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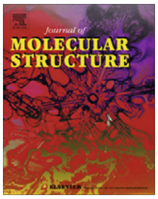

Microwave, infrared, and Raman spectra, r_0 structural parameters, conformational stability, and vibrational assignment of ethynylcyclohexane

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ABSTRACT

The FT-microwave spectrum of ethynylcyclohexane, c-$C_6H_{11}CCH$ has been investigated from 11,000 to 21,000 MHz and 32 transitions for the chair-equatorial conformer and 22 transitions for the chair-axial form have been observed and assigned from which the rotational constants and five centrifugal distortion constants have been obtained. By utilizing the six 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 conformers. The determined heavy atom structural parameters for the equatorial[axial] conformer are: the distances (Å) $C_1{-}C_{9,10} = 1.532(3)[1.537(3)]$, $C_{9,10}{-}C_{15,16} = 1.544(3)[1.534(3)]$, $C_4{-}C_{15,16} = 1.541(3)[1.545(3)]$, $C_6{\equiv}C_7 = 1.210(3)[1.212(3)]$ and angles in degrees: $\angle C_1C_{9,10}C_{15,16} = 111.0(5)[111.2(5)]$, $\angle C_6C_4C_{15,16} = 110.7(5)[110.3(5)]$ and $\tau C_1C_{9,10}C_{15,16}C_4 = 56.4(10)[55.3(10)]$. Variable temperature (−60 to −100 °C) studies of a xenon solution were carried out and by using 10 conformer pairs an enthalpy difference of $124 \pm 13\ cm^{-1}$ (1.48 ± 0.16 kJ/mol) was obtained with the more stable form the chair-equatorial conformer. At ambient temperature, the abundance of the chair-equatorial conformer is 55 ± 3%. By measuring the temperature dependency of the Raman spectrum of the liquid of the conformer pair at 822 (axial)/842 (equatorial) cm^{-1}, a standard enthalpy difference of $172 \pm 32\ cm^{-1}$ (2.06 ± 0.38 kJ/mol) was obtained again with the chair-equatorial conformer the more stable form. From MP2(full)/6-311 + G(d,p) *ab initio* calculations the chair-axial conformer is predicted to be more stable by 135 cm^{-1} (1.62 kJ/mol) whereas in contrast the density functional theory calculations by the B3LYP method with the same basis set gives the chair-equatorial conformer more stable by 289 cm^{-1} (3.46 kJ/mol). A complete vibrational assignment is given for the chair-equatorial conformer and most of the fundamentals for the chair-axial form have been assigned. To support the vibrational assignments, normal coordinate calculations with two scaling factors for the force constants from MP2(full)/6-31G(d) calculations were carried out to predict the fundamental vibrational frequencies, infrared intensities, Raman activities, depolarization values and infrared band contours. The results of these spectroscopic and theoretical studies are discussed and compared to the corresponding results for some similar molecules.

1. Introduction

In the 1960s through the 1980s there was extensive research for the determination of the energy or enthalpy difference between the commonly obtained axial and equatorial conformers of the monosubstituted chair-form of cyclohexane. Since many different techniques such as infrared, Raman, microwave, and NMR spectroscopies as well as electron diffraction and theoretical predictions were utilized to obtain the relative stabilities of the two conformers there were very large variations in the reported values with many of them with quite large uncertainties [1]. Additionally, for some of the molecules there was also 1,4-disubstitution, which makes comparison of the energy or enthalpy differences of the chair-axial and chair-equatorial conformers to the values obtained for the monosubstituted molecules difficult. One such molecule is 4-t-butylcyclohexanecarbonitrile [2] where the conformational preference of the cyano group was determined in t-butyl alcohol solvent to be the equatorial form from the Gibbs free energy difference. However, the temperature dependence of the equilibrium indicated that the small free energy difference is largely due to a

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[1] Taken in part from the thesis of R.M. Ward, which will be submitted in partial fulfillment for the Ph.D. degree.

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positive entropy term with a near zero enthalpy difference. However, the effect of the substitution of the t-butyl group at the 4-position was not known nor the effect of the t-butyl alcohol as the solvent. In order to obtain an enthalpy difference for cyanocyclohexane, we initiated conformation studies utilizing variable temperature infrared studies of xenon gas solutions [3]. From this study we obtained an enthalpy difference of 63 ± 9 cm^{-1} (0.75 ± 0.11 kJ/mol) but with the chair-axial form the more stable conformer. This values was supported by *ab initio* calculations, MP2(full)/6-311 + G(d,p), where a predicted energy difference of 120 cm^{-1} (1.44 kJ/mol) was obtained. Also the standard enthalpy difference of 46 ± 16 cm^{-1} (0.54 ± 0.19 kJ/mol) for the liquid was obtained from the variable temperature Raman spectra. This result was in marked contrast to the enthalpy differences we had previously obtained for chloro- and bromocyclohexane [4,5] as well as methyl- and silylcyclohexane [6,7] where for all of these molecules the chair-equatorial conformer was the more stable form. The enthalpy differences ranged from a low value of 132 ± 13 cm^{-1} (1.58 ± 0.16 kJ/mol) for chlorocyclohexane to a high value of 712 ± 71 cm^{-1} (8.52 ± 0.85 kJ/mol) for methylcyclohexane.

In general the predicted increases in the enthalpy differences from *ab initio* calculations by MP2(full) with moderate size basis sets and similar results were obtained from density functional theory calculation by the B3LYP method with similar basis sets. However in our recent enthalpy determination for cyanocyclohexane the experimental value of 63 ± 9 cm^{-1} (0.75 ± 0.11 kJ/mol) with the axial conformer more stable was significantly lower than the *ab initio* predicted values which were larger with values ranging from 255 cm^{-1} (MP2/6-311G(d,p)) to 120 cm^{-1} (MP2/6-311 + G(2d,2p)) with the arithmetic average from five basis sets of 175 ± 42 cm^{-1} (2.09 ± 0.50 kJ/mol), but with all predictions giving the axial conformer as the more stable form. However the most interesting prediction was from the B3LYP calculation where the chair-equatorial form was predicted to be more stable by 180 cm^{-1} (2.15 kJ/mol) than the axial form. It was surprising that the density functional calculations predicted the wrong conformer to be so stable. As a continuation of our studies to obtain conformational stabilities of a molecule with a significantly different substituent, except for cyanocyclohexane, we chose ethynylcyclohexane. Previous vibrational and microwave studies [8,9] of this molecule have already been performed, but the conformational energy difference had not been determined and only limited structural information obtained. In particular the predictions from *ab initio* and density functional theory calculations should be quite interesting compared to the corresponding ones from the cyano- compound.

In this study we sought to obtain the enthalpy difference between the chair-axial and chair-equatorial conformers of this substituted cyclohexane by variable temperature Raman spectra of the liquid and variable temperature infrared spectra of xenon solutions. In addition to the conformational stability studies we were interested in the effect of the ethynyl group on the cyclohexyl group particularly with respect to the r_0 structural parameters recently obtained for cyclohexane [10], silylcyclohexane [7] and cyanocyclohexane [3]. We obtained the parameters for these molecules by combining *ab initio* predicted parameters with microwave rotational constants. To support the vibrational study we have carried out *ab initio* calculations at the MP2 level with full electron correlation by the perturbation method [11] utilizing a variety of basis sets up to 6-311G(2d,2p) as well as those with the diffuse functions, i.e. 6-311 + G(2d,2p). The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay [12]. We have calculated the optimized geometries, conformational stabilities, harmonic force fields, infrared intensities, Raman activities, and depolarization ratios. Additionally, we have initialized the *ab initio* predicted force constants to obtain the centrifugal distortion constants for comparison to the experimental values from the microwave data. The results of these spectroscopic and theoretical studies are reported herein.

2. Experimental

The ethynylcyclohexane sample was purchased from Aldrich, Miluakee, WI with a stated purity of 98% and it was utilized without further purification.

The microwave spectra of ethynylcyclohexane were recorded using a “mini-cavity” Fourier-transform microwave spectrometer [13,14] at 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 2-in. range of travel. 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 ethynylcyclohexane sample was entrained in 70:30 Ne–He carrier gas mixture at 2 atm and expanded into the cavity using a reservoir nozzle [14] made from a modified Series-9 General Valve. The reservoir nozzle is mounted in a recessed region of the mirror flange, 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 is irradiated by microwave radiation generated by an Agilent Technologies E8247C PSG CW synthesizer; details of the irradiation and heterodyne detection circuitry can be found in Ref. [13]. 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, governed by the sampling rate and the length of the free induction decay record, is 2.5 kHz. Rotational transitions are split into Doppler doublets 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 is typically 13 kHz. The vacuum system can accommodate pulse repetition rates of up to 15 s^{-1} while maintaining a pressure below 10^{-4} torr, and the instrument can scan 450 MHz in 6 h while averaging 100 shots per scan segment. The frequencies for the measured transitions in the region of 11,000–21,000 MHz for the two conformers of ethynylcyclohexane are listed in Table 1 along with their assignments. Also listed are the frequency differences between the measured values and the values obtained from the determined rotational constants and the centrifugal distortion constants (Table 2).

The mid-infrared spectrum of the gas was obtained from 4000 to 230 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 1.0 cm^{-1}. One hundred and twenty-eight interferograms were added and transformed with a boxcar truncation function. All of the observed fundamental bands in the infrared spectra of the gas along with their proposed assignments are listed in Tables 3 and 4 for the equatorial and axial conformers, respectively.