Conformational stability, infrared and Raman spectra, vibrational assignments, and theoretical calculations of cyclohexylamine

Ikhlas D. Darkhalil, Joshua J. Klaassen, Bhushan S. Deodhar [1], Todor K. Gounev, James R. Durig *

Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110, USA

HIGHLIGHTS

- Conformational analysis has been determined between the possible conformers of cyclohexylamine.
- Vibrational assignments are given for the molecule.
- Ab initio and density functional theory calculations have been carried out for all possible conformers.

GRAPHICAL ABSTRACT

Temperature dependent mid-infrared spectrum of cyclohexylamine dissolved in liquefied xenon.
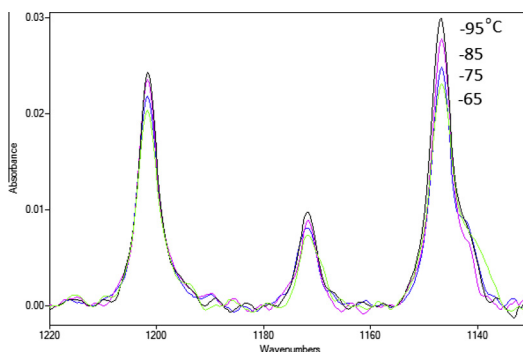
ABSTRACT

The infrared spectra (4000–400 cm^{-1}) of the gas and Raman spectra (4000–50 cm^{-1}) of the liquid have been recorded. Additionally, the variable temperature (−65 to −100 °C) infrared spectra of the sample dissolved in liquefied xenon was recorded from (3800–400 cm^{-1}). The three possible conformers have been identified and their relative stabilities obtained with enthalpy difference relative to trans-Axial (t-Ax) of 58 ± 15 cm^{-1} for gauche-Equatorial (g-Eq) ⩾ 65 ± 12 cm^{-1} for trans-Equatorial (t-Eq). The percentage of the three conformers is estimated to be 31% for the t-Ax, 47 ± 2% for g-Eq and 22 ± 1% for t-Eq at ambient temperature. The conformational stabilities have been predicted from theoretical calculations by utilizing several different basis sets up to 6-311+G(2df, 2pd) from both MP2(full) and density functional theory calculations by the B3LYP method. Vibrational assignments have been provided for the observed bands for all three conformers which are predicted by MP2(full)/6-31G(d) ab initio calculations to predict harmonic force constants, wavenumbers, infrared intensities, Raman activities and depolarization ratios for all of the conformers. The results are discussed and compared to the corresponding properties of some related molecules.

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Introduction

The cyclohexane molecule has been structurally interesting for many decades since they are two stable conformers, i.e., the chair and boat forms, however, the boat form has been such a high energy compared to the chair form therefore, there is irrelevant

* Corresponding author. Tel.: +1 816 235 6038; fax: +1 816 235 2290.
  E-mail address: durigj@umkc.edu (J.R. Durig).
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amount of this form present at ambient temperature. The conformational analysis of cyclohexane and its derivatives have been of interest to molecular spectroscopists since the studies Hassel reported [1,2]. The investigation of six-membered rings with non-substituted cyclohexane started in our laboratory by studying the relative intensities of the Raman active fundamentals and the potential function governing the conformational interchange between the chair and twisted boat form [3]. Studies were initiated to spectroscopically investigate monosubstituted chloro- [4], bromo- [5] and fluorocyclohexane [6] to further understand the conformational stability of the chair form, since there are only two conformers, equatorial and axial forms, which exist at ambient temperature. Due to the repulsive non-bonded nature of the interaction between the axial and the equatorial substituent, the equatorial conformation is generally favored according to two studies reported previously [2,7] and these monosubstituted cyclohexanes exist mostly in the equatorial form. By using vibrational spectroscopy and theoretical calculations such as infrared, Raman, nuclear magnetic resonance, and microwave spectroscopy, a significant number of studies have been carried out on the enthalpy differences for these halocyclohexanes. However, the enthalpy values differ over a wide range and for several cases the uncertainties were large i.e., 140 ± 105 cm^{-1} for fluorocyclohexane [6]. In some cases the enthalpy differences were obtained for solutions with polar solvents which could have a significant effect on the value determined. Additionally, several pseudohalogen substituted cyclohexanes i.e., cyanocyclohexane [8] and ethynylcyclohexane [9] have been studied and the lowest energy forms have been reported. However, the most stable conformation for cyanocyclohexane is an axial form [8,10] compared to the lowest energy equatorial form determined for all other substituted cyclohexanes in our investigations.

There are various predicted values from the ab initio as well as from force constants where the values varied over a very, very large range. Therefore, it has been difficult to provide a rational and consistent explanation for the effect of the various substituents on the conformational analysis for the equatorial and axial conformers of mono-substituted chair cyclohexanes. As a continuation of our spectroscopic analysis of cyclohexanes, extensive rotational, vibrational and conformational analysis studies have been carried out on cyclohexylamine. The results of this infrared spectroscopic study along with the ab initio predicted values are reported herein.

Experimental and theoretical methods

The sample of cyclohexylamine was purchased from Sigma–Aldrich Chemical Co., with stated purity of ⩾99%. The sample was used without any further purification.

The mid-infrared spectrum of the gas was 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 spectrum of the gas was obtained with a theoretical resolution of 0.5 cm^{-1} for the gas with 128 interferograms added and truncated (Fig. 1). A comparison between the observed and calculated wavenumbers, along with the calculated infrared intensities, Raman activities, depolarization ratios and potential energy distributions for the t-Ax, g-Eq, and t-Eq conformers of the cyclohexylamine are listed in Tables 1–3, respectively.

The mid-infrared spectra (4000–400 cm^{-1}) of the sample dissolved in liquid xenon (Fig. 1) 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,
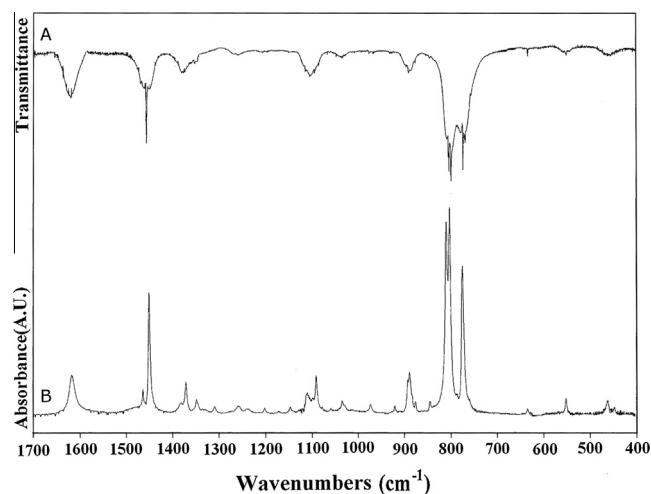

Fig. 1. Mid-infrared spectra of cyclohexylamine (Top) spectrum of gas; (Bottom) spectrum of xenon solution.

100 interferograms were collected at 1.0 cm^{-1} resolution, averaged and transformed with a boxcar truncation function. For these studies, a specially designed cryostat cell was used. It consists of a copper cell with a path length of 4 cm with wedged silicon windows sealed to the cell with indium gaskets. The copper cell was enclosed in an evacuated chamber fitted with KBr windows. The temperature was maintained with boiling liquid nitrogen and monitored by two Pt thermo resistors. After cooling to the designated temperature, a small amount of the sample was condensed into the cell and the system was then pressurized with the noble gas, which condensed in the cell, allowing the compound to dissolve. All of the observed bands in the infrared spectra of the gas along with their proposed assignments of the t-Ax, g-Eq, and t-Eq conformers are listed in Tables 1–3, respectively.

The Raman spectra 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 (Fig. 2) along with their proposed assignments and depolarization values are listed in Tables 1–3.

The LCAO–MO–SCF restricted Hartree–Fock calculations were performed with the Gaussian-03 program [11] with Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters by using the gradient method of Pulay [12]. Several basis sets as well as the corresponding ones with diffuse functions were employed with the Møller–Plesset perturbation method [13] to second order (MP2(full)) as well as with the density functional theory by the B3LYP method. The predicted conformational energy differences are listed in Table 4.

The vibrational spectra were predicted from the MP2(full)/6-31G(d) calculations. The predicted scaled wavenumbers were used together with a Lorentzian function to obtain the simulated spectra. Infrared intensities were obtained based on the dipole moment derivatives with respect to Cartesian coordinates. The derivatives were transformed with respect to normal coordinates by $(\partial \mu_u / \partial Q_i) = \sum_j (\partial \mu_u / \partial X_j) L_{ij}$, where Q_i is the ith normal coordinate, X_j is the jth Cartesian displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and the normal coordinates. The infrared intensities were then calculated by $(N\pi)/(3c^2) [(\partial \mu_x / \partial Q_i)^2 + (\partial \mu_y / \partial Q_i)^2 + (\partial \mu_z / \partial Q_i)^2]$.