



Conformational stability, r_0 structural parameters, and vibrational assignments of mono-substituted cyclobutanes: Fluorocyclobutane

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ABSTRACT

Variable temperature (-55 to -100°C) studies of the infrared spectra (3500 – 400 cm^{-1}) of fluorocyclobutane, $\text{C}_4\text{H}_7\text{F}$, dissolved in liquid xenon have been carried out as well as the infrared spectra of the gas. By utilizing eight pairs of conformers at 10 different temperatures, the enthalpy difference between the more stable equatorial conformer and the axial form has been determined to be $496 \pm 40\text{ cm}^{-1}$ ($5.93 \pm 0.48\text{ kJ/mol}$). The percentage of the axial conformer present at ambient temperature is estimated to be $8 \pm 1\%$. The *ab initio* MP2(full) average predicted energy difference from a variety of basis sets is $732 \pm 47\text{ cm}^{-1}$ ($9.04 \pm 0.44\text{ kJ/mol}$) and the average value of $602 \pm 20\text{ cm}^{-1}$ from density functional theory predictions by the B3LYP method are significantly larger than the experimentally determined enthalpy value. By utilizing previously reported microwave rotational constants for the equatorial and axial conformers combined with *ab initio* MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained. The determined heavy atom structural parameters for the equatorial [axial] conformer are: distances (Å) C–F = $1.383(3)$ [$1.407(3)$], C_α – C_β = $1.543(3)$ [$1.546(3)$], C_β – C_γ = $1.554(3)$ [$1.554(3)$] and angles ($^\circ$) $\angle\text{C}_\alpha\text{C}_\beta\text{C}_\gamma$ = $85.0(5)$ [$89.2(5)$], $\angle\text{C}_\beta\text{C}_\alpha\text{C}_\beta$ = $89.3(5)$ [$89.2(5)$], $\angle\text{F}-(\text{C}_\beta\text{C}_\alpha\text{C}_\beta)$ = $117.4(5)$ [$109.2(5)$] and a puckering angle of $37.4(5)$ [$20.7(5)$]. The conformational stabilities, harmonic force fields, infrared intensities, Raman activities, depolarization ratios and vibrational frequencies have been obtained for both conformers from MP2(full)/6-31G(d) *ab initio* calculations and compared to experimental values where available. The results are discussed and compared to the corresponding properties of some other monosubstituted cyclobutanes with halogen and pseudo-halogen substituents.

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1. Introduction

The cyclobutane molecule is puckered in the ground vibrational state which results from the steric forces being larger than the ring strain forces. The structural parameters of cyclobutane have been determined from a microwave investigation of four different deuterated isotopomers and the puckering angle was determined [1] to be $29.55(9)^\circ$. Prior to this study only the structural parameters of the equatorial chlorocyclobutane had been reported [2] from a microwave study but the reported A rotational constants were found to differ significantly from those parameters obtained by the weighted least-squares adjusted method from *ab initio* predicted

values [3]. However, from a more recent microwave investigation of both the equatorial and axial conformers of chlorocyclobutane [4] it has been possible to obtain the complete structural parameters [5] from the revised rotational constants of the equatorial conformer along with those for axial conformer combined with those predicted from the *ab initio* MP2(full)/6-311+G(d,p) calculations. By utilizing the *ab initio* predicted parameters in combination with previously reported microwave rotational constants it has been possible to obtain complete r_0 structural parameters in addition to chlorocyclobutane for cyclobutylamine [6], bromocyclobutane [7], cyanocyclobutane [8], and cyclobutanol [9]. All of these molecules have at least two conformers present at ambient temperature. By variable temperature infrared investigations of rare gas solutions [5–9] the enthalpy differences have been determined after confident vibrational assignments have been made by using *ab initio* predicted frequencies, infrared band contours and intensities, along with Raman activities and depolarization values. From far infrared and low frequency Raman spectra of the gases it has been possible to obtain the potential function governing the conformational interchange for many of these molecules. A comparison of the dif-

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ferent values of the heavy atom structural parameters and the barrier to inversion and enthalpy differences has been made along with predicted energy differences.

As a continuation of our conformational and structural determination of monosubstituted cyclobutanes with halogen and pseudo-halogen substituents we have investigated the temperature dependent infrared spectra of fluorocyclobutane in xenon solutions to obtain the enthalpy difference between the two conformers. In the initial study [2] of the microwave spectrum of fluorocyclobutane the structural parameters could not be obtained from the three experimentally obtained rotational constants. Therefore, corresponding parameters from chlorocyclobutane were used for fluorocyclobutane along with an estimated C–F bond distance of 1.37 Å. These parameters were sufficient to provide rotational constants which satisfactorily agreed with the experimentally determined ones [2].

Later by weighted least-squares adjustment method the C–F distance and the angle of the fluorine atom to the plane of the ring were determined [10], by utilizing the three experimentally determined rotational constants from the initial microwave study [2] along with the remaining parameters, to be the same as the corresponding parameters obtained for chlorocyclobutane [3]. Therefore, to obtain a more complete structural parameter determination for fluorocyclobutane we have combined the *ab initio* MP2(full)/6-311+G(d,p) predicted parameters with the six experimentally determined rotational constants [4] for the two forms to obtain the complete structural parameters for both conformers of fluorocyclobutane.

2. Experimental

The fluorocyclobutane sample was prepared by replacing the chlorine atom in chlorocyclobutane (Sigma–Aldrich Chemical Co., with stated purity of 97%) with a fluorine atom by allowing the chlorocyclobutane to drip onto powdered AgF_2 which had been dried under vacuum at 110 °C for 24 h. The sample was purified by a low-temperature, low-pressure fractionation column and the purity of the sample was verified by comparing the infrared spectrum with that previously reported [11].

The mid-infrared spectrum of the gas (Fig. 1B) was obtained from 4000 to 250 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 cm^{-1} . One hundred twenty-eight interferograms were added and transformed with a boxcar truncation function. The frequencies for the predicted and observed fundamentals are listed in Tables 1 and 2.

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

3. *Ab initio* calculations

The *ab initio* calculations were performed with the Gaussian-03 program [12] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the

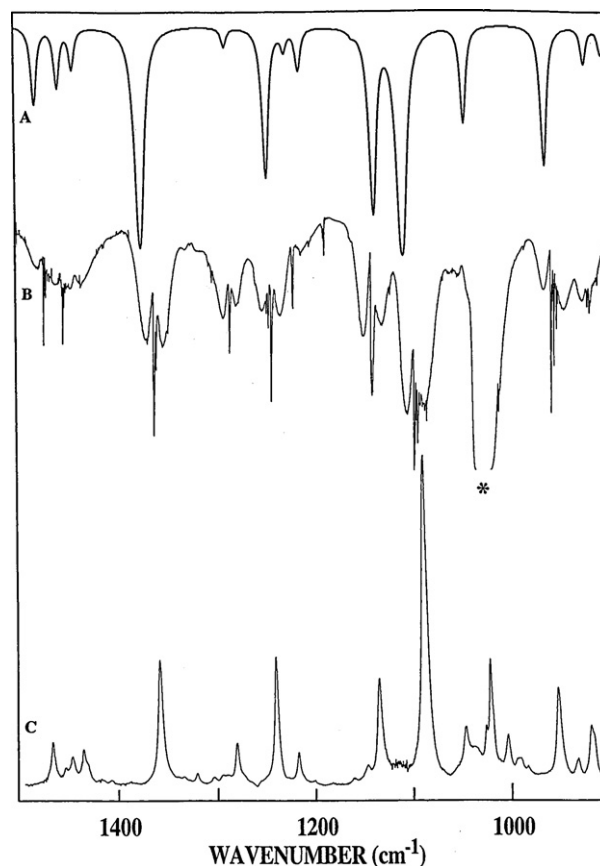


Fig. 1. Comparison of experimental and predicted mid-infrared spectra of fluorocyclobutane: (A) simulated spectrum of equatorial conformer; (B) observed infrared spectrum of the gas, asterisk denotes an impurity and (C) Xe solution at -70°C .

simultaneous relaxation of all geometric parameters using the gradient method of Pulay [13]. A variety of basis sets as well as the corresponding ones with diffuse functions were employed with the Møller–Plesset perturbation method [14] to the second order MP2 with full electron correlation as well as with the density functional theory by the B3LYP method. The predicted conformational energy differences are listed in Table 3.

In order to obtain descriptions of the molecular motions involved in the fundamental modes of fluorocyclobutane, a normal coordinate analysis was carried out. The force field in Cartesian coordinates was obtained with the Gaussian 03 program at the MP2(full) level with the 6-31G(d) basis set. The internal coordinates used to calculate the **G** and **B** matrices are given in Table 4 with the atomic numbering shown in Fig. 2. By using the **B** matrix [15], the force field in Cartesian coordinates was converted to a force field in internal coordinates. Subsequently, 0.88 was used as the scaling factor for the CH stretches and CH_2 scissors whereas 0.90 was used as the scaling factor for all other modes to obtain

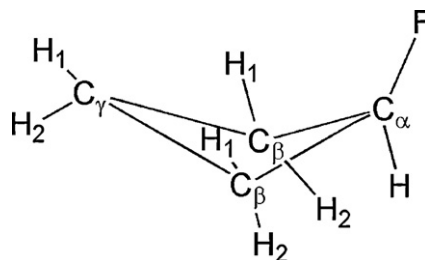


Fig. 2. Fluorocyclobutane showing atomic numbering.

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