# Microwave, structural, conformational, vibrational studies and ab initio calculations of isocyanocyclopentane

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HIGHLIGHTS

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

GRAPHICAL ABSTRACT
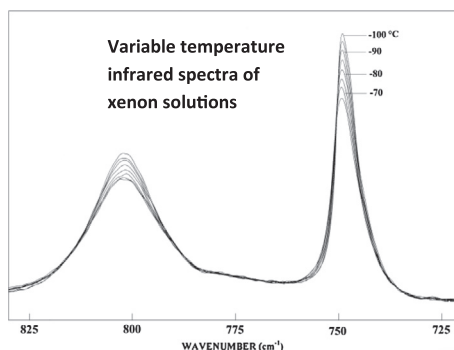
Variable temperature infrared spectra of xenon solutions

ARTICLE INFO

ABSTRACT

The infrared and Raman spectra (3200–50 cm^{-1}) of the gas, liquid or solution, and solid have been recorded of isocyanocyclopentane, c-C$_5$H$_9$NC. FT-microwave studies have also been carried out and 23 transitions were recorded for the envelope-axial (Ax) conformer. Variable temperature (−65 to −100 °C) studies of the infrared spectra (3200–400 cm^{-1}) dissolved in liquid xenon have been carried out. From these data, both the Ax and envelope-equatorial (Eq) conformers have been identified and their relative stabilities obtained. The enthalpy difference has been determined to be 102 ± 10 cm^{-1} (1.21 ± 0.11 kJ mol^{-1}) with the Ax conformer the more stable form. The percentage of the Eq conformer is estimated to be 38 ± 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 structural parameter values for the Ax form are; for the heavy atom distances (Å): C≡N = 1.176 (3); C$_\alpha$—N = 1.432 (3); C$_\alpha$—C$_\beta$,C$_{\beta'}$ = 1.534 (3); C$_\beta$—C$_\gamma$,C$_{\gamma'}$ = 1.542 (3); C$_\gamma$—C$_{\gamma'}$ = 1.554 (3) and angles (°):∠C$_\alpha$—N≡C = 177.8 (5); ∠C$_\beta$C$_\alpha$—N = 110.4 (5); ∠C$_\beta$C$_\alpha$C$_{\beta'}$ = 102.9 (5); ∠C$_\alpha$C$_\beta$C$_\gamma$ = 103.6 (5); ∠C$_\beta$C$_\gamma$C$_{\gamma'}$ = 105.9 (5). The results are discussed and compared to the corresponding properties of some related molecules.

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Introduction

Monosubstituted cyclopentanes have been of interest for many decades since the cyclopentane ring vibration was proposed to have a motion described as pseudorotation [1]. After

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the initial prediction of the pseudorotational motion in saturated five-membered rings twelve years later Pitzer and Donath [2] proposed that several mono-substituted cyclopentanes should have the bent conformation (envelope) as the preferred form. Relatively complete vibrational [3,4] studies of the cyclopentyl halides (F, Cl and Br) 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 envelope-equatorial (Eq) and envelope-axial (Ax) conformers for the envelope form of these halo 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 the axial conformer the more stable form for both molecules. Also from the initial study [3,4] of fluorocyclopentane it was also concluded that both the Ax and Eq forms were present in the fluid phases but from a later Raman study [7] it was determined there was only a single conformer present in the fluid states but it's conformation was not determined. However from CNDO/2 calculations [8] the predicted result were only one conformer and it was the Eq 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]. Again a single stable conformer was found in the fluid phases but it is neither the Ax nor Eq form, but the twisted form. Based on these results it was expected that there may be several other monosubstituted cyclopentane molecules where the previously determined conformer stability is in error. Therefore we initiated some studies of cyclopentane molecules which might be expected to have more than one conformer present at ambient temperature. Cyanocyclopentane [10] was the first of these molecules to be investigated and from the variable temperature studies of the infrared spectra of rare gas solutions two conformers were identified. It was determined that the conformers were the axial and equatorial forms and the axial conformer was determined to be the more stable form. A similar variable temperature study was carried out on ethynylcyclopentane [11] molecule and it was found that the equatorial conformer was the stable form in contrast to the axial conformer which was the more stable form for cyanocyclopentane. Currently it is not clear what factors are important to determine the conformer that is the most stable form for these monosubstituted cyclopentane molecules. Therefore, as a continuation of these studies of the monosubstituted cyclopentane molecules we have chosen isocyanocyclopentane, c-C_5H_9NC as the next molecule to be investigated for the conformational stabilities and structural parameters.

There has not been a previous report of the conformational stability of isocyanocyclopentane and there is, in general, limited conformational and structural data of organoisocyanides in the vapor state. We believe it is desirable to obtain an accurate enthalpy difference between the expected two conformers (Fig. 1) and obtain structural parameters, if possible, as well as to obtain the identity of the most stable conformer. Therefore we have investigated the vibrational spectrum of isocyanocyclopentane with a study of the infrared spectra of the gas, xenon solutions and solid. Additionally we have investigated the Raman spectra of the liquid as well as infrared spectra of the variable temperatures of the 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.

Experimental methods

The sample of isocyanocyclopentane was purchased from Acros Organics, with stated purity of ⩾96%. 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.

Microwave spectra of isocyanocyclopentane were recorded on a "mini-cavity" Fourier-transform microwave spectrometer [12,13] at the Kent State University. The Fabry–Perot resonant cavity is established by two 7.5-in. diameter diamond-tip finished aluminum mirrors with a 30.5-cm spherical radius. The Fabry–Perot cavity resides inside a vacuum chamber formed by a 6-way cross and a 15-in. long, 8-in. diameter extension tube. One of the cavity mirrors is formed on an 8-in. diameter vacuum flange and mounted on the 6-way cross. The second mirror is mounted on 0.75-in. diameter steel rails that pass through ball bearing brackets mounted inside the extension arm. A motorized micrometer is used to position the movable mirror over a two-inch travel range. The two cavity mirrors are nominally separated by 30 cm. The vacuum chamber is pumped by a Varian VHS-6 diffusion pump (2400 L s^{-1}) backed by a two-stage Edwards E2M30 rotary pump.

The isocyanocyclopentane sample was entrained in 70:30 Ne–He carrier gas mixtures at 2 atm and expanded into the cavity with a reservoir nozzle [13] made from a modified Series-9 General Valve. The reservoir nozzle is mounted in a recessed region of the mirror flange which is external to the vacuum chamber and the expansion passes through a 0.182-in. diameter hole into the resonant cavity. The center of the expansion is offset from the center of the mirror by 1 in.

The sample was irradiated by microwave radiation generated by an Agilent Technologies E8247C PSG CW synthesizer and details of the irradiation and heterodyne detection circuitry can be found in Ref. [14]. Labview software controls the timing of the gas and irradiation pulses, as well as the detection of any free induction decay signal. The software performs signal averaging and can scan the spectrometer by stepping both the frequency source and the cavity. Microwave circuit elements allow for a spectral range from 10.5 to 26 GHz. The digital frequency resolution is 2.5 kHz and governed by the sampling rate and by the length of the free induction decay record. Rotational transitions are split into Doppler doublets by typically 13 kHz centered at the transition frequency due to the coaxial orientation of the gas expansion to the cavity axis and the FWHM of each Doppler component. The assigned microwave lines are listed in Table 1 and the rotational and centrifugal distortion constants are listed in Table 2.

The mid-infrared spectrum of the gas and solid (Fig. 2) were obtained from 4000 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. It needs to be noted that annealing was attempted multiple times with reduction in some band intensities in the spectra however a polycrystalline solid of single conformer could not be obtained.

The mid-infrared spectra (3600–400 cm^{-1}) of the sample dissolved in liquefied xenon (Fig. 2B) at ten different temperatures (−65 to −100 °C) were recorded on a Bruker model IFS-66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beamsplitter and a DTGS detector. In all cases, 100 interferograms