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Vibrational spectroscopy of 3,4-difluorocyclobutenes: *cis*-d_0, *trans*-d_0 and *trans*-d_4 species

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Abstract

Infrared and Raman spectra were recorded for *cis*-3,4-difluorocyclobutene (cDFCB) and *trans*-3,4-difluorocyclobutene-d_4. Unscaled density functional theory (DFT) calculations of frequencies and intensities at the B3LYP/6-311++G(d,p) level supported the complete assignment of the vibrational fundamentals. The previous assignment of fundamentals of *trans*-3,4-difluorocyclobutene was revised. An unusual blue shift occurs for the methylenic CH-stretching frequencies of *cis*-3,4-difluorocyclobutene in going from the gas phase to the liquid phase. This hydrogen bond effect is related to similar observations recently reported and interpreted. The blue shift does not occur for the vinylic C—H bonds of the *cis* isomer and does not occur for either type of C—H bond in the *trans* isomer.

Keywords: Infrared spectra; Raman spectra; DFT predictions of frequencies and intensities; Vibrational fundamentals; Blue-shifted CH-stretching frequencies; Fluorocarbons

1. Introduction

A study of *cis*-3,4-difluorocyclobutene (cDFCB) has been missing from the investigations of the vibrational spectra of the 3,4-difluorocyclobutenes and 3,4-dichlorocyclobutenes. Suzuki and Nibler reported an assignment of vibrational fundamentals for *cis*-3,4-dichlorocyclobutene (cDClCB) [1]. Craig et al. developed a vibrational assignment for *trans*-3,4-dichlorocyclobutene (tDClCB) and made some revisions in the assignment of the *cis* isomer [2]. Our laboratory also reported an assignment for *trans*-3,4-difluorocyclobutene (tDFCB) [3]. A microwave investigation has provided a complete structure of tDFCB [4].

The earlier studies of dihalocyclobutenes were made without the benefit of quantum chemical (QC) calculations to reinforce the vibrational assignments and to explore the *cis*–*trans* isomerization equilibrium. The present study incorporates hybrid density functional theory (DFT) calculations done with the B3LYP/6-311++G(d,p) model. Raman intensities and depolarization ratios as well as infrared intensities are predicted. These calculations have led to some revisions in the assignments of the vibrational fundamentals of tDFCB and have aided the new assignments for cDFCB and tDFCB-d_4.

The investigation of the vibrational spectra of cDFCB has provided another example of an unusual blue shift in a CH-stretching frequency in going from the gas phase to a condensed phase. Good examples of this effect, which is opposite to the well-known red shift for hydrogen bonding, have recently been reported and investigated theoretically [5,6].

Access to full spectra of cDFCB was delayed by the synthetic challenge to making this substance. For the DClCB isomers, the *cis* isomer is the product of the published synthesis [7,8]. The *trans* isomer of DClCB, which is the dominantly more stable isomer, is readily made by catalysis of the isomerization of the *cis* isomer with the Lewis acid aluminum chloride [9]. In contrast to the outcome for cDClCB, the principal product of the published synthesis of DFCB is the *trans* isomer [3]. The *cis* isomer of difluorocyclobutene

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is formed as a minor product (approximately, 5% or less) in the synthesis of the *trans* isomer. Without success we investigated several alternative routes to producing cDFCB and finally returned to its painstaking synthesis as the byproduct in the synthesis of the *trans* isomer. Likely catalysts for the *cis*–*trans* isomerization of DFCB faled to give an observable amount of the *cis* isomer. The vibrational spectroscopy of cDFCB reported in this paper was done with only about 0.2 mmol of almost pure material.

Contributing to the evidence in support of the assignment of fundamentals of the DFCB isomers is the assignment of the fundamentals of the d_4 isotopomer of tDFCB, as reported here. tDFCB-d_4 became available when it was prepared for use in the microwave investigation of the structure of tDFCB [4]. tDFCB-d_4 was prepared by making perdeuterocyclooctatetraene (COT-d_8) from acetylene-d_2 by the Reppe method [10,11] and using COT-d_8 in the synthesis that leads to cDClCB-d_4 and thence to tDFCB-d_4 by reaction with AgF_2.

We had hoped that cDFCB-d_4 would be obtained in a useful amount as a byproduct of the synthesis of tDFCB-d_4 but were disappointed.

2. Experimental

2.1. Syntheses

cDFCB was prepared in variable, small amounts (5% or less) as a byproduct of the repeated small scale syntheses of tDFCB by the reaction of cDClCB with AgF_2 [3]. In preparative gc the peak for cDFCB follows and overlaps the peak of byproduct *trans*-3-chloro-4-fluorocyclobutene (tClFCB) [3]. Repeated gc separation was required to obtain a reasonably pure sample of cDFCB, which retained a bit of tClFCB. cDFCB was dried by distillation through P_2O_5.

tDFCB-d_4 was the product of reaction of AgF_2 with cDClCB-d_4 [3]. The precursor cDClCB-d_4 was obtained from the thermal decomposition in vacuo of the Diels–Alder adduct of the reaction of dimethyl acetylenedicarboxylate and the product of adding chlorine to COT-d_8 [4,7].[1] COT-d_8 was prepared in a bomb by first dissolving acetylene-d_2 and the nickel acetylacetonate (Aldrich) catalyst in tetrahydrofuran in the absence of moisture [8,9]. Our experience with this challenging reaction was described in detail previously [4]. The desired production of a useful amount of cDFCB-d_4 as a byproduct of the production of tDFCB-d_4 gave a gc peak that was largely *trans*-3-chloro-4-fluorocyclobutene-d_4.

NMR spectra of cDFCB, which confirmed its structure, were reported before [3]. From vapor pressure measurements from 0–15 °C and a $\ln P$ versus $1/T$ extrapolation, the b.p. of cDFCB was estimated as 96 °C. The m.p. is about −59 °C. The vapor pressure at 25 °C is approximately 40 Torr.

2.2. Spectroscopy

IR spectra were recorded on a Perkin-Elmer 1760 FT mid-IR instrument and a PE 1700X far-IR instrument. Gas cells were stopcock-equipped Wilmad minicells with 10 cm path lengths and a potassium bromide or a polyethylene window of 2.5 cm diameter. In the mid-IR region the reported spectra were the difference between 25 scans of the cell background and at least 9 scans of the sample at 0.5 cm^{-1} resolution. In the far-IR region, the reported spectra are the difference between 100 scans each of the cell background and the sample at 1 cm^{-1} resolution. Mid-IR spectra of cDFCB were also recorded at 0.1 cm^{-1} resolution on a Nicolet 760 Magna spectrometer.

Raman spectra were obtained with a Spex Ramalog 5 instrument, an associated Nicolet 1180 computer, and a Coherent Innova 70 argon-ion laser. The exciting line, which was at 514.5 nm, was isolated with a homebuilt Amici prism-slit system. Laser power was about 270 mW. Resolution was approximately 2.5 cm^{-1}. Observations were made with 90° geometry and the polarization analyzer in the scattered beam. Samples were sealed in 1.8 mm Kimax capillaries and studied as liquids at low temperature in a Harney–Miller-type cooling jacket. The uncertainty in the frequency measurements in the Raman spectra was $\pm 2\ cm^{-1}$. Depolarization ratios were the dividends of peak heights for perpendicular and parallel settings of the polarization analyzer.

2.3. Calculations

Quantum chemical (QC) calculations were done with Gaussian98 software on a Gateway PC with a Pentium 4 processor [12]. The hybrid DFT calculations used a B3LYP/6-311++G(d,p) model. The tight convergence criterion and a grid of 99 radial shells around each atom and 302 angular points in each shell were used. No scaling of the calculated force constants or frequencies was done. The Cartesian coordinates for cDFCB and tDFCB from the geometry optimizations are in Table 1.

3. Results and discussion

3.1. Equilibrium

For the isomerization reaction:

$$\text{cDFCB(g)} \rightarrow \text{tDFCB(g)}$$

The QC-calculated electronic energy difference is $-13.6\ kJ\ mol^{-1}$, and the calculated entropy difference

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[1] An interesting observation regarding the addition of Cl_2 to cyclooctatetraene in CCl_4 should be investigated further. In reference [7], it is suggested that Cl_2 addition occurs on the double bond in the four-membered ring of the small amount of bicyclooctatetraene in equilibrium. Our observations show that the proton and ^{13}C NMR spectra change dramatically during the first 24 h after this reaction. Thus, it is likely that Cl_2 does a *cis* addition to one double bond in the cyclooctatetraene ring, and this monocyclic product converts to the bicycle ring system and then slowly to the *trans* isomer.