



NMR & Electronic Spectra, NLO, FMO, NBO and Thermodynamic Properties of Pentachlorophenol: An Experimental and Theoretical Investigation

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Proton (¹H) and Carbon-13 (¹³C) nuclear magnetic resonance spectra of pentachlorophenol were measured. Corresponding chemical shifts were generated using Gauge Independent Atomic Orbital (GIAO) approach, as a part of density functional theory (DFT) application. UV-visible spectrum was measured in the spectral range 200-400 nm and compared with its simulated counterpart generated, using time-dependent density functional theory (TD-DFT). Frontier molecular orbital (FMO) approach was used to understand origin of UV-visible spectrum and chemical reactivity of the molecule. The non-linear (NLO) behaviour was studied by evaluating the values of dipole moment, polarizability and hyperpolarizability. Molecular electrostatic potential (MESP) surface was drawn to locate reactive sites of pentachlorophenol. Natural bond orbital (NBO) analysis of the molecule was made to examine stability of the molecule arising from charge delocalization. Thermodynamic parameters of the molecule were also calculated.

Keywords: Pentachlorophenol, DFT, Gauge independent atomic orbital, Chemical reactivity, FMO, NLO, NBO.

INTRODUCTION

Pentachlorophenol is a chlorinated aromatic compound, widely used as a biocide and could also be found in ropes, paints, adhesives, canvas, insulating materials and brick walls [1]. Pentachlorophenol is produced *via* two pathways, either by stepwise chlorination of phenols in the presence of catalysts (Lewis acid) or alkaline hydrolysis of hexachlorobenzene [1]. Toxicities of this biocide compound showed that pentachlorophenol is rapidly and efficiently absorbed from the gastrointestinal and respiratory tracts [2]. Once absorbed, pentachlorophenol exhibits a small volume of distribution. Metabolism occurs primarily in the liver, to a limited extent, *via* oxidative dechlorination and conjugation.

Pentachlorophenol can be metabolized by several aquatic and soil microorganisms, but environmental conditions are usually unfavourable for biodegradation [3-5]. Slow elimination in surface waters, high persistence in sediments, formation of stable metabolites and the limited adaptation of microorganisms to chlorophenols owing to their high microbial toxicity

imply that chlorophenols are practically non-biodegradable in the aquatic environment [6].

By adopting classical inverse vibrational problem approach, the investigations regarding vibrational spectra, normal coordinate analysis and transferability of force constants of some substituted phenols were already reported in our earlier work [7,8]. At present, we are engaged with addressing problems associated with structure, vibrational properties, electronic characteristics, frontier molecular orbital (FMO) utility, non-linear optical (NLO) behaviour, natural bond orbital (NBO) analysis and thermodynamic parameters using both experimental (X-ray, ¹H NMR, ¹³C NMR, FT-IR, FT-Raman, UV-vis) and theoretical (density functional theory *i.e.* DFT) tools [9,10], in addition to anticancer activity. Recently, the structural and vibrational properties for pentachlorophenol [11] and pentabromophenol [12] are reported. However, results of ¹H & ¹³C NMR, UV-Vis spectrum, FMO, NLO, NBO and thermodynamic analysis for pentachlorophenol are yet to be reported. In present work, the results of ¹H & ¹³C NMR, NLO properties, UV-visible spectrum (both experimental and simulated), frontier