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Vibrational spectra, UV–vis spectral analysis and HOMO–LUMO studies of 2,4-dichloro-5-nitropyrimidine and 4-methyl-2-(methylthio)pyrimidine

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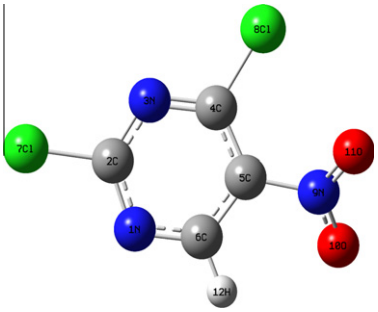
HIGHLIGHTS

- A complete vibrational analysis of DCNP and MTP are performed.
- DCNP has the smallest HOMO–LUMO gap.
- DCNP is thermodynamically stable, MTP is more reactive.
- The predicted β value reveals that both molecules are an attractive object for future studies of NLO properties.
- We have found that the conformer 2 (b) is more stable for MTP.

GRAPHICAL ABSTRACT

The FTIR and FT Raman vibrational spectra of 2,4-dichloro-5-nitropyrimidine (DCNP) and 4-methyl-2-(methylthio)pyrimidine (MTP) have been recorded using BRUKER RFS 100 s^{-1} spectrometer in the range 4000–400 and 3600–50 cm^{-1}, respectively. A detailed vibrational spectral analysis has been carried out, and assignments of the observed fundamental bands have been proposed on the basis of peak positions and relative intensities. The optimized molecular geometry and vibrational frequencies in the ground state are calculated using density functional B3LYP method with 6-31+G(d,p) and 6-311++G(d,p) basis set combinations. With the help of specific scaling procedures, the observed vibrational wave numbers in FTIR and FT Raman spectra are analyzed and assigned to different normal modes of the molecule. UV–vis spectral analysis of the title compounds has been researched by theoretical calculations. The frontier orbital energies, absorption wavelengths (λ), oscillator strengths (f) and excitation energies (E) studied using TD-DFT (B3LYP) with 6-311++G(d,p) basis set are calculated in this work.



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ABSTRACT

The FT-IR and FT-Raman vibrational spectra of 2,4-dichloro-5-nitropyrimidine (DCNP) and 4-methyl-2-(methylthio)pyrimidine (MTP) have been recorded in the range 4000–400 and 3600–50 cm^{-1}, respectively. A detailed vibrational spectral analysis has been carried out and assignments of the observed fundamental bands have been proposed on the basis of peak positions and relative intensities. The optimized molecular geometry and vibrational frequencies in the ground state are calculated using density functional B3LYP method with 6-31+G(d,p) and 6-311++G(d,p) basis set combinations. With the help of specific scaling procedures, the observed vibrational wavenumbers in FT-IR and FT-Raman spectra are analyzed and assigned to different normal modes of the molecules. The predicted first hyperpolarizability reveals that the molecules are an attractive object for future studies of non-linear optical properties. And also HOMO–LUMO energy gap explains the eventual charge transfer interaction taking place within the molecules. UV–vis spectral analysis of the title compounds has been researched by theoretical calculations. The frontier orbital energies, absorption wavelengths (λ), oscillator strengths (f) and excitation energies (E) studied using TD-DFT (B3LYP) with 6-311++G(d,p) basis set are calculated in this work.

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Introduction

Pyrimidines occupy a distinct and unique place in our life. This heterocyclic moiety has great biological and medicinal significance. Pyrimidine is a heterocyclic aromatic organic compound similar to benzene and pyridine, containing two nitrogen atoms at position 1 and 3 of the six-member ring. It is isomeric with two other forms of diazine. Purines and pyrimidines are two of the building blocks of nucleic acids. Only two purines (adenine, guanine) and three pyrimidines (cytosine, thymine and uracil) occur widely in nucleic acids [1]. Pyrimidine containing 4 carbon and 2 nitrogen atoms and is pharmacologically inactive but its synthetic derivatives possess an important role in modern medicine. In medicinal chemistry pyrimidine derivatives have been very well known for their therapeutic applications. Pyrimidine also shows antifungal properties. Flucytosine is a fluorinated pyrimidine used as nucleosidal anti-fungal agent for the treatment of serious systemic infections caused by susceptible strains of candida and cryptococcus. The pyrimidine moiety with some substitution shows promising antitumor activity as there are large numbers of pyrimidine based antimetabolites. The structural modification may be on the pyrimidine ring or on the pendant sugar groups [2]. Pyrimidines have a long and distinguished history extending from the days of their discovery as important constituents of nucleic acids to their current use in the chemotherapy of AIDS. Sulfonamide–trimethoprim combinations are used extensively for opportunistic infections in patients with AIDS.

A large array of pyrimidine drugs possesses a variety of medicinal properties. These properties include anticancer, antibacterial, antiprotozoal, antimicrobial, antiviral, antihypertensive, antihistaminic, anti-inflammatory, analgesic and CNS-active to metabolic adjuvants [3]. Numerous works had been reported related to the assignment of the vibrational spectrum of pyrimidine and its derivatives [4–8].

After going through the literature, to the best of our knowledge, neither quantum chemical calculation, nor the vibrational spectra of 2,4-dichloro-5-nitropyrimidine and 4-methyl-2-(methylthio)pyrimidine (here after they are referred as DCNP and MTP, respectively) have been reported. Therefore, the present investigation was undertaken to study the vibrational spectra of the title compounds completely and to identify the various modes with greater wavenumber accuracy. Density functional theory (DFT) calculations have been performed to support our wavenumber assignments.

Methods

DFT calculation

The molecular geometry optimizations, energy and vibrational frequency calculations are carried out for DCNP and MTP with the GAUSSIAN 09W software package using the B3LYP hybrid density functional method [9,10] combined with the 6-31+G(d,p) and 6-311++G(d,p) basis set combinations. The B3LYP scheme, considered as the most appropriated method for structure calculations. The 6-311++G(d,p) basis replaces the 1s through 2p electrons of the heavy atoms with a potential field for a considerable computational savings. A double-δ quality dunning basis was used for the light atoms and the remaining heavy atom electrons. The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming C_1 point group symmetry. The symmetry of the molecules was also helpful in making vibrational assignments. By combining the results of the GAUSSVIEW program [11] with symmetry considerations, vibrational frequency assignments are made with a high degree of confidence.

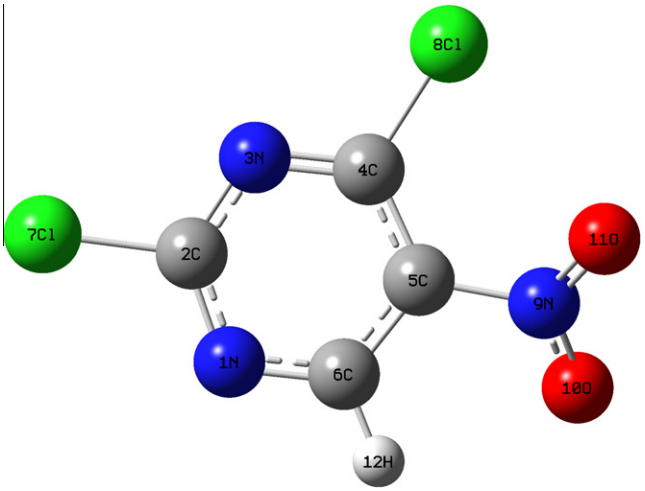

Fig. 1a. The optimized structure of 2,4-dichloro-5-nitropyrimidine.

The atoms in Figs. 1a and 1b are labeled to define the internal coordinates employed in the calculation of vibrational spectra of DCNP and MTP, respectively. There is always some ambiguity in defining internal coordinates. However, the defined coordinate form complete set and matches quite well with the motions observed using the GAUSSVIEW program. The systematic comparison of the results from DFT theory with results of experiments have shown that the method using B3LYP functional is the most promising in providing correct vibrational wavenumbers. The symmetry analysis for the vibrational modes of DCNP and MTP are presented in order to describe the basis for the assignments. Transformation of the force field and the subsequent normal coordinate analysis (NCA) including the least squares refinement of the scaling factors, calculation of total energy distribution (TED) are done on a PC with the MOLVIB program (version 7.0-G77) written by Tom Sundius [12–14]. UV–vis spectra, the excitation energy, absorbance and oscillator strengths are studied using TD-DFT (B3LYP) with 6-311++G(d,p) basis set in this work.

Spectroscopic measurements

The compounds under investigation DCNP and MTP are purchased from Lancaster Chemical Company, UK, and used as such without further purification to record FT-IR and FT-Raman spectra.

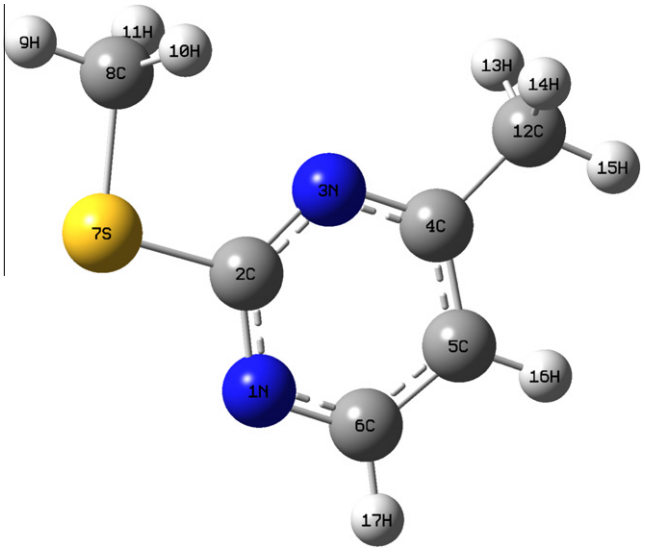

Fig. 1b. The optimized structure of 4-methyl-2-(methylthio)pyrimidine.