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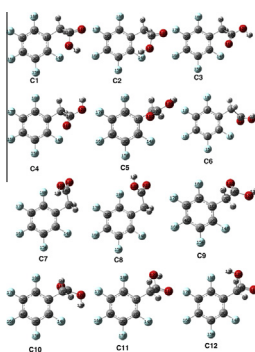
Molecular structure, vibrational spectroscopic, hyperpolarizability, natural bond orbital analysis, frontier molecular orbital analysis and thermodynamic properties of 2,3,4,5,6-pentafluorophenylacetic acid

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HIGHLIGHTS

- The FT-IR and FT-Raman spectra of 2,3,4,5,6-pentafluorophenylacetic acid were analyzed.
- The calculations were carried out for 2,3,4,5,6-pentafluorophenylacetic acid at DFT/LSDA and B3LYP levels.
- A comparison with the IR and Raman spectra of 2,3,4,5,6-pentafluorophenylacetic acid have been constructed.

GRAPHICAL ABSTRACT



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ABSTRACT

The FT-IR (4000–400 cm^{-1}) and FT-Raman spectra (3500–100 cm^{-1}) of 2,3,4,5,6-pentafluorophenylacetic acid (PAA) have been recorded. Density functional theory calculation with LSDA/6-31+G(d,p) and B3LYP/6-31+G(d,p) basis sets have been used to determine ground state molecular geometries (bond lengths and bond angles), harmonic vibrational frequencies, infrared intensities, Raman intensities and bonding features of the title compound. The assignments of the vibrational spectra have been carried out with the help of normal coordinate 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 PAA are calculated using B3LYP/6-31+G(d,p) method on the finite-field approach. The calculated first hyperpolarizability shows that the molecule is an attractive molecule for future applications in non-linear optics. The stability of molecule has been analyzed by using NBO analysis. The calculated HOMO and LUMO energies show that charge transfer occurs within this molecule. Mulliken population analysis on atomic charges is also calculated. Thermodynamic properties (heat capacity, enthalpy, Gibb's free energy and entropy) of the title compound at different temperatures were calculated.

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Introduction

Phenylacetic acid is a white crystal with a disagreeable odor, boiling point 262 °C, soluble in alcohol and ether. It serves as an

ingredient in perfume to provide honey-like odor. It is found as a moiety in some alkaloids and plant hormones. It is formed as catabolite of phenylalanine. In toluic acid name system, phenylacetic acid is alpha-toluic acid which one of the hydrogen atoms in the methyl group has been substituted instead of the substitution in the benzene ring. Substituted phenylacetic acid molecule at alpha position and phenylacetate esters can serve as a drug with a wide

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variety of effects including anticholinergic, muscarinic antagonist, antidote to cholinesterase inhibitors or toxins, cycloplegic and mydriatic. Phenylacetic acid is used to prepare a nonsteroidal anti-inflammatory drug like diclofenac. It is used in the manufacturing of penicillin. Mandelic acid, phenylglycolic acid, can be produced from phenylchloroacetic acid. Phenoxyacetic acid is one of the well-known aryloxyacetic acid, which is useful in the treatment of insulin resistance, and hyperglycemia, which has been investigated by various researchers [1–3]. Phenoxyacetic acid and substituted phenoxyacetic acids have potential biological properties. These acids are widely used in herbicide [4] and pesticide [5] formulations. Antimicro-bioactivity [6], anticancer, antitumour, analgesic, anti-inflammatory, plant growth regulation, inhibition of tillage are some of their reported properties.

Detailed literature survey showed that a considerable amount of work has been done on the vibrational analysis of phenols [7]. However, for phenoxyacetic acid such a kind of work are limited. Only IR spectral assignments and normal coordinate analysis have been carried out for some phenoxyacetic acids [8]. The molecular and crystal structure of 4-chlorophenoxy acetic acid was reported by Vijakumar and Rao [9]. Karthikeyan and Saravanan [10] reported tentative Raman spectral assignments of phenoxyacetic acid and chlorine substituted phenoxyacetic acid with the aid of *ab initio* theoretical calculations using HF/3-21G⁺ basis set, however some of its assignment was ambiguous and also they reported vibrational analysis without performing the calculation of potential energy distribution (TED). Recently vibrational spectral studies related to this molecule were reported [11]. Vibrational spectroscopy is an efficient tool for the characterization of bioactive materials. It is effectively used to identify functional groups and determine the molecular structure of the crystals. During the past decade, the density functional theory (DFT) [12] has been accepted by the *ab initio* quantum chemistry community as a popular approach for the computation of molecular structure, vibrational frequencies and energies of chemical reactions, which provide a potential cost-effective approach for calculating vibrational spectra of large molecules. In the recent theoretical studies, the harmonic vibrational frequencies for a larger number of small and well-studied organic molecules were computed with HF, MP2 and DFT methods [13–16].

The inter- and intramolecular hydrogen bonding interactions (O–H...O and C–H...O) have practical and theoretical significance in determining the structure and activity of biological molecules [17]. To the best of our knowledge, no DFT calculations of 2,3,4,5,6-pentafluorophenylacetic acid have been reported so far. Therefore, the present work focuses on the study of the effect of fluorine substitution in the benzene ring of the phenylacetic acid and its influence on the intramolecular charge transfer (ICT), p-conjugation, electron delocalization, hydrogen bonding and spectral investigation using FT-Raman and IR spectra, along with the density functional theory (DFT) calculations.

Experimental details

2,3,4,5,6-Pentafluorophenylacetic acid (PAA) was procured by M/s Aldrich Chemicals, USA, which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The room temperature Fourier transform infrared spectrum of PAA was measured in the region 4000–400 cm⁻¹ at a resolution of ±1 cm⁻¹ using a BRUKER IFS-66V FT-IR spectrometer equipped with a cooled MCT detector for the mid-IR range. KBr pellets were used in the spectral measurements. The FT-Raman spectra of PAA were recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory in the region 3500–100 cm⁻¹ using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mW power. The reported frequencies are expected to be accurate within ±1 cm⁻¹.

Computational methods

The molecular structure of PAA and corresponding vibrational harmonic frequencies were calculated using DFT/LSDA and Becke3–Lee–Yang–Parr (B3LYP) combined with 6-31+G(d,p) basis set using GAUSSIAN 09 program package [18] without any constraint on the geometry. The harmonic vibrational frequencies have been analytically calculated by taking the second-order derivative of energy using the same level of theory. Transformation of force field from Cartesian to symmetry coordinate, scaling, subsequent normal coordinate analysis, calculations of TED, IR and Raman intensities were made on a PC with the version V7.0-G77 of the MOLVIB program written by Sundius [19,20]. To achieve a close agreement between observed and calculated frequencies, the least-square fit refinement algorithm was used. By combining the results of the GAUSSVIEW [21] program with symmetry considerations, along with the available related molecules, vibrational frequency assignments were made with a high degree of accuracy.

Prediction of Raman intensities

The Raman intensities (I_i) were calculated from the Raman activities (S_i) obtained with the Gaussian 09 program, using the following relationship derived from the intensity theory of Raman scattering [22–24].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i)] / kT}$$

where ν_0 is the exciting frequency (in cm⁻¹ units), ν_i is the vibrational frequency if the i th normal mode, h , c and k are the universal constants and f is the suitably chosen common scaling factor for all the peak intensities. The simulated IR and Raman spectra have been plotted using Lorentzian band shapes with FWHM bandwidth of 10 cm⁻¹.

Results and discussion

Molecular geometry

In order to find the most optimized geometry, the energy calculations were carried out for PAA, using LSDA/6-31+G(d,p) and B3LYP/6-31+G(d,p) methods for various possible conformers. The computationally predicted various possible conformers obtained for the title compound are shown in Fig. 1. The total energies obtained for these conformers are listed in Table 1. The structure optimizations have shown that the conformer of Fig. 1 (C9) have produced the global minimum energy. The optimized molecular structure with the numbering of atoms of the title compound is shown in Fig. 2. The most optimized geometrical parameters were also calculated by DFT (LSDA/B3LYP) level with the 6-31+G(d,p) basis set are listed in Table 2.

From the structural point of view of the molecule belongs to C₁ point group symmetry. The 18 atoms with 48 fundamental modes of vibrations are same symmetry species. The optimized geometrical parameter of the title compound was compared with other similar system *p*-chlorophenoxy acetic acid for which the crystal structure has been solved [9]. From theoretical values, we can find that most of the optimized bond lengths and bond angles are slightly longer and shorter than experimental values, due to the theoretical calculations belong to isolated molecule in gaseous phase and the experimental results belong to molecule in solid state. Comparing bond angles and bond lengths of PAA at B3LYP/6-31+G(d,p) level of theory leads to geometrical parameters, which are much closer to experimental values.

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