



# FT-IR, FT-Raman spectra, density functional computations of the vibrational spectra, molecular geometry, conformational stability and some molecular properties of 1-Bromo-2,3-dimethoxynaphthalene



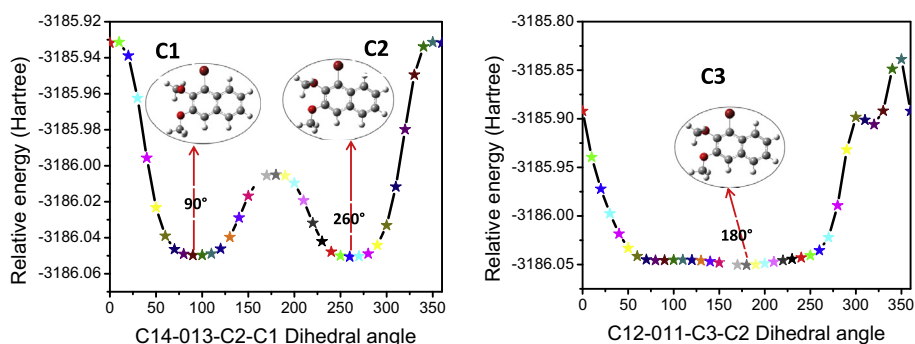
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## HIGHLIGHTS

- Conformational stability of the 1-Bromo-2,3-dimethoxynaphthalene have been calculated.
- Geometric structure and Vibrational assignments of 1-Bromo-2,3-dimethoxynaphthalene were analyzed.
- UV–Visible spectrum was recorded and analyzed.
- The planarity of the molecule with respect to methoxy group is discussed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work of theoretical structural analysis, a comprehensive screening of the recent DFT theoretical approach to structural analysis is presented for the molecule 1-Bromo-2,3-dimethoxynaphthalene which has abbreviated as 1B23DMN. The molecular structure, harmonic vibrational frequencies, molecular properties, molecular electrostatic potential (MEP) mapping, natural bond orbital (NBO) analysis and electronic spectra of 1B23DMN have been reported along with a combination of experimental spectroscopic measurements. DFT calculations using B3LYP method and 6-31G(d,p) as basis set were found to yield results that are very comparable to experimental IR and Raman spectra. Computed geometrical parameters and frequencies of the fundamentals were found in satisfactory agreement with the experimental data. The UV–Visible spectrum of molecule has been recorded and the electronic properties such as HOMO & LUMO energies and a few low lying excited states were carried out using time dependent density functional theory (TD-DFT) approach. NBO analysis has been performed for analyzing charge delocalization throughout the molecule. MEP map has also been used for quantitative measurement of the chemical activities of various sites of the molecule.

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## Introduction

Naphthalene is an organic and simplest polycyclic aromatic hydrocarbon. It can be viewed as the fusion of a pair of benzene

rings. Naphthalene substituted with a combination of strongly electron-donating functional groups, such as alcohols and amines, and strongly electron-withdrawing groups, especially sulfonic acids, are intermediates in the preparation of many synthetic dyes. Naphthalene is used as a moth repellent, though this use is decreasing in favor of p-dichlorobenzene. It has also been used in the manufacture of phthalic anhydride, phthalic and anthranilic

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acids, naphthols, naphthylamines, 1-naphthyl-N-methylcarbamate insecticide, naphthalene sulfonates, synthetic resins, celluloid, lampblack, smokeless powder, anthraquinone, indigo, perylene, and hydronaphthalenes [1]. Because of their spectroscopic properties and chemical significance, naphthalene and its derivatives were studied extensively by spectroscopic and theoretical methods.

The present investigation has been undertaken to provide satisfactory vibrational analysis of a yellow colored solid sample 1B23DMN through FT-IR and FT-Raman spectra. The molecule 1B23DMN is a compound having one halogen (Br) in  $\alpha$  position and two methoxy groups in  $\beta$  position substituted to naphthalene ring system. There are positional isomers differing by the location of the methoxy group. The different positions provide various chemical structures which offer important roles to each characteristic. From the spectroscopic point of view, in recent years numerous experimental and theoretical studies have been made on the vibrational spectra of naphthalene and its mono- and disubstituted derivatives [2–12]. Most recently, Govindarajan et al. [13,14] investigated the FT-IR and FT-Raman spectra of 1-methoxynaphthalene and the FT-IR, FT-Raman and UV spectral investigation, performed frequency analysis and electronic structure calculations on 1-nitronaphthalene respectively. Spectroscopic (FT-IR and FT Raman) analysis and vibrational study on 2,3-dimethyl naphthalene were made by Prabhu et al. [15]. However, a spectroscopic analysis on 1B23DMN has not been completely and rigorously carried out yet. Therefore, the present work aims to provide a complete description on the molecular geometry, molecular vibrations and electronic features of 1B23DMN.

## Experimental

1-Bromo-2,3-dimethoxynaphthalene sample was purchased from Sigma–Aldrich Chemical Company with a stated purity of 99% and it was used as such without further purification. The sample was prepared to carryout IR spectral analysis using a KBr disk technique because of solid phase. The FT-IR spectra were recorded employing Perkin Elmer FT-IR spectrometer in the middle infrared region, 4000–400  $\text{cm}^{-1}$  on calibration using polystyrene bands. FT-Raman spectrum of the sample was also recorded using 1064 nm line of Nd:YAG laser as excitation source with wave length in the region 3500–50  $\text{cm}^{-1}$  on a Bruker RFS 100/S FT-Raman spectrometer. The detector was a liquified nitrogen cooled Ge detector. Five hundred scans were accumulated at 4  $\text{cm}^{-1}$  resolution using a laser power of 100 mW. UV–Visible (ultraviolet and visible light) absorbance spectra were recorded over a range of 800–200 nm with a Shimadzu UV-1650 PC spectrophotometer, operated at a resolution of 0.5 nm. The samples were filled in a quartz cuvette of 1 cm light path-length, and the light absorption spectra were given in reference to methanol and ethanol. Data were analyzed by UV PC personal spectroscopy software, version 3.91.

## Computational details

The optimized geometry of 1B23DMN and vibrational frequencies were calculated at the B3LYP/6-31G(d,p) level with the Gaussian 03 program [16]. The basis set 6-31G(d,p) augmented by 'd' polarization functions on heavy atoms and 'p' polarization functions on hydrogen atoms were used for better description of polar bonds of molecules [17,18]. It should be emphasized that 'p' polarization functions on hydrogen atoms are useful not only for reproducing the out-of-plane vibrations involving hydrogen atoms but also for a better description of the molecular geometry and other normal vibrational modes. Another common addition to basis sets is the addition of diffuse functions which are known

to be critical in describing the electron distribution of anions, but they are also quite important in describing weak interactions, like hydrogen bonds, and can be critical in evaluating activation barriers and other properties. These additional basis functions can be important when considering anions and other large, "soft" molecular systems. The vibrational assignments of the normal modes were also made on the basis of the PED calculated using the VEDA 4 program [19]. The graphical presentation of the calculated Raman and IR spectra were made using Gauss View program [20]. The absence of imaginary frequency modes for the optimized structure of 1B23DMN at DFT level confirms a true minimum on the potential energy surface. As the hybrid B3LYP functional tends to overestimate the fundamental normal modes of vibration, the computed frequencies in the harmonic approximation were scaled to closer reproducible experimental values [21]. In our present study, the scale factor of 0.9608 [22,23] was used for B3LYP/6-31G(d,p) method. The TD-DFT calculations were also performed by considering the molecule as dissolved in two different solvents, namely methanol and ethanol. To simulate the solvent effect, the IEFPCM (Polarization Continuum Model) is used [24,25]. To investigate the reactive sites of the title compound, the MEP were evaluated using B3LYP/6-31G(d,p) method. In this work, the first task of the computational study was to determine the optimized geometry of the 1B23DMN molecule. The optimum geometry was determined by minimizing the energy, with respect to all geometrical parameters without imposing molecular symmetry constraints. The second task was to perform the frequency analysis which was completed again with DFT method. Thereafter, vibrational frequencies, infrared intensities and Raman scattering activities of 1B23DMN have been calculated at the B3LYP/6-31G(d,p) level of theory. It is [26] demonstrated that the B3LYP method gives excellent results in predicting vibrational spectra of aromatic molecules. The theoretical Raman intensity (IR), which simulates the measured Raman spectrum can be calculated using RAIN program [27].

## Results and discussion

### Conformational stability

One of the problems in theoretical calculations of large molecules such as biopolymers is that it is not possible with certainty to find the global energy minimum with a general method. This is especially annoying for systems with more than a few hundred conformers, where all minima may not realistically be screened separately. In order to find the most optimized geometry, the energy calculations were accomplished for 1B23DMN with respect to naphthalene and methoxy groups, using B3LYP method with 6-31G(d,p) as basis set for various possible conformers along with this inconsistency. The minima on the potential surface were found by completely relaxing the geometry. The computationally predicted several possible conformers obtained for the compound are shown in Fig. 1(a) and (b). From the total energies obtained for these conformers it is clear from the DFT structure optimizations that the conformer Fig. 1(b) of 1B23DMN has produced the global minimum energy. Fig. 2 depicts the potential energy curve for the torsion around the central O–C bond of the 1B23DMN obtained from B3LYP/6-31G(d,p) calculations, in which the geometry was relaxed for each value of the C14–O13–C2–C1 (left in the Fig. 2) and C12–O11–C3–C2 (right in the Fig. 2) torsional angles. During the calculation all the geometrical parameters were simultaneously relaxed while the C14–O13–C2–C1 and C12–O11–C3–C2 torsional angles were varied in steps of 10° up to 360°. For the C14–O13–C2–C1 rotation, the minimum energy were obtained at 90° and 260° in the potential energy curve of energy –3186.04969 and –3186.05053 Hartrees respectively whereas

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