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Conformational and structural studies of 2,2-difluoroethylamine from temperature dependent infrared spectra of xenon solution and *ab initio* calculations

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ABSTRACT

Variable temperature (−55 to −100 °C) studies of the infrared spectra (4000–400 cm^{-1}) of 2,2-difluoroethylamine, $F_2CHCH_2NH_2$ dissolved in liquid xenon have been carried out. From these data three of the five possible conformers have been identified and their relative stabilities obtained. The enthalpy differences have been determined among the most stable *Tt* conformer and the second stable conformer, *Gg*, to be 83 ± 8 cm^{-1} (0.99 ± 0.10 kJ/mol), the third stable conformer, *Gt*, to be 235 ± 11 cm^{-1} (2.81 ± 0.13 kJ/mol). The percentage of each conformer at ambient temperature is estimated to be with *Tt* (34 ± 1%), *Gg* (45 ± 1%), *Gt* (22 ± 1%). The first indicator is the NCCH 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. The conformational stabilities have been predicted from *ab initio* calculations utilizing several different basis sets up to aug-cc-pVTZ for 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 two most stable conformers. The determined heavy atom structural parameters for the *Tt*[*Gg*]{*Gt*} conformers are: the distances (Å) $C_1–C_2$ = 1.514(3) [1.507(3)] {1.512(3)}, $C_2–N_3$ = 1.452(3) [1.458(3)] {1.453(3)}, $C_1–F_4$ = 1.368(3) [1.370(3)] {1.369(3)}, $C_1–F_6$ = 1.368(3)[1.365(3)] {1.366(3)} and angles in (°) $\angle N_3C_2C_1$ = 115.0(5)[108.8(5)]{114.8(5)}, $\angle F_4C_1C_2$ = 110.3(5) [109.3(5)] {109.7(5)}, $\angle F_6C_1C_2$ = 110.3(5) [110.0(5)] {109.9(5)}, $\angle F_4C_1F_6$ = 106.5(5) [107.0(5)] {107.1(5)} and $\tau F_4C_1C_2N_3$ = 58.6(5) [64.5(5)] {61.2(5)}. Vibrational assignments have been provided for most of the observed bands which have been supported by MP2(full)/6-31G(d) *ab initio* calculations to predict harmonic force fields, frequencies, infrared intensities, Raman activities and depolarization ratios for the three conformers. The results are discussed and compared to the corresponding properties of some similar molecules.

1. Introduction

We recently initiated a study of the conformational stability and determined the structural parameters of several organoamines. In these studies we have been utilizing variable temperature infrared spectra of rare gas solution to obtain the enthalpy differences of the conformers. For the structural values we have obtained adjusted r_0 structural values by utilizing *ab initio* MP2(full)/6-311+G(d,p) predicted parameters for the heavy atoms which are then adjusted to agree with the microwave determined rotational constants. The parameters for the hydrogen atoms are taken from the *ab initio* calculations. By this method we [1] obtained the conformational stability of ethylamine which was determined to have the *trans* conformer more stable by 54 ± 4 cm^{-1} (0.65 ± 0.05 kJ/mol) than the *gauche* form. This value was in agreement with earlier determined values of 107 ± 70 cm^{-1} (1.28 ± 0.84 kJ/mol) from electron diffraction study [2], 110 ± 50 cm^{-1} (1.32 ± 0.60 kJ/mol) from a microwave investigation [3], and 100 ± 10 cm^{-1} (1.20 ± 0.12 kJ/mol) 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). However, without the diffuse functions the *trans* form is predicted to be the more stable conformer by 32 cm^{-1}(0.38 kJ/mol).

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 theoretical

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predictions for organoprimary amines. Nevertheless, it is of scientific interest to determine the effect of substituting one or more of the hydrogen atoms on β-carbon. One of the earliest molecules of this type studied was *n*-propylamine, $CH_3CH_2CH_2NH_2$ [9] for which the conformational stability was determined. The most stable conformer was determined to be the *Tt* form but this determination was for the solid. However the most stable conformer in the gas or the liquid need not be the same as found in the solid so it would be of interest to obtain the relative stabilities of the conformers of *n*-propylamine in the gaseous state. However, we have determined the conformational stabilities of all five of the conformers of 2-fluoroethylamine [10] where the fluorine atom might be expected to have a significant effect on the carbon–carbon distance.

For $FCH_2CH_2NH_2$, the most stable conformer was the *Gg′* form with the *Gt* conformer the second most stable form with an enthalpy difference of $62 \pm 8\ \mathrm{cm^{-1}}$ (0.74 ± 0.10 kJ/mol), 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* ($262 \pm 26\ \mathrm{cm^{-1}}$), *Tt* ($289 \pm 45\ \mathrm{cm^{-1}}$), and *Gg* ($520 \pm 50\ \mathrm{cm^{-1}}$), respectively, where it was not possible to determine whether the *Tg* or *Tt* were the more stable one. Thus the fluorine atom appears to have an effect on the conformer stability of the ethylene group so we have continued our investigations of substitutions on the β-carbon atom of ethylamine with the determination of the conformational stabilities and structural parameters of 2,2-diflouroethylamine. For these conformational and structural studies of 2,2-difluoroethylamine, $F_2CHCH_2NH_2$, we have recorded variable temperature mid-infrared spectra of xenon solutions. To support these experimental studies we have also obtained the harmonic force fields, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies from MP2(full)/6-31G(d) *ab initio* calculations with full electron correlation. To obtain predictions on the conformational stabilities we have carried out MP2(full) *ab initio* and density functional theory (DFT) calculations by the B3LYP method by 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 microwave study [11]. The results of these spectroscopic, structural and theoretical studies of 2,2-difluoroethylamine are reported herein.

2. Experimental and theoretical methods

The sample of $F_2CHCH_2NH_2$ was prepared by the reduction of 2,2-difluoroacetamide (Oakwood Chemical Co.) with lithium aluminum hydride in dry dibutyl ether. The volatile material was collected in a tube immersed in liquid nitrogen and first purified by trap-to-trap distillation and then finally by using a low-pressure, low-temperature purification column.

The mid-infrared spectrum of the gas (Fig. 1A) and solid (Fig. 2A) were obtained from 3500 to 300 $\mathrm{cm^{-1}}$ 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 theoretical resolution used to obtain the spectrum of the gas was 0.5 $\mathrm{cm^{-1}}$ and 128 interferograms were added and transformed with a boxcar truncation function. For the spectrum of the solid theoretical resolution of 2 $\mathrm{cm^{-1}}$ was used with 128 interferograms added and truncated. Multiple annealings were required to obtain satisfactory spectra of the solid.

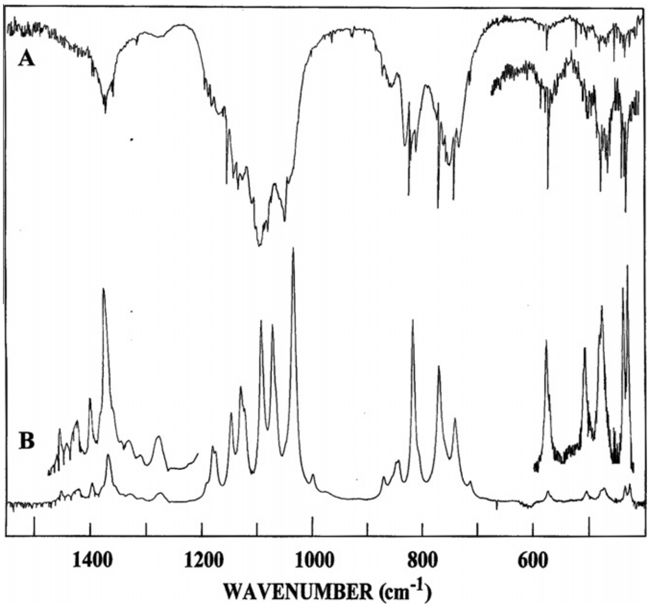

Fig. 1. Mid-infrared spectra of 2,2-difluoroethylamine (A) gas; (B) Xe solution at −65 °C.

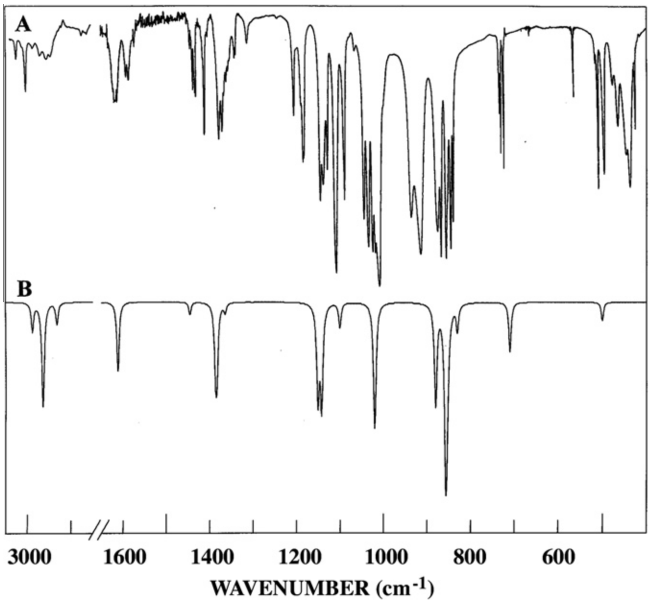

Fig. 2. Comparison of experimental and predicted infrared spectra of 2,2-difluoroethylamine: (A) infrared spectra of the solid; (B) simulated spectrum of *Tt* conformer.

The mid-infrared spectra (3500–400 $\mathrm{cm^{-1}}$) of the sample dissolved in liquefied xenon (Fig. 1B) at ten different temperatures (−55 °C 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 were collected at 1.0 $\mathrm{cm^{-1}}$ 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 temperature was maintained with boiling liquid nitrogen and monitored by two Pt thermoresistors. After cooling to the designated temperature, a small amount of the sample was condensed into the cell and the system was then