contour map show the various electrophilic region of the title molecules. However, molecular hyperpolarizability is also calculated by DFT method. Finally, the correlations between thermodynamic properties with various temperatures are reported.

Experimental details

The compound under investigation namely PC, and MPC are purchased from M/S Aldrich Chemicals, (USA) with spectroscopic grade and it is used as such without any further purification. The FT-IR spectrum of the compounds were recorded in Perkin–Elmer 180 Spectrometer between 4000 and 100 cm^{-1}. The spectral resolution is ±2 cm^{-1}. The FT-Raman spectra of the compounds were also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1064 nm line width with 200 mW power. The spectra were recorded with scanning speed of 30 cm^{-1} min^{-1} of spectral width 2 cm^{-1}. The frequencies of all sharp bands are accurate to ±1 cm^{-1}.

Quantum chemical calculations

The quantum chemical calculations have been performed at B3LYP/cc-pvdz and B3PW91/cc-pvdz basis sets using the Gaussian 09W program [5]. The optimized structural parameters have been evaluated for the calculations of vibrational frequencies by assuming C_s point group symmetry. At the optimized geometry for the title molecules no imaginary frequency modes were obtained, therefore there is a true minimum on the potential energy surface was found. As a result, the unscaled calculated frequencies, infrared intensities, Raman activities and depolarization ratios are obtained. In order to fit the theoretical wavenumbers to the experimental, the scaling factors have been introduced by using a least square optimization of the computed to the experimental data. Vibrational frequencies are scaled [6] by 0.985, 0.992 used up to 1700 cm^{-1} and 0.981, 0.9512 greater than 1700 cm^{-1} for B3LYP and B3PW91, respectively. The assignments of the calculated normal modes have been made on the basis of the corresponding PEDs. The PEDs are computed from quantum chemically calculated vibrational frequencies using MOLVIB program [7]. Gaussview Program [8] has been considered to get visual animation and for the verification of the normal modes assignment. The electronic absorption spectra for optimized molecules calculated with the time dependent DFT (TD-DFT) at B3LYP/cc-pvdz level in gas phase and solvent (DMSO (dimethyl sulfoxide) and chloroform). Furthermore, in order to show nonlinear optic (NLO) activity of title molecules, the dipole moment, linear polarizability and first hyperpolarizability were obtained. Moreover, the changes in the thermodynamic functions (the heat capacity, entropy, and enthalpy) were investigated for the different temperatures from the vibrational frequency calculations of title molecules.

The Raman activities (S_i) calculated with the help of GAUSSIAN 09W program were converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [9–12].

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

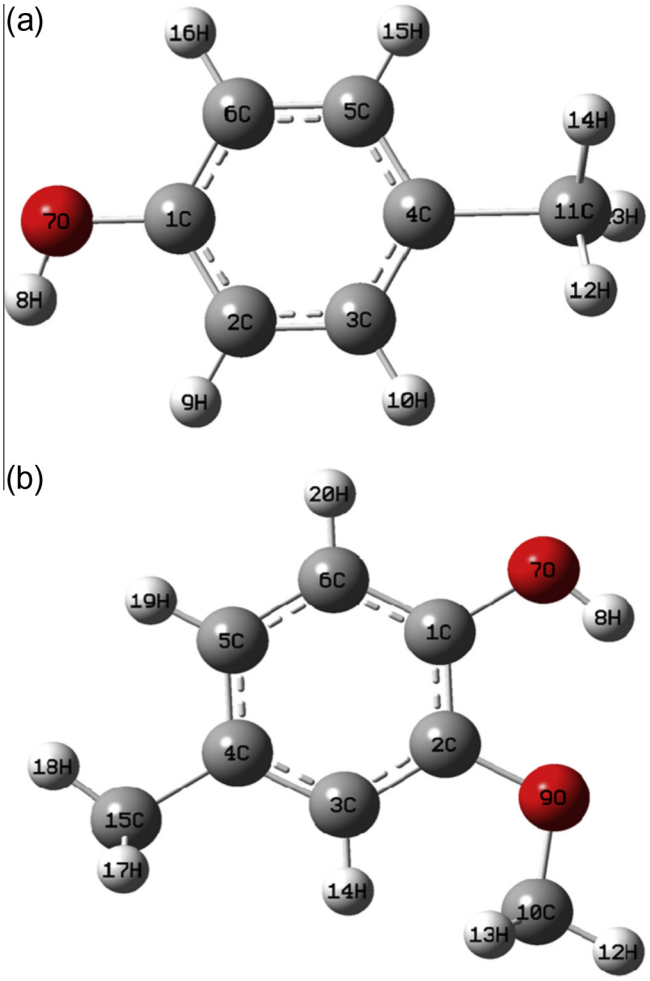

Fig. 1. Optimized structure of (a) p-cresol and (b) 2-methoxy-p-cresol.