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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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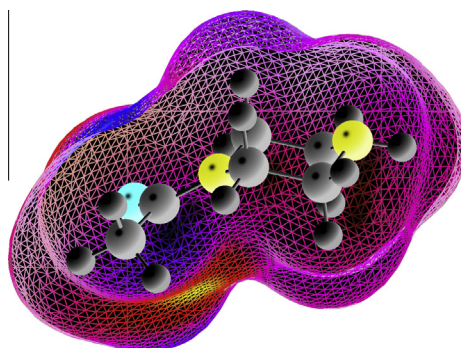
## A joint theoretical and experimental study of 1-acetylpiperazine: Conformational stability, infrared and Raman spectra

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### HIGHLIGHTS

- Infrared, Raman and quantum chemical calculations of 1-ap.
- Normal chair form with e–e substituents is not preferred.
- Conformational energy barrier is independent of the solvent.
- Vibrational frequencies and intensities change when going from nonpolar to polar solvents.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Infrared and Raman spectra of 1-acetylpiperazine (1-ap) have been recorded in the region of 4000–40 cm<sup>-1</sup>. The conformational isomers, optimized geometric parameters, normal mode frequencies and corresponding vibrational assignments of 1-ap (C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O) have been examined by density functional theory (DFT), with the Becke–3–Lee–Yang–Parr (B3LYP) functional and the 6-31++G(d,p) basis set. Reliable conformational investigation and vibrational assignments have been performed by the potential energy surface (PES) and potential energy distribution (PED) analyses, respectively. Computations are carried out in both gas phase and solution using benzene and methanol. There is a good agreement between the theoretically predicted structural parameters and vibrational frequencies and those obtained experimentally. The normal chair conformation with equatorial substituents is not preferred due to the steric interaction.

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### Introduction

1-Acetylpiperazine, called in the literature by different names such as 1-piperazinoethanone, 1-(piperazin-1-yl)ethan-1-one and 1-oxo-1-(piperazin-1-yl)ethane, is a very versatile molecule. It has been the subject of many scientific studies. For example,

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1-ap has been used in synthesizing some novel anticancer agent [1], inhibitors of hepatitis C virus [2] and the human pregnane X receptor [3], metal salts [4], mononuclear 3d-transition metal complexes [5], dialkylaminoalkyl derivatives [6], dual cholinesterase and ab-aggregation inhibitors [7]. 1-ap has also been employed in the researching structure–activity relationship on two novel and potent cognition enhancing drugs [8], optimization of surfaces for antibody immobilization using metal complexes [9], HIV-1 integrase inhibitors [10].

In the literature, there are ample examples of 1-ap being used as an intermediate material in both organic and medicinal chemistry. However, there is lack of information on the vibrational and structural studies of 1-ap in the literature. In the present study, the structure of 1-ap was characterized by vibrational spectroscopy. Further, DFT in conjunction with the B3LYP/6-31++G(d,p) was employed to predict the structural and spectroscopic parameters of the compound in the both gas phase and solution. The findings of these spectroscopic and theoretical studies are herein reported.

## Experimental

A commercially available sample of 1-ap in solid form was purchased from Aldrich (99%) and used without further purification. FT-MIR and FT-FIR spectra of 1-ap were recorded in the region of 4000–400  $\text{cm}^{-1}$  and 400–40  $\text{cm}^{-1}$  with Bruker Optics IFS66v/s FTIR spectrometer at a resolution of 2  $\text{cm}^{-1}$ . Raman spectrum was obtained using a Bruker Senterra Dispersive Raman microscope spectrometer with 532 nm excitation from a 3B diode laser having 2  $\text{cm}^{-1}$  resolution in the spectral region of 4000–40  $\text{cm}^{-1}$ .

## Computational details

All the computations were performed using Gaussian 09.A1 program package [11]. GaussView 5.0.8 [12] was used for visualization of the structure and simulation of the vibrational spectra. Several possible isomers could be proposed for 1-ap. However, the discussions are limited only to six isomers, four of them (A: a–e (axial-equatorial), B: a–a, C: e–e, D: e–a, where the former represents NH while the latter stands for acetyl group) from the conformations of piperazine [13] and the other two (E and F) from PES analysis (Fig. 1). A–D forms are considered in axial and equatorial positions according to plane formed by C2, C3, C5 and C6 carbon atoms of 1-ap. We performed the potential energy surface (PES) analysis on the rotations of 6C–5C–4N–13H and 5C–6C–1N–7C torsion angles, scanning from 0° to 180°, with 10° increments. Scan

process were conducted for different isomers and it was found that the molecule under investigation is the most stable in the conformer F (Fig. 2, Table 1). Fig. 2 shows PES graphics for 1-ap which allowed us to determine its conformational composition with a high accuracy.

For all the computations, the six isomers of 1-ap were optimized using B3LYP functional in conjunction with the 6-31++G(d,p) basis set both in the gas phase and in benzene and methanol solvent environments. Harmonic vibrational frequencies and their corresponding vibrational intensities were also computed using the same functional and basis set. Vibrational frequencies scaled to generate the corrected frequencies, by 0.955 (>1800  $\text{cm}^{-1}$ ) and 0.977 (<1800  $\text{cm}^{-1}$ ) [14–16]. The fundamental normal modes were assigned. PED calculations were carried out by the VEDA 4 (Vibrational Energy Distribution Analysis) as described earlier [17]. Calculated Raman activities are converted to relative Raman intensities using the relationship derived from the intensity theory of Raman scattering [18,19]. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the compound were analyzed.

## Results and discussion

The results of the electronic computations on the isomers and geometrical parameters of 1-ap are reported and discussed. This is followed by discussion of the experimental and theoretical vibrational frequencies and their intensities.

### Geometrical structures

The energetic and some molecular parameters of the six forms of 1-ap listed in Table 1. Regarding the calculated energies, the F conformer is more stable than others for the all medium. The A–D forms could be neglected for calculation of equilibrium constant since their energy differences are larger than 2 kcal/mol [14,18,20,21]. The F form is more stable than E by 0.704, 0.532

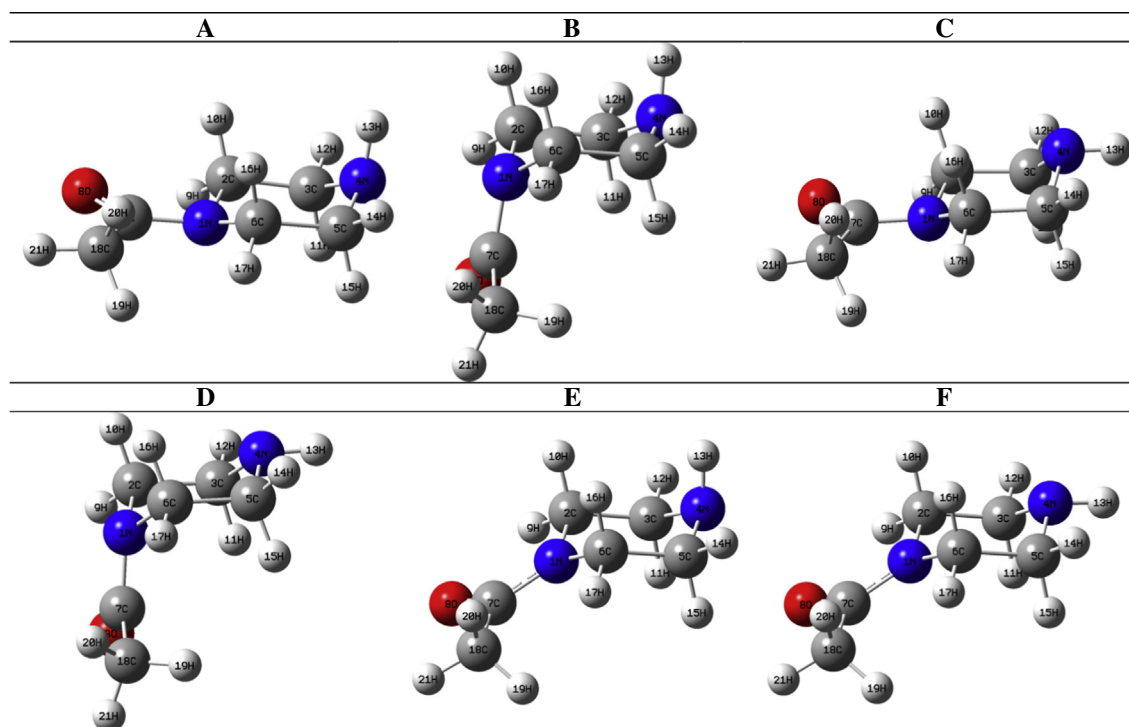


Fig. 1. Optimized structures of the investigated isomers.

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