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DFT analysis of P-nitrobenzotrifluoride – A combined study of experimental (FT-IR and FT-Raman) and theoretical calculations

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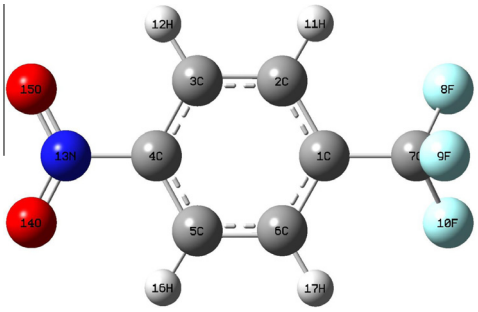
HIGHLIGHTS

- To obtain the molecular motions of PNBTF, NCA has been done.
- For PNBTF, electrophilic reactivity region is around O atom.
- The nucleophilic reactivity region is around H atom.
- The $\mu \times \beta$ value shows the optical non-linearity of PNBTF.
- The bioactivity of PNBTF is analyzed by HOMO–LUMO energy gap.

GRAPHICAL ABSTRACT



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ABSTRACT

In this, a combined experimental and theoretical study on molecular structure and vibrational analysis of P-nitrobenzotrifluoride (PNBTF) is reported. The Fourier transform infrared and FT-Raman was recorded in the solid phase. The molecular geometry and vibrational frequencies of PNBTF in the ground state have been calculated by using density functional method (B3LYP) with 6-311++G(d,p) as basis set. Comparison of the observed fundamental vibrational frequencies with calculated results by density functional methods indicates that B3LYP/6-311++G(d,p) is superior to other methods for molecular vibrational problems. The bioactivity of the compound is analyzed by the HOMO–LUMO analysis. The reactivity sites are identified by mapping of electron density into electrostatic potential surface (MEP). Besides, ^{13}C and ^{1}H nuclear magnetic resonance (NMR) chemical shifts are calculated by using the gauge-invariant atomic orbital (GIAO) method. Furthermore, the compound can be used as a good nonlinear optical material due to the higher value of first hyperpolarizability. Solventation effect of NMR spectra by CPCM model of P-nitrobenzotrifluoride has been analyzed.

Introduction

P-nitrobenzotrifluoride (PNBTF) (4-nitro-alpha, alpha, alpha-trifluorotoluene; 1-nitro-4-trifluoromethyl-benzene; 1-nitro-4-(trifluoromethyl)benzene; benzene, 1-nitro-4-(trifluoromethyl)) is a thin, oily straw colored liquid with a fish like odor used to make other chemicals. It is a stable, incompatible with strong bases, strong oxidizing and strong reducing agents.

The aromatic nitro compounds may explode in the presence of a base such as sodium hydroxide or potassium hydroxide even in the presence of water or organic solvents. The explosive tendencies of aromatic nitro compounds are increased by the presence of multiple nitro groups. This perspective explores the origins of both fluorine and medicinal chemistry a century ago and traces the early history of the intersection of these areas and the subsequent roles that fluorine has played in advancing medicinal innovations and diagnoses during the past 60 years. The overview highlights remarkable breakthroughs in many diverse areas of medicinal chemistry, including inter alia, anesthetics, steroidal, nonsteroidal

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anti-inflammatory drugs, anticancer, antiviral agents, CNS medications, antibacterial and cholesterol biosynthesis inhibitors. The increasing use of fluorine-18-labeled radiotracers in PET is for diagnostic imaging of the brain, heart in oncology. The signature roles of fluorine in medicinal chemistry are now firmly established. The presence of fluorine in pharmaceuticals has a major impact on the plethora of important medical applications. Fluorine will very likely continue to contribute significantly by playing multifaceted roles in enhancing future medical advances.

Toluene, formerly known as toluol, is a clear, water-insoluble liquid with the typical smell of paint thinners. It is a monosubstituted benzene derivative, i.e., one in which a single hydrogen atom from a group of six atoms from the benzene molecule has been replaced by a univalent group, in this case CH_3. It is an aromatic hydrocarbon that is widely used as an industrial feedstock as a solvent. Like other solvents, toluene is sometimes also used as an inhalant drug for its intoxicating properties; however, inhaling toluene has potential to cause severe neurological harm [1,2]. Toluene is an important organic solvent, but is also capable of dissolving a number of notable inorganic chemicals such as sulfur [3], iodine, bromine, phosphorus and other non-polar covalent substances.

Toluene is a common solvent, able to dissolve paints, paint thinners, silicone sealants [4], many chemical reactants, rubber, printing ink, adhesives (glues), lacquers, leather tanners and disinfectants. It can also be used as a fullerene indicator, and is a raw material for toluene diisocyanate (used in the manufacture of polyurethane foam) and TNT. In addition, it is used as a solvent to create a solution of carbon nanotubes. It is also used as a cement for fine polystyrene kits (by dissolving and then fusing surfaces) as it can be applied very precisely by brush and contains none of the bulk of an adhesive. Industrial uses of toluene include dealkylation to benzene and the disproportionation to a mixture of benzene and xylene. When oxidized it yields benzaldehyde and benzoic acid, two important intermediates in chemistry. It is also used as a carbon source for making Multi-Wall Carbon Nanotubes. Toluene can be used to break open red blood cells in order to extract hemoglobin in biochemistry experiments.

Toluene can be used as an octane booster in gasoline fuels used in internal combustion engines. Toluene at 86% by volume fueled all the turbo Formula 1 teams in the 1980s, first pioneered by the Honda team. The remaining 14% was a "filler" of *n*-heptane, to reduce the octane to meet Formula 1 fuel restrictions. Toluene at 100% can be used as a fuel for both two-stroke and four-stroke engines; however, due to the density of the fuel and other factors, the fuel does not vaporize easily unless preheated to 70 °C (Honda accomplished this in their Formula 1 cars by routing the fuel lines through the muffler system to heat the fuel). Toluene also poses similar problems as alcohol fuels, as it eats through standard rubber fuel lines and has no lubricating properties, as standard gasoline does, which can break down fuel pumps and cause upper cylinder bore wear.

In Australia, toluene has been found to have been illegally combined with petrol in fuel outlets for sale as standard vehicular fuel. Toluene attracts no fuel excise, while other fuels are taxed at over 40%, so fuel suppliers are able to profit from substituting the cheaper toluene for petrol. This substitution is likely to affect engine performance and result in additional wear and tear. The extent of toluene substitution has not been determined [5,6]. Toluene is another in a group of fuels that have recently been used as components for jet fuel surrogate blends [7]. Toluene is used as a jet fuel surrogate for its content of aromatic compounds. Toluene has also been used as a coolant for its good heat transfer capabilities in sodium cold traps used in nuclear reactor system loops. Toluene had also been used in the process of removing the cocaine from coca leaves in the production of Coca-Cola syrup [8].

Spectroscopic investigations on isomeric toluidines, nitro toluenes were reported by earlier researchers [9,10]. The structural stability of toluene molecules has also been investigated in the past years by several researchers [11–13]. But, the analysis of vibrational spectra using DFT method is very few. The analysis of vibrational spectra of α-chlorotoluene based on HF and DFT theory calculations has been carried out by Nagabalasubramanian et al. [13], Ramalingam et al. [14] and Herna'ndez-Rivera and Castillo-Chara [15] have studied the HF and DFT theory calculations of 4-nitrotoluene and 2,4,6-trinitrotoluene (TNT). Vibrational spectroscopic analysis of 2-chlorotoluene and 2-bromotoluene has been studied by Govindarajan et al. [16].

A literature survey suggests that PNBTF molecule is not examined before. As a continuation of the recent studies on structural and theoretical investigations of some substituted toluene derivatives, the main aspects of this investigation are: (i) Structural investigation of PNBTF by FT-IR and FT-Raman spectra, (ii) The molecular geometries and vibrational spectra of PNBTF compound are calculated by applying density functional theory (DFT) computations, (iii) The solvent effect on ^{13}C and ^{1}H NMR data is introduced by applying the conductor-like polarizable continuum model (CPCM), (iv) HOMO–LUMO analysis has been used to give more information regarding charge transfer within the molecule. One key approach to understand solvent effects is the solvent-induced changes in the electronic transition of solutes generally referred to as solvatochromism. This paper aims at reporting the effect of various solvents on the NMR spectra of PNBTF molecule.

Experimental part

Measurement of the vibrational spectra

PNBTF molecule was obtained from Lancaster chemical company, UK and used as such for the spectral measurements without further purification.

Infrared spectra

The infrared spectrum was recorded with a BRUKER IFS 66V model FT-IR spectrometer equipped with a room temperature MCT detector. The spectrum of the PNBTF molecule was recorded by using KBr pellets in the 4000–400 cm^{-1} spectral region.

Raman spectra

The Raman spectrum (3500–50 cm^{-1}) was measured with a BRUKER IFS 66V model interferometer equipped with FRA-106 FT-Raman spectrometer. 1064 nm of an Nd:YAG laser was used for excitation at 200 mW output power. The reported wavenumbers are expected to be accurate within ±1 cm^{-1}.

Computational methodology

The gas phase geometry of PNBTF in the ground state is optimized by DFT 6-311++G(d,p) methods using GAUSSIAN 09W [17,18] program. For this optimized geometry, vibrational frequencies are calculated analytically at the same level of theory to ensure it to be a true local minimum.

In NMR calculations, the optimized molecular geometry of PNBTF molecule is obtained at B3LYP/6-311++G(d,p) basis level in Acetone, DMSO and in CCl_4 solvents by using conductor-like polarizable continuum model (CPCM) method. Then, ^{1}H and ^{13}C NMR chemical shifts for PNBTF are calculated at B3LYP/6-311++G(d,p) levels in solvent by using gauge invariant atomic orbital (GIAO) method.

Additionally, HOMO and LUMO energy values and energy gap for PNBTF are calculated by using B3LYP method with 6-311++