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r_0 Structural parameters, conformational, vibrational studies and *ab initio* calculations of cyanocyclopentane

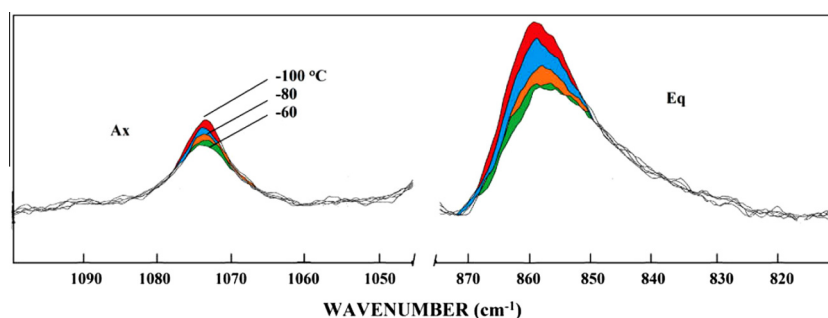
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HIGHLIGHTS

- Experimental enthalpy difference has been determined between the two conformers.
- Vibrational assignments have been obtained for both conformers.
- r_0 structural parameters have been determined for both conformers.
- *Ab initio* calculations have been performed for both stable conformers and the twist and planar forms.

GRAPHICAL ABSTRACT



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ABSTRACT

The infrared and Raman spectra (3100–50 cm^{-1}) of the gas, liquid or solution, and solid have been recorded of cyanocyclopentane, $\text{c-C}_5\text{H}_9\text{CN}$. Variable temperature (–60 to –100 °C) studies of the infrared spectra (3100–400 cm^{-1}) of the sample dissolved in liquid xenon have been carried out. From these data, both the envelope-equatorial (Eq) and Ax conformers have been identified and their relative stabilities obtained. The enthalpy difference has been determined to be $55 \pm 12 \text{ cm}^{-1}$ ($0.66 \pm 0.14 \text{ kJ/mol}$) with the Eq conformer the more stable form. The percentage of the Ax conformer is estimated to be $45 \pm 1\%$ at ambient temperature. The conformational stabilities have been predicted from *ab initio* calculations by utilizing several different basis sets up to aug-cc-pVTZ from both MP2(full) and density functional theory calculations by the B3LYP method. Vibrational assignments have been made for the observed bands for both conformers with initial predictions by MP2(full)/6-31G(d) *ab initio* calculations to obtain harmonic force constants, wavenumbers, infrared intensities, Raman activities and depolarization ratios for both conformers. The r_0 structural parameter values for the Eq[Ax] form are; for the heavy atom distances (Å): $\text{C}\equiv\text{N} = 1.160$ [1.160] (3); $\text{C}_\alpha\text{-C} = 1.463$ [1.463] (3); $\text{C}_\alpha\text{-C}_\beta$, $\text{C}_\beta = 1.543$ [1.545] (3); $\text{C}_\beta\text{-C}_\gamma$, $\text{C}_\gamma = 1.540$ [1.541] (3); $\text{C}_\gamma\text{-C}_\gamma = 1.552$ [1.553] (3) and angles (°): $\angle\text{C}_\alpha\text{-C}\equiv\text{N} = 179.0$ [178.9] (5); $\angle\text{C}_\beta\text{C}_\alpha\text{-C} = 113.1$ [110.1] (5); $\angle\text{C}_\beta\text{C}_\alpha\text{C}_\beta = 103.0$ [102.1] (5); $\angle\text{C}_\alpha\text{C}_\beta\text{C}_\gamma = 104.1$ [104.8] (5); $\angle\text{C}_\beta\text{C}_\gamma\text{C}_\gamma = 106.3$ [106.0] (5). The results are discussed and compared to the corresponding properties of some related molecules.

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1. Introduction

Some very interesting results were observed in the spectroscopic study of monosubstituted cyclopentane derivatives like fluoro, chloro, bromo, ethynyl and isocyanocyclopentane. From the

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earlier studies it was concluded that fluorocyclopentane exist in envelop-axial (Ax) form [1]. Further studies of chloro and bromo cyclopentane for both molecules the Ax conformer was found to be the most stable form with the enthalpy difference of $145 \pm 15 \text{ cm}^{-1}$ ($1.73 \pm 0.18 \text{ kJ/mol}$) for chlorocyclopentane [2] and enthalpy difference of $233 \pm 23 \text{ cm}^{-1}$ ($2.79 \pm 0.28 \text{ kJ/mol}$) for bromocyclopentane [3]. At ambient temperature for chlorocyclopentane $67 \pm 2\%$ of the conformer and for bromocyclopentane $75 \pm 2\%$ of the conformer are estimated to be in the Ax form [2,3]. Later in a detail spectroscopic study of fluorocyclopentane, the twist conformer was observed to be the most stable conformer [4]. From the comparison of conformational stability data obtained for fluoro and chlorocyclopentane as the atomic size of substituents on the cyclopentane ring increases the conformational stability of molecules changed from twist to Ax form. Similarly for chloro and bromocyclopentane as the atomic size increases the enthalpy difference between the two conformers also increases.

In a recent study of ethynylcyclopentane the Eq conformer was observed to be the most stable form with the enthalpy difference of $94 \pm 9 \text{ cm}^{-1}$ ($1.12 \pm 0.11 \text{ kJ/mol}$) and at ambient temperature $62 \pm 1\%$ of the conformer is present in Eq form [5]. However for isocyanocyclopentane, the Ax conformer was observed to be the most stable form with the enthalpy difference of $102 \pm 10 \text{ cm}^{-1}$ ($1.21 \pm 0.11 \text{ kJ/mol}$) and at ambient temperature $62 \pm 1\%$ is estimated for the Ax form [6]. Thus in the study of ethynylcyclopentane and isocyanocyclopentane, two different conformers were observed in the most stable form.

In the microwave study of normal and 1-D isotopic species of cyanocyclopentane only the Ax and Eq conformers were observed and rotational constants were reported for both conformers [7]. By utilizing rotational constants obtained from the microwave study authors also determined structural parameters for both Ax and Eq conformers of cyanocyclopentane. Based on relative intensity measurements the ground state energy difference between Ax and Eq conformers was reported to be $0 \pm 200 \text{ cal/mol}$ ($0 \pm 70 \text{ cm}^{-1}$) [7]. The reported enthalpy difference between the two conformers of cyanocyclopentane is very low compared to enthalpy differences obtained for other similar molecules like fluoro, chloro, bromo, ethynyl and isocyanocyclopentane. Additionally authors were not able to determine the most stable conformer, but they proposed that Eq conformer may be the most stable form [7]. In another infrared study at variable temperature of cyanocyclopentane, authors reported Ax conformer to be most stable form with the enthalpy difference of $109 \pm 37 \text{ cm}^{-1}$

($312 \pm 106 \text{ cal/mol}$) and at ambient temperature Ax conformer was estimated to be $59 \pm 7\%$ [8]. However in this study the vibrational assignments were made for both Ax and Eq conformers but the assignments were incomplete. Also for determining the enthalpy difference between the two conformers of cyanocyclopentane the authors used only one band pair from the infrared spectrum of sample dissolved in liquid Xe solution [8]. Hence the results obtained from this infrared study of cyanocyclopentane are highly doubtful and therefore we have reinvestigated the conformational stability and enthalpy difference between the Eq and Ax conformer (Fig. 1) of cyanocyclopentane. Results obtained from this investigation will be useful for understanding the effect of $\text{C}\equiv\text{N}$ group on conformational stability and enthalpy difference between different conformers of cyanocyclobutane, cyanocyclopentane and cyanocyclohexane. Additionally this study will be also helpful for understanding the effect of different substituents on cyclopentane ring.

For identifying fundamental vibrational modes of cyanocyclopentane, the Raman spectrum of the liquid and infrared spectra of the gas, amorphous and annealed solid were investigated. For determination of enthalpy difference between two possible conformers the infrared spectra of the variable temperature of the sample dissolved in xenon solution was investigated. To support the vibrational study, *ab initio* calculations with basis sets up to aug-cc-pVTZ as well as those with diffuse functions, i.e., 6-311 + G(2df,2pd) have been carried out. Density functional theory (DFT) calculations by the B3LYP method with the same basis sets have also been carried out. Optimized geometries, conformational stabilities, harmonic force fields, infrared intensities, Raman activities and depolarization ratios are also calculated. The results of these spectroscopic, structural and theoretical studies of cyanocyclopentane are reported herein.

2. Experimental and theoretical methods

The sample of cyanocyclopentane was purchased from Alfa Aesar, with stated purity of $\geq 98\%$. The sample was further purified by low-temperature, low-pressure fractionation column. The purity of the sample was checked and verified by the infrared spectra.

The mid-infrared spectrum of the gas and solid (Figs. 2 and 3) were obtained from 3100 to 400 cm^{-1} on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beam splitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry

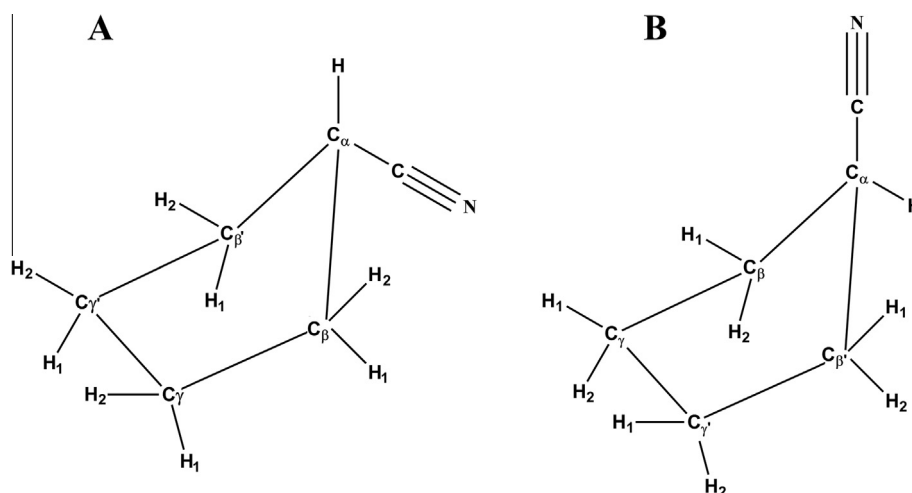


Fig. 1. Conformers of cyanocyclopentane (A) Eq (B) Ax.

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