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A comparative spectroscopic, electronic structure and chemical shift investigations of *o*-Chloronitrobenzene, *p*-Chloronitrobenzene and *m*-Chloronitrobenzene

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ABSTRACT

The structural characteristics and substituent effects of *o*-Chloronitrobenzene, *m*-Chloronitrobenzene and *p*-Chloronitrobenzene have been analysed by experimental FTIR, FT-Raman and FT-NMR spectroscopic studies. A detailed quantum chemical calculations have been performed using DFT/B3LYP method with 6-311++G**, 6-31G** and cc-pVTZ basis sets. Complete vibrational analyses of the compounds were performed. The temperature dependence of thermodynamic properties has been analysed. The atomic charges and charge delocalisation of the molecule have been performed by natural bond orbital (NBO) analysis. Molecular electrostatic surface potential (MESP), total electron density distribution and frontier molecular orbitals (FMOs) are constructed at B3LYP/6-311++G** level to understand the electronic properties. The charge density distribution and site of chemical reactivity of the molecules has been obtained by mapping electron density isosurface with electrostatic potential surfaces (ESPs). The electronic properties, HOMO and LUMO energies were measured by time-dependent TD-DFT approach. ^{1}H and ^{13}C NMR spectra were recorded and ^{1}H and ^{13}C nuclear magnetic resonance chemical shifts of the molecule were calculated. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts of the molecules in chloroform solvent were calculated by using the Gauge-Independent Atomic Orbital (GIAO) method and are found to be in good agreement with experimental values.

1. Introduction

Aromatic nitro compounds and their derivatives are used as solvents, analytical reagents, and are important intermediates in organic synthesis of perfumes, drugs, pesticides, and explosives [1–4]. Aromatic nitro compounds are convertible into primary amines, which are valuable intermediates in the synthesis of dyes, pharmaceuticals, photographic developers and antioxidants [5]. Haloaromatic compounds are well known building blocks in the synthesis of pharmaceuticals and agrochemicals. Traditionally, the chlorine aromatics are assuming greater importance as the cost-effectiveness of biologically-active chlorine containing products and the synthesis value of chlorine substituents becomes more widely acknowledged. *o*-Chloronitrobenzene (*o*-CNB), *m*-Chloronitrobenzene (*m*-CNB) and *p*-Chloronitrobenzene (*p*-CNB) are used as an intermediate for organic compounds; pharmaceuticals, pesticides and dyes.

o-Chloronitrobenzene is an important organic synthesis intermediates, can generate variety of intermediates. The dye industry for system – GC yellow, orange – GR; in regard additives used in the manufacture of rubber accelerator M and DM; the perfume industry for the synthesis of vanillin; pesticides used in the production of industrial Topsin and thiophanate-methyl carbendazim; it is also used as benzotriazole UV absorption agent raw materials. *o*-CNB is used in the synthesis of azo dye intermediates, e.g. *o*-chloroaniline (Fast Yellow G Base), *o*-nitroaniline (Fast Orange GR Base), *o*-anisidine (Fast Red BB Base), *o*-phenetidine and *o*-aminophenol. It also is used in corrosion inhibitors, pigments, and agricultural chemicals. *m*-Chloronitrobenzene is an organic compound raw material and is used as dye intermediate. It is mainly applicable for manufacturing *m*-Chloroaniline, also serves in pharmaceutical, pesticide, accessory ingredient, dichlorobenzene and spice industry.

p-CNB is an intermediate in the preparation of a variety of derivatives, including *p*-chloroaniline, *p*-nitrophenol, *p*-nitroanisole, *p*-nitroaniline, 2,4-dinitrochlorobenzene, and 3,4-dichloronitrobenzene [6]. The electron-withdrawing nature of the appended nitro-group makes the benzene ring especially susceptible to

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nucleophilic aromatic substitution, unlike related chlorobenzene. Another major use of *p*-CNB is its condensation with aniline to produce *p*-nitrodiphenylamine. Reductive alkylation of the nitro group affords secondary aryl amines, which are useful antioxidants for rubber [6]. *p*-CNB is used principally in the production of intermediates for azo and sulphur dyes. Other uses include pharmaceuticals, photo chemicals, rubber chemicals, and insecticides. Typical intermediates manufactured from *p*-CNB are *p*-phenylenediamine (Fast Red GC Base), *p*-anisidine, *p*-aminophenol, *p*-nitrophenol, *p*-phenylenediamine, 2-chloro-*p*-anisidine (Fast Red R Base), 2,4-dinitro-1-chlorobenzene, and 1,2-dichloro-4-nitrobenzene.

The resulting demand of chloroaromatics has led to search for commercially attractive and flexible compounds and to investigate the entire properties. The complete FT-IR and FT-Raman vibrational studies on the fundamental modes and the electronic property investigations by NMR and NBO analysis, FMO's and thermodynamic properties are inadequate in the literature. Thus, a detailed investigation have been attempted using DFT-B3LYP method with 6-311++G**, 6-31G** and cc-pVTZ basis sets to provide more satisfactory and valuable informations on electronic structure, molecular orbitals, potential energy distribution and NMR spectral characteristics of *o*-CNB, *m*-CNB and *p*-CNB. The optimised geometry, frontier molecular orbitals (FMOs) and their energy gaps, molecular electrostatic potential map (MESP), total density region and electrostatic potential contour (ESP) map have been constructed at B3LYP/6-311++G** level to understand the electronic properties, electrophilic and nucleophilic active centres of *o*-CNB, *m*-CNB and *p*-CNB.

2. Experimental section

The compounds *o*-Chloronitrobenzene (*o*-CNB), *m*-Chloronitrobenzene (*m*-CNB) and *p*-Chloronitrobenzene (*p*-CNB) were obtained from Aldrich Chemicals, USA and used as such to record FTIR, FT-Raman and FT-NMR spectra. The FTIR spectra of the compounds were recorded by KBr pellet method in the region 4000–400 cm^{-1} using Bruker IFS 66 V spectrometer with a Globar source, Ge/KBr beam splitter, and a MCT detector. The frequencies for all sharp bands are accurate to 2 cm^{-1}. The FT-Raman spectra were also recorded in the range 4000–100 cm^{-1} by the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source with 200 mW powers operating at 1064 nm. A liquid nitrogen cooled-Ge detector was used. The spectral resolution is 2 cm^{-1}. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) (400 MHz; $CDCl_3$) spectra were recorded on a Bruker HC400 instrument. The chemical shifts for protons are reported in parts per million scales (δ scale) downfield from tetramethylsilane.

3. Computational details

The stable molecular structures of *o*-CNB, *m*-CNB and *p*-CNB in the ground state is optimised and the structural parameters have been computed by Becke's three parameter hybrid functional (B3) [7,8] combined with gradient corrected correlation functional of Lee–Yang–Parr (LYP) [9] with high level triple zeta 6-311++G**, the standard split-valence polarised 6-31G** [10] and Dunning's cc-pVTZ basis sets on a Intel core-i5 processor using Gaussian 03W program [11,12]. The optimised structural parameters of *o*-CNB, *m*-CNB and *p*-CNB were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarisation ratios. The potential energy distribution of the vibrational modes of the compounds are also calculated through normal coordinate analysis [13–15] using the force constants obtained from the B3LYP/6-311++G** method utilising the program of Fuhrer et al. [16].

The Raman scattering activities (S_i) calculated by Gaussian 03 W program were suitably converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [17].

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

where v_0 is the exciting frequency (cm^{-1}), v_i is the vibrational wavenumber of the *i*th normal mode, *h*, *c* and *k* are universal constants, and *f* is the suitably chosen common scaling factor for all the peak intensities.

The thermodynamic parameters entropy, heat capacity at constant pressure and enthalpy change of *o*-CNB, *m*-CNB and *p*-CNB at different temperatures ranging from 100 to 1000 K were determined to study the dependence of these properties with temperature using B3LYP/6-311++G** method. Isoelectronic molecular electrostatic potential surfaces (MEPSs) and electron density surfaces [18] were calculated using 6-311++G** basis set. The molecular electrostatic potential (MEP) at a point '*r*' in the space around a molecule (in atomic units) can be expressed as:

$$V(r) = \sum_A \frac{Z_A}{\left|\vec{R}_A - \vec{r}\right|} - \int \frac{\rho(\vec{r}')dr'}{|\vec{r}' - \vec{r}|}$$

where Z_A is the charge on nucleus A, located at R_A and $\rho(r')$ is the electronic density function for the molecule. The first and second terms represent the contributions to the potential due to nuclei and electrons, respectively. $V(r)$ is the resultant at each point *r*, which is the net electrostatic effect produced at the point *r* by both the electrons and nuclei of the molecule. The molecular electrostatic potential (MEP) serves as a useful quantity to explain hydrogen bonding, reactivity and structure–activity relationship of molecules including biomolecules and drugs [19]. Structures resulting from the plot of electron density surface mapped with electrostatic potential surface depict the shape, size, charge density distribution and the site of chemical reactivity of a molecule. Gauss View 5.0.8 visualisation program [20] has been used to construct the MESP surface, the shape of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbitals. The energies of the HOMO and LUMO molecular orbitals [21] and HOMO–LUMO energy gap have also been measured by TD-B3LYP/6-311++G** method, while taking solvent effect into account [22–25].

The isotropic chemical shifts are frequently used as an aid in identification of organic compounds and accurate predictions of molecular geometries are essential for reliable studies of magnetic properties. The ^{1}H and ^{13}C NMR isotropic shielding were calculated with the GIAO method using the optimised parameters obtained from B3LYP/6-311++G** method. The effect of solvent $CHCl_3$ on the theoretical NMR parameters were included using the IEF–PCM model. The isotropic shielding values were used to calculate the isotropic chemical shifts (δ) with respect to tetramethylsilane. $\delta_{iso}(X) = \sigma_{TMS}(X) - \sigma_{iso}(X)$, where δ_{iso} – isotropic chemical shift and σ_{iso} – isotropic shielding.

4. Results and discussion

4.1. Structural properties

The most stable optimised molecular structure of *o*-CNB, *m*-CNB and *p*-CNB at B3LYP/6-311++G** method is shown in Fig. 1. The optimisation of the geometry of these molecules by B3LYP/6-311++G** method yield energies −896.48, −896.49 and −896.50 Hartrees, respectively for *o*-CNB, *m*-CNB and *p*-CNB. Thus, the structure of *p*-CNB is most stable than that of others. The more