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

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ABSTRACT

The Raman and infrared spectra (4000–50 cm^{-1}) of the gas, liquid or solution, and solid have been recorded of isopropylamine, $(CH_3)_2CHNH_2$. Variable temperature (−50 to −100 °C) studies of the Raman spectra (3500–100 cm^{-1}) dissolved in liquid xenon have been carried out. From these data, both the *trans* and *gauche* conformers have been identified and their relative stability obtained. The enthalpy difference has been determined to be 113 ± 11 cm^{-1} (1.35 ± 0.13 kJ mol^{-1}) with the *trans* conformer the more stable form. The percentage of the *gauche* conformer is estimated to be 54 ± 1% at ambient temperature. The conformational stabilities have been predicted from *ab initio* calculations utilizing several different basis sets up to aug-cc-pVTZ from both MP2(full) and density functional theory calculations by the B3LYP method. By utilizing previously reported microwave rotational constants along with *ab initio* MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained for the *trans* conformer. The determined heavy atom and NH_2 distances are (Å) C–C = 1.530(3), C–N = 1.465(3), N–H = 1.019(3) and angles in degrees (°) ∠NCC = 108.9(5), ∠CCC = 111.0(5), ∠HNC = 110.3(5). The structural parameters for the *gauche* conformer were estimated by using the same adjustment differences to the *gauche* form as those obtained for the corresponding *trans* parameters. Vibrational assignments have been provided for the observed bands for both conformers which are supported by MP2(full)/6-31G(d) *ab initio* calculations to predict harmonic force constants, wavenumbers, infrared intensities, Raman activities and depolarization ratios for both conformers. The results are discussed and compared to the corresponding properties of some related molecules.

1. Introduction

Many organoamine molecules are extremely important biomaterials including pharmaceuticals, pesticides, cleaners, food additives, etc. Recently there has also been a great deal of interest in organoamines in the material sciences and nano-technology fields where organoamines are used for organic light emitting diodes (OLED) and solar cells, as well as, simple nano-machine structures and molecular scaffolding for precision nano-engineering.

Many of these molecules have been extensively studied to determine their most stable conformation and to obtain the energy or enthalpy differences between or among the conformers present at ambient temperature. Additionally, there has been significant interest in the structural parameters for many of the small organoamines and for some of them the carbon–nitrogen or nitrogen–hydrogen bond distances are reported significantly different. Since the organoamines are such important molecules we embarked again on the infrared, Raman and microwave studies of several of them which have been supported by *ab initio* calculations and rare gas solutions to determine the enthalpy differences between or among the conformers identified. We began this study [1] with a vibrational spectroscopic investigation of ethylamine in which it was determined to have the *trans* conformer more stable by 54 ± 4 cm^{-1} (0.65 ± 0.05 kJ mol^{-1}) than the *gauche* form. This value was in agreement with earlier determined values of 107 ± 70 cm^{-1} (1.28 ± 0.84 kJ mol^{-1}) from electron diffraction study [2], 110 ± 50 cm^{-1} (1.32 ± 0.60 kJ mol^{-1}) from a microwave investigation [3], and 100 ± 10 cm^{-1} (1.20 ± 0.12 kJ mol^{-1}) from an infrared study of ethylamine in an argon matrix [4]. However, several of the earlier studies [5–8] reported the *gauche* conformer as the more stable form, and it is rather interesting that MP2(full)/6-311+G(2d,2p) calculations predict [1] the *gauche* conformer to be the more stable form by 66 cm^{-1} (0.79 kJ mol^{-1}). However, without the diffuse functions the *trans* form is predicted to be the more stable conformer by 32 cm^{-1} (0.38 kJ mol^{-1}).

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These results clearly indicate that the enthalpy difference between the *gauche* and *trans* conformers of the NH_2 moiety will need to be determined experimentally rather than by theoretical predictions of organoprimary amines. Thus, it is of scientific interest to determine the effect of substituting one or more of the hydrogen atoms on β-carbon. One of the first molecules we investigated was 2-fluoroethylamine [9] where one of the hydrogen atoms on the β-carbon was replaced by a fluorine atom which is expected to have a significant effect on the C–C distance and it has potential to have five stable conformers, instead of two. With the utilization of variable temperature infrared spectra of xenon solutions we were able to determine the conformational stabilities of all five of the conformers of 2-fluoroethylamine [9].

The most stable conformer was the *Gg′* form with the *Gt* conformer the second most stable form with an enthalpy difference of $62 \pm 8\ cm^{-1}$ ($0.74 \pm 0.10\ kJ\ mol^{-1}$), where the first indicator is the NCCF dihedral angle (G = *gauche* or T = *trans*) and the second one (g = *gauche* or t = *trans*) is the relative position of the lone pair of electrons on the nitrogen atom with respect to the β-carbon atom [*Gg′* is noted by the N–H eclipsing the fluoride]. The third, fourth, and fifth conformers in relative energy are the *Tg* ($262 \pm 26\ cm^{-1}$), *Tt* ($289 \pm 45\ cm^{-1}$), and *Gg* ($520 \pm 50\ cm^{-1}$), respectively, where it was not possible to determine whether the *Tg* or *Tt* was the more stable one. Thus the fluorine atom appears to have an effect on the conformer stability of the ethylene groups so we have continued our investigations of molecules with substitutions on the β-carbon atom of ethylamine with the determination of the conformational stabilities and structural parameters of *n*-propylamine which has a substitution of the methyl groups which is replacing one of the hydrogen atoms on the β-carbon. However this study is in progress and at the same time we have also replaced one of the hydrogen atoms on the α-carbon of ethylamine with a methyl group, i.e. isopropylamine to evaluate the effect of substitution on this carbon atom.

Therefore as a continuation of our study of the organoamines, we have again investigated vibrational spectra of isopropylamine with particular attention to the assignments for the fundamentals for both conformers, the enthalpy difference between the conformers and the structural parameters. In the first relatively complete vibrational investigation, the Raman spectra of gas, liquid and solid and the infrared spectra of the gas and solid of the normal species as well as the ND_2 isotopologue were investigated from 4000 to $50\ cm^{-1}$ by Durig et al. [10]. From this study the enthalpy differences of 156 and $183\ cm^{-1}$ ($1.87\ kJ\ mol^{-1}$ and $2.19\ kJ\ mol^{-1}$) for the d_0 and ND_2 species was found from the potential function obtained from the assignment of the far infrared spectra with the fundamentals of 236 and $221\ cm^{-1}$ for NH_2 torsional modes of the *trans* and *gauche* conformers, respectively. These values were significantly different from the value of $42\ cm^{-1}$ ($0.50\ kJ\ mol^{-1}$) reported by Krueger and Jan [11] from a dilute CCl_4 solution with the *trans* conformer more stable.

The other studies up to this time of the first extensive spectroscopic investigations were detailed in this article [10] with energy differences ranging with the *gauche* conformer more stable to values near zero between the two forms. However, a more recent study [12] by using high-resolution infrared spectra of the gas and low temperature Argon matrix investigation resulted in some significantly different assignments for the fundamentals of both conformers and significantly larger enthalpy difference than the value from the previously reported [10] potential function. In addition to our interest in the enthalpy difference and the vibrational assignments we were interested in the structural parameters since only limited data have been reported. In the initial microwave study [13] the authors point out that the structure of the isopropyl group is relatively constant in a wide variety of substances, therefore, it was assumed that the structural parameters of the isopropyl group was nearly the same as those of the groups of seven other molecules so the ∠CCC was taken as 111.8° and the two C–C distances were equal for the *trans* conformer at 1.527 Å which reproduced the observed planar moment when the substitution value for the amine H–H distance. The nine moments of inertia from $(CH_3)_2CHNH_2$, $(CH_3)_2CHNHD$, and $(CH_3)_2CHND_2$ were fit with $r(C–N) = 1.49$ Å, $\angle CCN = 108°$ and $\angle HNC = 109°$ with estimated uncertainties of ±0.02 Å and ±2°. In a later microwave study [14] of $(CH_3)_2CHNH_2$ and $(CH_3)_2CHND_2$ by FT-microwave spectroscopy both centrifugal distortion constants and corrected quadrupole coupling constants as well as more accurate rotational constants were reported but no information was given for the structural parameters. However a more recent electron diffraction investigation [15] was reported where the parameters were further refined by combining the moments of inertia from the microwave studies. In this study it was assumed that the molecule was 100% *trans* since the NH_2 change to the *gauche* form was not expected to affect significantly the heavy atom parameters. However, we believed that it is possible to obtain the structural parameters for the *trans* conformer more accurately than the values previously reported and estimate those for the *gauche* form which is in large abundance at ambient temperature. Therefore, the three major goals were to correct some of the earlier vibrational assignments, obtain a reliable enthalpy difference between the two conformers from which the concentrations of the two forms could be obtained at ambient temperature, and determine reliable structural parameters for both conformers.

In order to obtain a more reliable experimental value for the conformational enthalpy difference, we have investigated the variable temperature (−50 to −100 °C) Raman spectra (3500–$100\ cm^{-1}$) of the sample dissolved in the liquified xenon. We have also reinvestigated the infrared spectra (4000–$220\ cm^{-1}$) of the gas and solid. To support these experimental studies we have also obtained the harmonic force constants, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies from MP2(full)/6-31G(d) *ab initio* calculations. To obtain predictions on the conformational stabilities we have carried out MP2(full) *ab initio* and density functional theory (DFT) calculations by B3LYP method utilizing a variety of basis sets. The r_0 structural parameters have been obtained by combining the MP2(full)/6-311+G(d,p) *ab initio* predicted parameters with the previously reported rotational constants obtained from the most recent microwave study [14]. The results of these spectroscopic, structural, and theoretical studies of isopropylamine are reported herein.

2. Experiment and theoretical methods

The sample of isopropylamine was purchased from Sigma–Aldrich Chemical Co., with stated purity of ⩾99.5%. The sample was used with no further purifications.

The mid-infrared spectrum of the gas (Fig. 1A) and solid (Fig. 1E) 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 gas and solid spectra 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 (3500–$100\ cm^{-1}$) of the sample dissolved in liquefied xenon (Fig. 2) 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 lines mm^{-1} grating, a $f = 70$ cm spectrograph equipped with a 2400 lines mm^{-1} grating, and a back-illuminated LN2-cooled PI Acton Spec-10:2 kB/LN 2048 × 512 pixel CCD detector. For all experiments, the 514.5 nm line of a 2017-Ar S/N 1665 Spectra-Physics argon