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Spectroscopic investigation and natural bond orbital analysis on 4-ethylmorpholine

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HIGHLIGHTS

- The FT-IR and FT-Raman spectra of 4-ethylmorpholine have been recorded.
- The complete assignments are performed on the basis of the potential energy distribution (PED).
- HOMO–LUMO energies, molecular electrostatic potential distribution of the molecule were calculated.
- Stability of the chair conformation has been analyzed using NBO analysis.

ARTICLE INFO

ABSTRACT

This study is an analysis of FT-IR (4000–400 cm^{-1}) and FT-Raman (4000–0 cm^{-1}) spectra of 4-ethylmorpholine (4EM). The molecular geometry, vibrational frequencies, infrared intensities, Raman activities and atomic charges have been calculated by using *ab initio* HF and density functional theory calculation (B3LYP) with 6-311+G(d,p) basis set. Complete vibrational assignment and analysis of the fundamental modes of the compound were carried out using the observed FT-IR and FT-Raman spectra for 4EM. NBO analysis has been performed on the before and after flipping the chair conformation of 4EM at DFT method. The formation of the hydrogen bond was investigated using NBO calculations. The dipole moment (μ) and polarizability (α), anisotropy polarizability ($\Delta\alpha$) and hyperpolarizability (β) of the molecule have been reported. The theoretical UV–Visible spectrum of the compound was computed in the region 200–400 nm and the electronic properties HOMO and LUMO energies were measured by time-dependent TD-DFT approach. Thermodynamic properties (heat capacity, entropy and enthalpy) of the title compound at different temperatures were calculated.

1. Introduction

Morpholine derivatives are used as analgesics and local anaesthetics [1–4], antibiotics [5,6], antimycotics [7,8] and for plaque control in dentistry [9,10]. Several morpholine derivatives, e.g., morpholinium salts of certain acylated sulfonamides, possess bactericidal activity. Morpholine hydroperiodide has been used as a water disinfectant [1]. Morpholine fungicides are used for agricultural purposes [11], as foliar fungicides with protective and curative properties for the control of powdery mildew and rust [12,13], and as foliar fungicides for cereals [14]. Morpholine is also used in the preparation of herbicides that can be applied either to the soil before the weeds emerge or to the growing plants [1].

4-Ethylmorpholine is used as a catalyst in the manufacture of urethane foam, as an intermediate for dyestuffs, pharmaceuticals, rubber accelerators and emulsifying agents, as well as a pH regulator [15]. Besides, it can be used in purification of Penicillin G or as a substitute for enzyme reactions. It is applied in polymer technology as a promoter for resin surface curing. It is used in polymer technology as a stabilizer for fiber spinning solutions. It can be applied in organic synthesis as a special solvent for fats and fatty oils.

Literature survey reveals that to the best of our knowledge, the results based on quantum chemical calculations, FT-IR and FT-Raman spectral studies, HOMO–LUMO and NBO analysis on 4-ethylmorpholine (4EM) have no reports. Herein, we reported detailed interpretations of the Infrared and Raman spectra based on the experimental and theoretical results, which are acceptable and supportable to each other. Density functional theory calculations are reported to provide excellent vibrational frequencies of organic

compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation for the basis set deficiencies and for the anharmonicity [16–18]. Reliable vibrational assignments associated with these molecules are made on the basis of potential energy distribution (PED) results.

In the present investigation, the delocalization of an electron density (ED) from the filled lone pairs of Lewis base to the unfilled Lewis sites of 4EM and the corresponding changes in bond lengths and ED are being reported. The optimized geometrical parameters, vibrational assignments, and certain non-linear optical properties (dipole moment, polarizability, hyperpolarizability) for the title molecule are analyzed. The electronic properties, such as HOMO–LUMO energies, absorption wavelengths and oscillator strengths were calculated using B3LYP method of the time dependent TD-DFT, basing on the optimized structure in solvent and gas phase. Density plots over the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy surface directly identified the donor and acceptor atoms in the title molecules. It also provides information about the charge transfer within the molecule. The molecular quantities as vertical ionization energy (A), ionization potential (I), electronic chemical potential (μ), global softness (S), electronegativity (χ) and electrophilicity indices (ω) are calculated and discussed. Moreover, molecular electrostatic potential (MEP) surface is plotted over the optimized geometry to elucidate the reactivity of 4EM molecule. Molecular electrostatic potential is considered as additional molecular characteristic. Furthermore, reactive nucleophilic and electrophilic sites in the MEP surface are compared with the fitting point charges to electrostatic potential. On the basis of vibrational analysis, the thermodynamic properties of the 4EM at different temperatures have been calculated, revealing correlation of different thermodynamic functions such as heat capacity (C), entropy (S), enthalpy (H), Gibb's free energy (ΔG), molecular energy (E), vibrational partition functions ($V = 0$ and $V = $ Bot) and temperature.

2. Experimental

The title compound4-EM in the liquid form was obtained from Sigma Aldrich, USA with a purity of greater than 98% and it was used as such without purification. The FT-IR spectrum of 4EM was recorded in the region 4000–400 cm^{-1}on a NEXUS 670 spectrophotometer equipped with an MCT detector, a KBr pellet technique. The FT Raman spectrum of 4-EM was also recorded in the frequency region 4000–0 cm^{-1} on a NEXUS 670 spectrophotometer equipped with Raman module accessory with Nd:YAG laser operating at 1.5 W power continuously with 1064 nm excitation.

3. Computational methods

The entire vibrational assignments and optimized geometrical parameters of 4-EM is predicted by means of HF and density functional B3LYP level with 6-311+G(d,p) basis setin Gaussian 09W software package [19]. B3LYP represents Becke's three-parameter hybrid functional method [20] with Lee–Yang–Parr correlation functional (LYP) [21] of DFT yield a good description of harmonic vibrational wavenumbers for small and medium sized molecules. The DFT potentials symmetrically over estimate the vibrational wavenumbers. These discrepancies are corrected either by computing anharmonic corrections explicitly [22] or by introducing a scale factor. The vibrational frequencies calculated at B3LYP method with 6-311+G(d,p) level of basis set were scaled by 0.9222 for wavenumbers above 1000 cm^{-1} and 0.9122 for higher wavenumbers. The scaled values used in HF/6-311+G(d,p) were 0.8571 for wavenumbers less than 1000 cm^{-1} and 0.9212 for higher wavenumbers. After scaling factor, the deviation from the experiment

is more reliable. The potential energy distribution (PED) was calculated by using the scaled quantum mechanical (SQM) method [23] and MOLVIB program (Version V7.0-G77) written by Sundius [24,25]. The fundamental vibrational modes were characterized by their PED. For the plots of stimulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of ±10 cm^{-1}.

From the basic theory of Raman scattering, Raman activities (S_i) calculated by Gaussian 09 program has been converted to relative Raman intensities (I_i) using the following relationship:

$$I_i = \frac{f(\upsilon_0 - \upsilon_i)^4 S_i}{\upsilon_i[1 - \exp(-hc\upsilon_i)]/kT}$$

where υ_0 is the laser exciting wavenumber in cm^{-1} (in this work, we have used the excitation wavenumber $\upsilon_0 = 9398.5$ cm^{-1}, which corresponds to the wavelength of 1064 nm of Nd:YAG laser), υ_i is the vibrational wave number of the ith normal mode in cm^{-1}, h, c, and k are universal constants (is a constant equal to 10^{-12}) and f is a suitably chosen common normalization factor for all the peak intensities.

The non-linear optical properties such as dipole moment (μ), polarizability (α_{tot}), anisotropy of polarizability ($\Delta\alpha$) and molecular first hyperpolarizability ($\langle\beta\rangle$) of 4EM is computed with the aid of HF and B3LYP/6-311+G(d,p) level of theory.

The frontier molecular orbital energies, energy gap between various occupied and unoccupied molecular orbitals of 4EM are also calculated. NBO calculation is also performed on the 4EM with the same level of DFT theory with 6-311+G(d,p) basis set. For obtaining chemical reactivity of the molecule, the molecular electrostatic potential (MEP) surface is plotted over the optimized geometry of 4EM using Gaussian 09W software package [19]. The fitting point charges to the electrostatic potential on each atom of the optimized geometry are compared with MEP surface. Moreover, Mulliken atomic charges of atoms and certain thermodynamic properties such as entropy, enthalpy, rotational constants, vibrational constants and zero point vibrational energy of the title compound are also calculated at the same level of DFT calculation.

A detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, a full set of 57 standard internal coordinates containing 8 redundancies were defined as given in Table S1 (Supplementary Material). From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of local symmetry coordinates following the recommendations of Pulay et al. [26] and they are presented in Table S2 (Supplementary Material).

4. Results and discussion

The present compound under investigation has become a greater interest because it contains the chair conformation. Because all carbons are sp^3 hybridized the ring cannot be in a planar arrangement due to the bond angles nearly closer to the ideal bond angle 109.5°; all the carbon-hydrogen bonds are also fully staggered, eliminating the torsional strain. Thus, the ring is puckered as shown in Fig. 1 and is called a chair conformation. Note that carbon-1, 3, 5 are above the plane and carbon-2, 4, 6 are below the plane. Nitrogen in ring system involves in the introduction of sterically demanding asymmetric center to achieve effective stereo control.

4.1. Geometrical parameters

The calculated structural parameters for AMP are listed in Table 1. Among the different conformers of cyclohexanone, the chair form is energetically favored [27]. The computed values of torsion