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Raman and infrared spectra, quantum chemical calculations, conformations and spectral assignments of 1-chloro-1-methyl-1-silacyclohexane

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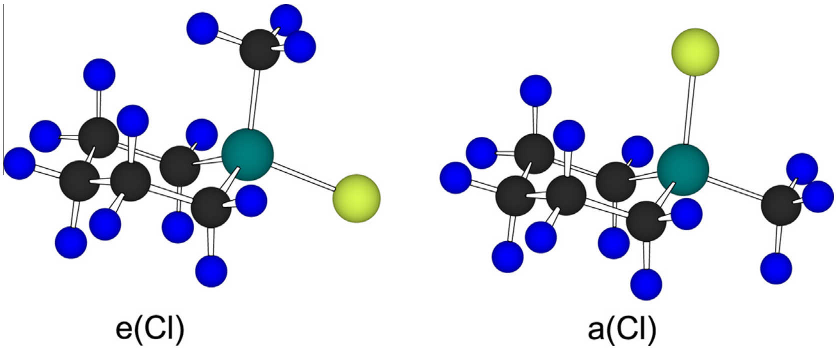
HIGHLIGHTS

- Infrared and Raman spectra of 1-chloro-1-methyl-1-silacyclohexane.
- Attribution of equatorial (*e*) and axial (*a*) conformers from spectra of the crystal.
- Assignments of the A′ and A″ modes of the *e* and *a* conformers.
- Determination of the enthalpy difference Δ*H* between the *e* and *a* conformers from variable temperature Raman spectra.
- DFT calculations of vibrational modes in the anharmonic approximation.

GRAPHICAL ABSTRACT

The infrared and Raman spectra of 1-chloro-1-methyl-1-silacyclohexane were recorded between 293 and 78 K, and a conformational equilibrium was established in the vapor, liquid, supercooled liquid and solid plastic phases. The *a*(Cl) had lower enthalpy than *e*(Cl); only *a*(Cl) was present in the crystal. DFT calculations revealed ΔH(*e*(Cl)–*a*(Cl)) to be in the range 3.2–2.4 kJ mol^{-1}. The 32 A′ and 25 A″ modes of both conformers were assigned from the spectra and supported by B3LYP/cc-PVTZ calculations in the anharmonic approximation.



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ABSTRACT

A 1,1-disubstituted silacyclohexane, 1-chloro-1-methyl-1-silacyclohexane, $C_5H_{10}SiClCH_3$, was synthesized and studied by infrared and Raman spectroscopy. The infrared spectra of the vapor and liquid were recorded at ambient temperature and the solid sample investigated at 78 K. Negligible spectral changes ocurred at 78 K compared with the fluid state, but after annealing to ca. 165 K an apparent crystal was formed.

Raman spectra of the liquid were recorded at 293 K and depolarization data obtained. Additional Raman spectra were recorded at various temperatures between 293 and 143 K. A supercooled liquid appeared after slow cooling, but an amorphous solid phase was observed after shock freezing to 78 K. After annealing, a plastic phase was observed and an anisotropic crystal appeared after further annealing. In the crystalline phase spectral shifts and some vanishing bands were observed and only the *a* (Cl) conformer remained.

The compound exists in two conformers, *equatorial* (*Cl*) (*e*) and *axial* (*Cl*)(*a*) in the liquid, amorphous and plastic phases, but only the *a*-conformer was present in the crystal. The experimental results suggest that the *a*-conformer has 1.5 ± 0.5 kJ mol^{-1} lower enthalpy than *e* in the liquid.

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B3LYP calculations with various basis sets and the G3 model chemistry gave conformational energy difference ΔE (a–e) in the range 3.2–2.4 kJ mol^{-1}. Infrared and Raman intensities, polarization ratios and vibrational frequencies for the two conformers were calculated. The 32 A′ and 25 A″ modes for the e(Cl) and a(Cl) conformations were assigned, supported by anharmonic B3LYP/cc-pVTZ calculations.

1. Introduction

The low energy form of the cyclohexane ring is the chair conformation while the additional boat and twist forms have much higher energies, and they are therefore not observed under ordinary conditions. In most monosubstituted cyclohexanes [1,2] the *equatorial* (e) conformers have lower enthalpy than the *axial* (a) conformer, leading to a larger abundance of the e-conformers in the vapor and in the liquid states. In the crystalline state obtained by cooling or compressing the liquids, most cyclohexanes exist in the e-form since the a-conformers are generally not accommodated in the crystal lattice.

If a carbon atom in cyclohexane is substituted with a silicon atom, a silacyclohexane is formed and the steric and electronic effects are changed. The silacyclohexanes are more unstable than the corresponding cyclohexanes and less experimental information is available. The parent molecule silacyclohexane has been studied by gaseous electron diffraction (GED) [3], microwave (MW) [4] and vibrational spectroscopy [5]. An important application of silacyclohexane is as a backbone in nematic liquid crystals and many patents have been made on liquid crystal displays involving derivatives of silacyclohexane. Some silacyclohexanes substituted on the silicon atom have been investigated [6]. From experimental methods involving MW [7], GED [8] and vibrational spectroscopy it has been established that most of the monosubstituted silacyclohexanes have the a-form as the preferred conformer. This conclusion has been verified by quantum mechanical calculations [9–11]. In recent years 1-fluoro-1-silacyclohexane [8,12], 1-chloro-1-silacyclohexane [13,14], 1-iodo-1-silacyclohexane [15], 1-trifluoromethyl-1-silacyclohexane [16] and 1-bromo-1-silacyclohexane [17] have been investigated by experimental methods. In 1-methyl-1-silacyclohexane, however, GED and NMR spectroscopy in solution supported by quantum chemical calculations revealed the e-conformer [18] to be more stable, while MW indicated a negligible energy difference between the conformers in the vapor phase [19]. Raman [20,21] and infrared spectral studies [21] of this compound in the liquid state confirmed that the e conformer has ca. 0.6 kJ mol^{-1} lower enthalpy than the a conformer. Moreover, a disubstituted silacyclohexane, 1-fluoro-1-methyl-1-silacyclohexane has been studied by various techniques [22], giving an enthalpy difference of 2.1 kJ mol^{-1} from variable temperature Raman spectra in the liquid, with the a (F) conformer being the more stable. We found it interesting to extend our vibrational spectral studies of the silacyclohexanes to include also the chloro analogue (Fig. 1) 1-chloro-1-methyl-1-silacyclohexane (CMSC). The results for this compound are compared with those from 1-chloro-1-silacyclohexane [14] and 1-methyl-1-silacyclohexane [21] and from infrared and Raman studies and comprehensive thermodynamic investigations of 1-chloro-1-methylcyclohexane [23].

2. Experimental

2.1. Preparation

The sample of CMSC was prepared by a modified version of an original procedure [24] involving the formation of a double Grignard of 1,5-dibromopentane in dry diethyl ether. The Grignard was then transferred to a solution of freshly distilled methyltrichlorosilane in dry ether under nitrogen atmosphere and refluxed overnight. The diethyl ether is distilled off under reduced pressure and dry pentane is added, the salt is filtered and washed twice with pentane under nitrogen. The pentane was distilled off at reduced pressure, and the final purification of the product was achieved by a trap to trap distillation.

The purity of the sample was checked by the presence of the very intense symmetric C–Si–C stretch in the Raman spectra at 628 cm^{-1}, close to the results for four related silacyclohexanes [5,12,14,21] situated between 606 and 653 cm^{-1}. The ^{13}C NMR spectrum of CMSC gave peaks at 1.001, 7.18, 23.88 and 29.55 ppm relative to TMS in agreement with the three carbon positions in the ring at the equivalent 1,5- and 2,4- positions and the 3- position relative to TMS. The methyl carbon attached to Si gives rise to the peak at 1.001 ppm.

2.2. Raman measurements

The Raman spectra were recorded with a multichannel spectrometer from Horiba (Jobin Yvon) model T 64000 employing both single and triple monochromators. The spectrometer had a CCD detector, cooled to ca. 130 K. The spectra were excited by a Millennia Pro diode-pumped (Nd:YVO$_4$ crystal) frequency-doubled laser from Spectra-Physics (Model J 40). The laser was adjusted to give approximately 50 mW of the 532 nm line on the sample, and was employed in 90° scattering geometry. The spectrometer was applied with: (1) a single monochromator using a notch filter, or a triple monochromator with (2) additive or (3) subtractive collection. The low wavenumber modes were recorded to 50 cm^{-1} employing the triple subtractive mode, compared to 120 cm^{-1} using the single monochromator and the notch filter.

The spectra were recorded at ca. 2 cm^{-1} resolution, and depolarization measurements were recorded in the 90° mode, employing a polarizer and a scrambler. The polarization unit was calibrated with carbon tetrachloride, filled into a cylindrical tube identical to that employed for CMSC. Except for very weak and/or overlapping bands, comprehensive depolarization data were obtained.

Raman spectra of the liquid, including depolarization measurements were obtained at room temperature, but additional spectra were recorded for each 10° between 293 K and 143 K in a tube of 2 mm inner diameter. The sample tube was surrounded by a glass Dewar and cooled with gaseous nitrogen evaporated from a tank [25]. It was controlled by an Eurotherm unit, using a calibrated Fe–constantan thermocouple in contact with the tube, giving approximately ±0.5 °C accuracy for the temperature of the sample tube.

From these spectra, the enthalpy difference $\Delta_{conf}H$ between the conformers in the liquid state was calculated. Various a/e band pairs were tested for determining the energy difference. The vapor of CMSC was also condensed on a copper finger at 78 K and a glassy phase was formed. The sample was heated in steps to 180 K and the amorphous deposit converted to an apparently plastic solid which crystallized around 165 K.