

EXPERIMENTAL AND THEORETICAL DETERMINATION OF STRUCTURAL, VIBRATIONAL, MOLECULAR, ELECTRONIC, NLO, NBO, AND THERMODYNAMIC CHARACTERISTICS OF PENTABROMOPHENOL AND PENTAFLUROPHENOL#.

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Fourier Transform Raman ($3500-100\text{ cm}^{-1}$) and Fourier Transform infrared spectra ($4000-400\text{ cm}^{-1}$) were measured for Pentabromophenol (PBP) and Pentafluorophenol (PFP). UV-Visible ($200-400\text{ nm}$) spectrum, along with ^1H and ^{13}C NMR spectra were also recorded, for PBP. Torsional potentials, optimized structure parameters, barrier height to internal rotation, harmonic vibrational frequencies, general valance force field, potential energy distribution (PED), along with infrared and Raman intensities were evaluated, for PBP and PFP. DFT was used in conjunction with B3LYP functional with 6-311++G(d,p) basis set, for the computations. Scaling process was employed to get a better fit between the measured and computed frequencies. The rms error between them was 9.7 and 7.0 cm^{-1} , for PBP and PFP, respectively. Unambiguous vibrational assignments were arrived at by using PED and eigenvectors. In order to understand the nature of intermolecular hydrogen bond in these molecules geometry optimization was made for dimers of PBP and PFP. Further, using Gauge Independent Atomic orbital (GIAO) approach ^1H and ^{13}C NMR chemical shifts were evaluated and compared with corresponding experimentally measured shifts for PBP. In the same way, Time-dependent Density Functional Theory (TD-DFT) was used to simulate UV-Visible spectrum of PBP and compared with its experimental spectrum. HOMO and LUMO energies along with associated electronic parameters were generated. In order to find reactive sites in PBP and PFP molecular electrostatic surface potential (MESP) diagrams were drawn. The values of dipole moment, polarizability and hyperpolarizability of these molecules were computed to determine their NLO behavior. To understand the stability of the molecules (PBP and PFP) caused by charge delocalization, natural bond orbital (NBO) analysis was made for both PBP and PFP. Thermodynamic parameters were also evaluated for both the molecules.

Key words: Pentabromophenol, Pentafluorophenol, Vibrational spectra, Intermolecular hydrogen bond, DFT, Hyperpolarizability # A part of this work appeared in J. Mol. Struct. 1180 (2019) 665-675