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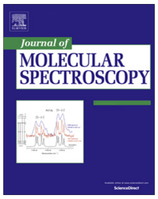

Effect of fluorination on methyl internal rotation barriers: Microwave spectra of cyclopropylfluoromethyl silane (c-$C_3H_5SiHFCH_3$) and cyclopropyldifluoromethyl silane (c-$C_3H_5SiF_2CH_3$)

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ABSTRACT

Rotational spectra for two conformers of c-$C_3H_5SiHFCH_3$ (cyclopropylfluoromethyl silane, CFMS) and one conformer of c-$C_3H_5SiF_2CH_3$ (cyclopropyldifluoromethyl silane, CDFMS) have been observed by a combination of chirped-pulse and resonant cavity Fourier-transform microwave spectroscopy in the 7.5–16.5 GHz range. All rotational transitions were doubled by up to several megahertz into *A* and *E* states as a result of methyl group internal rotation, and analysis of measured transitions using a combined axis method yielded internal rotation barriers of *ca.* 6.0 kJ mol^{-1} for the two conformers of CFMS and *ca.* 5.2 kJ mol^{-1} for CDFMS, revealing a systematic decrease in the barrier as fluorine atoms are added to the silicon. Dipole moment information is also available for the CDFMS species.

1. Introduction

Previous microwave [1] and IR [2] work explored conformational properties of cyclopropylmethylsilane (c-$C_3H_5SiH_2CH_3$, CMS) and its germanium analog cyclopropylmethylgermane (c-$C_3H_5GeH_2CH_3$, CMG) [3,4]. The microwave studies revealed that only a single conformer was observed for both molecules and that the methyl group internal rotation barrier was lower in the Ge species than in the Si species. In this work we present rotational spectroscopic assignments for two fluorinated analogs of CMS: cyclopropylfluoromethyl silane (c-$C_3H_5SiHFCH_3$, CFMS) and cyclopropyldifluoromethyl silane (c-$C_3H_5SiF_2CH_3$, CDFMS). Rotation about the Si—C(cyclopropyl) bond in both compounds gives rise to three possible staggered arrangements. In CDFMS two of these structures will be equivalent conformers with one F atom located over the cyclopropyl ring, with the third structure having the methyl group in that position, while in CFMS the H, F, or methyl group can be located over the cyclopropyl ring, leading to three unique conformers. In the present paper, relative stabilities of these different conformers will be assessed by ab initio calculations and any species present in a supersonic expansion will be characterized via their rotational spectra.

In addition, characterization of the title compounds provides a series of related molecules with none (CMS) [1], one (CFMS) or two (CDFMS) F atoms on the central Si atom, allowing examination of the effect of this fluorination on the barrier to internal rotation of the methyl group. In previous studies of methyl silane and its fluorinated analogs [5–7], fluorination was found to reduce the barrier, whereas monofluorination of the all-carbon analog, ethane, actually increases the barrier (see, for example, Table XI in Ref. [8]). Unfortunately, the all-carbon analog for CMS, ethylcyclopropane, is expected to have a small (<0.1 D) dipole moment, making it poorly suited for microwave characterization, hence only IR and Raman data [9] is available; no data on fluorine substituted ethylcyclopropanes exists.

The goal of the present study is therefore to identify which conformers are present in the supersonic expansion and to characterize their rotational spectra to furnish values for the barrier to methyl group rotation in each case to see how it varies as the degree of fluorination at the silicon atom is changed.

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2. Experimental

2.1. Microwave spectroscopic measurements

Samples of cyclopropylfluoromethyl silane (CFMS) and cyclopropyldifluoromethyl silane (CDFMS, CAS Registry Number 57522-86-8) were synthesized and purified at the College of Charleston, South Carolina, as described below, and then sent to Eastern Illinois University for microwave spectroscopic measurements. Rotational spectra for a single conformer of CDFMS and two conformers of CFMS were measured using both a 480 MHz bandwidth chirped-pulse [10] Fourier-transform microwave (FTMW) spectrometer (a scaled-down version of the original design by Pate [11]), and a Balle-Flygare type [12] resonant cavity FTMW spectrometer [13]. Initial scans over the 8–16 GHz region were carried out using the chirped-pulse spectrometer, with a total of 2000 free induction decays averaged within each 480 MHz frequency segment. Absolute transition frequencies were obtained from a LabView program which compares overlapping spectral segments that are offset by 240 MHz, and assembles the resulting scans into a full broadband spectrum. Gas samples for both molecules consisted of approximately 1% of the molecule of interest seeded in He/Ne (17.5%/82.5%, BOC Gases) and delivered to a General Valve Series 9 valve at a total pressure of 2.5 atm. In both chirped-pulse and resonant cavity instruments, the gas sample was introduced into the vacuum chamber perpendicular to the direction of microwave propagation, resulting in transitions with full-widths at half maximum height of around 130 kHz (chirped-pulse instrument) and 30 kHz (resonant cavity instrument). In both cases, transition frequencies were reproducible to 4 kHz or better. Once initial spectral assignments were made from the broadband scan, transitions were remeasured on the resonant cavity instrument to ensure all fine splittings were identified, and to allow measurement of less intense transitions.

Dipole moment measurements were carried out only for CDFMS (since this had more intense transitions) using a pair of steel mesh plates spaced ~31 cm apart and straddling the gas expansion in the resonant cavity instrument. Electric fields of up to approximately 330 V/cm were applied, and were calibrated using the $J = 1 \leftarrow 0$ transition of OCS, assuming a dipole moment of 0.71519(3)D [14].

2.2. Synthesis

The samples of c-$C_3H_5SiHFCH_3$, and c-$C_3H_5SiF_2CH_3$ were prepared in two steps. Firstly, cyclopropylbromide was reacted with magnesium in dry ether using the Grignard method and t hen coupled with methyldichlorosilane or methyltrichlorosilane in dry ether under dry nitrogen gas. Secondly, the product methyldichlorosilylcyclopropane or methylchlorosilylcyclopropane were obtained, respectively and were separated from the ether under reduced pressure and then fluorinated with freshly sublimed antimony trifluoride without solvent. The samples were purified twice by trap-to-trap distillation. The authenticity of the samples were verified by comparing the infrared, ^1H, ^{13}C, and ^{29}Si NMR, and microwave spectra.

2.3. Ab initio calculations

Initial rotational spectroscopic assignments for both compounds were guided by rotational constants obtained from ab initio optimizations using the Gaussian 09 [15] program suite at the MP2/6-311++G(2d,2p) level. No symmetry constraints were imposed during structure optimizations and default optimization thresholds were used. Harmonic vibrational frequency calculations provided zero-point energy corrected energies for identification of the most stable conformers. Principal axis coordinates for all five conformers considered for the two molecules are available as Supplementary Material.

3. Results

3.1. Ab initio optimizations

For the doubly fluorinated CDFMS, rotation around the Si–C(cyclopropyl) bond leads to only two possible staggered conformations, with either a fluorine atom (conformer A1, Fig. 1) or methyl group (A2, Fig. 1) over the cyclopropyl ring. As can be seen from the relative energies in Table 1, conformer A1 is predicted to be most stable, and dipole moment predictions suggest that transitions arising from all three dipole components should be easily visible in the rotational spectrum. Conformer A2, although having similar rotational constants to conformer A1, should be readily distinguishable from A1 based on its quite different dipole moment components.

For the singly fluorinated CFMS, Fig. 2 shows the three possible staggered conformers that result from rotation about the Si–C(cyclopropyl) bond, with an H atom (conformer B1), F atom (conformer B2) or methyl group (conformer B3) situated over the cyclopropyl ring; conformer B1 is predicted to be most stable (Table 1). These three conformers should be readily distinguishable by their rotational constants and dipole moment components.

3.2. Rotational spectra

The spectrum for CDFMS was scanned first since it was expected to be more intense due to larger predicted dipole moment components and the expectation that only a single conformer would likely be observed (Table 1). Patterns consistent with expected transitions for conformer A1 were located in the broadband scan close to predicted frequencies. Many transitions exhibited a small doubling (by up to 5 MHz) due to internal rotation of the methyl group; most of these fine splittings were sufficiently large to observe in the original broadband scan, although some required the higher resolution of the resonant cavity spectrometer to fully resolve (Fig. 3). After identification of the lowest energy conformer of CDFMS, a large number of additional transitions remained in the spectrum. These were eventually assigned to the most stable conformer B1 of CFMS (see Table 1) which was present as an impurity in the original CDFMS sample.

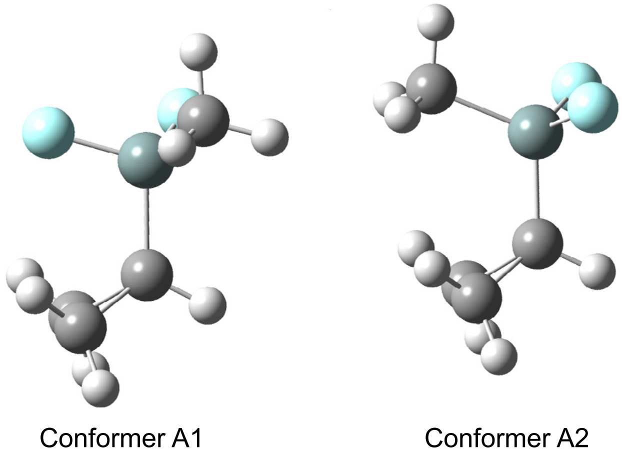

Fig. 1. Ab initio conformers A1 and A2 for cyclopropyldifluoromethyl silane (CDFMS).