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Conformational and structural studies of ethynylcyclopentane from temperature dependent Raman spectra of xenon solutions, infrared spectra, and *ab initio* calculations

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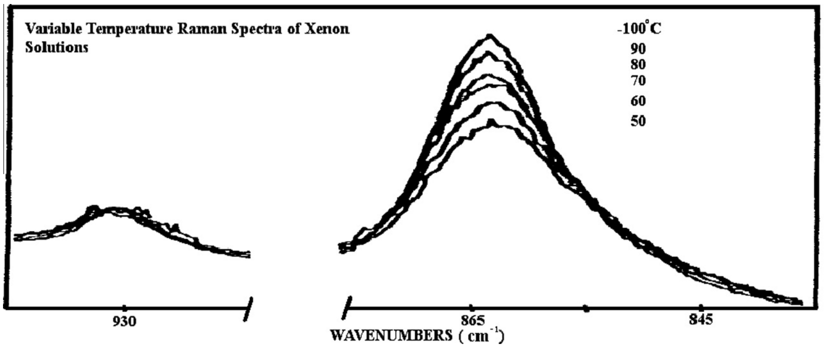
HIGHLIGHTS

- The heavy atom structural parameters have been determined for both forms.
- Vibrational assignments have been obtained for both conformers.
- Energy differences have been predicted for both forms and the planar transition state.
- Experimental enthalpy difference has been determined between the two conformers.

GRAPHICAL ABSTRACT



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ABSTRACT

Variable temperature (−50 to −100 °C) Raman spectra (3500–136 cm^{-1}) were recorded of ethynylcyclopentane, c-C_5H_9CCH in liquid xenon. The *envelope-equatorial* (*Eq*) conformer was determined more stable than *envelope-axial* (*Ax*) form with enthalpy difference of 94 ± 9 cm^{-1} (1.12 ± 0.11 kJ/mol) and 39 ± 2% Ax conformer present at ambient temperature. The conformational stabilities have been predicted from *ab initio* calculations with basis sets up to aug-cc-pVTZ. From previously reported microwave rotational constants and *ab initio* MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters are reported *Eq* [*Ax*] distances (Å) $r\mathrm{C{\equiv}C} = 1.211(3)$ [1.211(3)], $r\mathrm{C_\alpha{-}C{\equiv}C} = 1.461(3)$ [1.467(3)], $r\mathrm{C_\alpha{-}C_\beta} = 1.542(3)$ [1.542(3)], $r\mathrm{C_\beta{-}C_\gamma} = 1.541(3)$ [1.542(3)], $r\mathrm{C_\gamma{-}C_{\gamma'}} = 1.556(3)$ [1.555(3)] and angles (°) $\angle\mathrm{C_\alpha{-}C{\equiv}C} = 179.4(5)$ [179.9(5)], $\angle\mathrm{C_\beta C_\alpha{-}C{\equiv}C} = 113.7(5)$ [111.5(5)], $\angle\mathrm{C_\beta C_\alpha C_{\beta'}} = 102.6(5)$ [102.1(5)], $\angle\mathrm{C_\alpha C_\beta C_\gamma} = 103.7(5)$ [103.7(5)], $\angle\mathrm{C_\beta C_\gamma C_{\gamma'}} = 106.0(5)$ [105.9(5)] and $\tau\mathrm{C_\beta C_\alpha C_{\beta'} C_{\gamma'}} = 40.8(5)$ [41.6(5)]. Vibrational assignments are reported, supported by *ab initio* predictions and results are discussed.

1. Introduction

Mono-substituted cyclopentanes have been of interest for several decades since cyclopentane undergoes a ring vibration designated [1] as pseudorotation since there are two “out-of-plane” vibrational modes which are usually described qualitatively as ring-puckering and ring-twisting. After the initial prediction [1] of pseudorotation in saturated five-membered rings, a study followed [2] wherein the authors proposed that fluorocyclopentane as well as some other mono-substituted cyclopentanes should have the bent conformation (*envelope*) as the preferred form. Relatively complete vibrational [3,4] studies of the cyclopentyl halides

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(F, Cl, Br, and I) were carried out utilizing infrared and Raman spectra and it was concluded that the F, Cl, and Br compounds all had doublets for the carbon-halogen stretches arising from *equatorial* and *axial* conformers for the *envelope* form of these substituted cyclopentanes. We recently determined [5,6] the enthalpy differences between the two stable forms of the chloride and bromide by variable temperature studies of the infrared spectra of rare gas solutions with values of 145 ± 15 cm^{-1} (1.73 ± 0.18 kJ/mol) and 233 ± 23 cm^{-1} (2.79 ± 0.28 kJ/mol), respectively, with the *axial* conformer the more stable form for both molecules.

From the initial study [3,4] of fluorocyclopentane it was also concluded that both the *axial* and *equatorial* forms were present in the fluid phases. However from a later Raman study [7] it was concluded there was only a single conformer present in the fluid states and it was the *envelope-equatorial* (*Eq*) conformer. This conclusion was consistent with predictions from CNDO/2 calculations [8] that only the *Eq* conformer was a stable form. As a continuation of our studies of the conformational stabilities of mono-substituted cyclopentanes we reinvestigated the infrared and Raman spectra of fluorocyclopentane [9]. The results were quite interesting in that there is, in fact, a single stable conformer present in the fluid phases but it is neither the *envelope-axial* (*Ax*) nor *envelope-equatorial*, but the *twisted* form. These conclusions were based on infrared spectra of variable temperature xenon solutions, Raman spectra of the liquid and solid, and microwave spectrum which were supported by *ab initio* and density functional theory calculations. Therefore, as a continuation of these studies we have turned our attention to another mono-substituted cyclopentane, i.e. ethynylcyclopentane, c-C_5H_9CCH.

There has been a previous investigation of the conformational stability of ethynylcyclopentane from a microwave study [10] where the *Eq* conformer was reported to be more stable by 94 ± 24 cm^{-1} (1.12 ± 0.29 kJ/mol) than the *Ax* form. By transferring the parameters reported for cyanocyclopentane which were obtained from assumed parameters (four) transferred from analogous molecules and five parameters from the least squares fit of the two isotopic species of each conformer. The three parameters (angles) were reported for ethynylcyclopentane by fitting the experimental moments of inertia. However the heavy atom bond distances for cyanocyclopentane were reported not to be in error by more than 0.02 Å and the angles no more than 5°. Therefore it is desirable to obtain a more accurate enthalpy difference between the two conformers and obtain more accurate structural parameters for ethynylcyclopentane, so as to compare them to the corresponding cyanocyclopentane parameters. Therefore we have investigated the vibrational spectrum of ethynylcyclopentane with a study of the infrared spectra of the gas and solid. Additionally we have investigated the Raman spectra of the liquid as well as spectra of the variable temperatures of xenon solutions. To support the vibrational study, we have carried out *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). We have also carried out density functional theory (DFT) calculations by the B3LYP method with the same basis sets. We have calculated optimized geometries, conformational stabilities, harmonic force fields, infrared intensities, Raman activities and depolarization ratios. The results of these spectroscopic, structural, and theoretical studies are reported herein.

2. Experimental and theoretical methods

The sample of c-C_5H_9CCH was purchased from GFS Chemicals, Columbus, OH with a stated purity of 95%. The sample was further purified by a low-temperature, low-pressure fractionation column and the purity of the sample was verified from the infrared spectra of the gas and NMR spectrum of the liquid.

The infrared spectrum of the gas (Fig. 1A) and solid (Fig. 1E) were obtained from 3500 to 220 cm^{-1} on a Perkin–Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The spectra of the gas and solid were obtained with a theoretical resolution of 0.5 cm^{-1} for the gas and 2 cm^{-1} for the solid with 128 interferograms added and truncated. Multiple annealings were required to obtain satisfactory spectra of the solid.

The Raman spectra of the liquid (Fig. 2A) obtained from 3400 to 60 cm^{-1} were recorded on a Spex model 1403 spectrophotometer equipped with a Spectra-Physics model 2017 argon ion laser operating on the 514.5 nm line. The laser power used was 1.5 W with a spectral bandpass of 3 cm^{-1}. The spectrum of the liquid was recorded with the sample sealed in a Pyrex glass capillary. The measurements of the Raman frequencies are expected to be accurate to ±2 cm^{-1}. All of the observed bands in the Raman spectra of the liquid along with their proposed assignments and depolarization values are listed in Tables 1 and 2, for the *Eq* and *Ax* conformers, respectively.

The Raman spectra (3500–136 cm^{-1}) of the sample dissolved in liquefied xenon (Fig. 2B) at six different temperatures (−50 to −100 °C) were recorded on a Trivista 557 spectrometer consisting of a double $f = 50$ cm monochromator equipped with a 2000

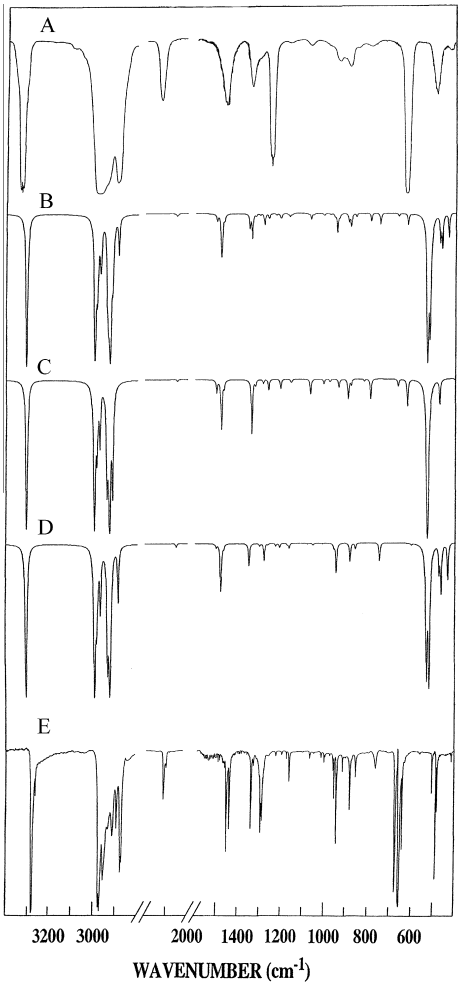

Fig. 1. Comparison of experimental and calculated infrared spectra of ethynylcyclopentane: (A) observed spectrum of gas; (B) simulated spectrum of a mixture of *Eq* and *Ax* conformers ($\Delta H = 94\ \text{cm}^{-1}$) at 25 °C; (C) simulated spectrum of *Ax* conformer; (D) simulated spectrum of *Eq* conformer; (E) observed spectrum of solid.