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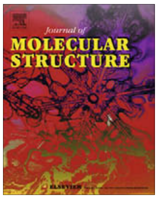

The r_0 structural parameters, conformational stability, and vibrational assignment of equatorial and axial cyanocyclobutane

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ABSTRACT

Variable temperature (−55 to −100 °C) studies of the infrared spectra (3500–400 cm^{-1}) of cyanocyclobutane, c-C_4H_7CN, dissolved in liquid xenon have been carried out. The infrared spectra of the gas and solid, as well as, the Raman spectrum of the liquid have also been recorded. 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 254 ± 12 cm^{-1} (3.03 ± 0.15 kJ/mol). The percentage of the axial conformer present at ambient temperature is estimated to be 23 ± 1%. The *ab initio* MP2(full) average predicted energy difference for a variety of basis sets is 238 ± 23 cm^{-1} in excellent agreement with the experimental ΔH value, but the average value of 331 ± 7 cm^{-1} from density functional theory predictions by the B3LYP method is significantly larger than the experimentally determined enthalpy value. By utilizing previously reported microwave rotational constants for both 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: the distances (Å) $C{\equiv}N = 1.160(3)$ [1.160(3)], $C_\alpha{-}(CN) = 1.461(3)$ [1.468(3)], $C_\alpha{-}C_\beta = 1.557(3)$ [1.562(3)], $C_\beta{-}C_\gamma = 1.549(3)$ [1.550(3)] and angles (°) $\angle C_\alpha C_\beta C_\gamma = 87.8(5)$ [89.1(5)], $\angle C_\beta C_\alpha C_\beta = 88.3(5)$ [87.9(5)], $\angle NC(C_\beta C_\alpha C_\beta) = 130.9(5)$ [120.0(5)] and a puckering angle of 28.5(5) [24.1(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 similar molecules.

1. Introduction

There has been interest in the conformational equilibrium of monosubstituted cyclobutanes for many years but from the initial microwave studies of flouro- [1], chloro- [1], bromo- [2], and cyanocyclobutane [3] only the single equatorial conformer was found. However, there was evidence from vibrational spectra that a second conformer was present at ambient temperature for some of the monosubstituted cyclobutanes [4–9]. Subsequent microwave studies of chloro- [10], fluoro- [11], and cyanocyclobutane [12] have resulted in the identification of the axial form for all three of these molecules. Additionally from the later study [10] of chlorocyclobutane significantly different values were obtained of the rotational constants for several of the isotopes originally reported [1] from which the structural parameters were obtained. In an attempt [13] to utilize the initially reported rotational constants for chlorocyclobutane to obtain the structural parameters it was not possible to obtain agreement with several of the values of the A rotational constants. However, with the newer A values it was possible to obtain the structural parameters from *ab initio* calculations with the microwave data for the complete structural determination of chlorocyclobutane [14] which was consistent with the corresponding parameters of chlorocyclobutane [10]. As a continuation of the determination of the structural parameters of monosubstituted cyclobutanes we turned our attention to cyanocyclobutane. From the initial microwave investigations [15,3] of cyanocyclobutane, which appeared almost at the same time, only the spectrum of the equatorial conformation was assigned. These results were consistent with the previously reported [5] potential function for the ring-puckering mode of cyanocyclobutane which had a single well. However from further microwave studies [12] the spectrum of the axial conformer was identified and assigned from which the rotational constants were obtained. Additionally a new potential function governing the ring-puckering

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mode was proposed [12] with three bound states of the axial conformer with an enthalpy difference of 258 ± 50 cm^{-1}. Later an infrared and Raman study of cyanocyclobutane was reported [16] and the enthalpy difference of 402 ± 33 cm^{-1} for the liquid was obtained from the temperature variation of the Raman spectrum. Also the barrier to ring conversion was proposed [16] to be less than 418 cm^{-1} and assignments were made for 12 of the 20 A' normal modes of the equatorial conformer along with 10 of the 13 A'' fundamentals. Thus, in addition to the structure parameters we were also interested in obtaining a complete vibrational assignment for the equatorial conformer as well as several of the axial fundamentals which would be supported by *ab initio* calculations for predictions of the barrier to ring inversion and fundamental frequencies for both conformers with infrared intensities and Raman activities. The results of these experimental and theoretical investigations of cyanocyclobutane are reported herein.

2. Experimental

The sample of cyanocyclobutane was purchased from Aldrich Chemical Co., with stated purity of 97%. The sample was further purified by low-temperature, low-pressure fractionation column and the purity of the sample was verified by comparing the infrared spectrum with that previously reported [16].

The mid-infrared spectra of the gas and solid 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 theoretical resolution used to obtain the spectrum of the gas was 0.5 and 2.0 cm^{-1} for the spectra of the solid. One hundred and 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. 1B) 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. A very small sample was introduced into the cell after cooling to the designated temperature. The system was then pressurized with the noble gases, which condensed in the cell, allowing the compound to dissolve.

The Raman spectrum (Fig. 2) was 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 fundamentals in the spectrum of the liquid with their proposed assignments are listed in Tables 1 and 2.

3. *Ab initio* calculations

The LCAO-MO-SCF restricted Hartree–Fock calculations were performed with the Gaussian 03 program [17] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay [18]. A variety of basis sets as well as the corresponding ones with diffuse functions were employed with the Møller–Plesset perturbation method [19] to the 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 3.

In order to obtain a complete description of the molecular motions involved in the fundamental modes of cyanocyclobutane, a normal coordinate analysis has been 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. 3. By using the B matrix [20], the force field in Cartesian coordinates was converted to a force field in internal coordinates. Subsequently, 0.90 for all coordinates were used, along with the geometric average of scaling factors for interaction force constants, to obtain the fixed scaled force field and resultant wavenumbers. A set of symmetry coordinates was used (Table 5) to determine the corresponding potential energy distributions (PEDs). A comparison between the observed and calculated wavenumbers, along with the calculated infrared intensities, Raman activities, depolarization ratios and potential energy distributions for the *equatorial* and *axial* conformers, which are given in Tables 1 and 2, respectively.

The infrared spectra were predicted from the MP2(full)/6-31G(d) calculations. The predicted scaled frequencies were used together with a Lorentzian function to obtain the calculated spectra. Infrared intensities determined from MP2(full)/6-31G(d) calculations 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 $[(N\pi)/(3c^2)][(\partial\mu_x/\partial Q_i)^2 + (\partial\mu_y/\partial Q_i)^2 + (\partial\mu_z/\partial Q_i)^2]$. In Fig. 1 a comparison of the experimental and simulated infrared spectra of cyanocyclobutane is shown. Infrared spectrum of the cyanocyclobutane at ambient temperature (Fig. 1A) and the predicted infrared spectra for the pure *equatorial* (Fig. 1E) and *axial* (Fig. 1D) conformers, as well as the mixture (Fig. 1C) of the two conformers with relative concentrations calculated for the equilibrium mixture at ambient by using the experimentally determined enthalpy difference are presented. The predicted spectrum is in relatively good agreement with the experimental spectrum which indicates the utility of the scaled predicted frequencies and intensities for supporting the vibrational assignment.

Also to further support the vibrational assignments, we have simulated the Raman spectra from the *ab initio* MP2(full)/6-31G(d) results. The evaluation of Raman activity by using the analytical gradient methods has been developed [21–24]. The activity S_j can be expressed as: $S_j = g_j(45\alpha_j^2 + 7\beta_j^2)$, where g_j is the degeneracy of the vibrational mode j, α_j is the derivative of the isotropic polarizability, and β_j is that of the anisotropic polarizability. To obtain the polarized Raman scattering cross-sections, the polarizabilities are incorporated into S_j by multiplying S_j with $(1-\rho_j)/(1+\rho_j)$, where ρ_j is the depolarization ratio of the jth normal mode. The Raman scattering cross-sections and calculated wavenumbers obtained from the Gaussian 03 program were used together with a Lorentzian function to obtain the simulated Raman spectra. Comparison of experimental Raman spectra of the liquid (Fig. 2A) and the predicted Raman spectra for the pure *equatorial* (Fig. 2D) and *axial* (Fig. 2C) conformers as well as the mixture (Fig. 2B) of the two conformers with relative concentrations calculated for the equilibrium mixture at 25 °C by using the experimentally determined enthalpy difference are shown. The predicted spectrum of