

THE VIBRATIONAL SPECTRA AND CONFORMATIONS OF POLYHALOGENATED CYCLOBUTANES

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ABSTRACT.

The vibrational spectra of 1-chloro-2,2,3,3-tetrafluoro- and 1-cyano-2,2,3,3-tetrafluorocyclobutane reveal that these compounds have a conformational equilibrium strongly shifted towards equatorial Cl and CN substituents, although to a smaller extent than for the chloro and cyanocyclobutane.

When a Cl and an F atom are attached to the same carbon, they will compete for the preferred equatorial position, giving relatively small enthalpy differences between the conformers. In 1-chloro-1-fluoro-, 1-chloro-1,2,2-trifluoro- and 1,1,2-trichloro-2,3,3-trifluorocyclobutane the enthalpy differences are 2.2, 2.9 and 0.9 kJ mol⁻¹ in the liquid, respectively. In 1-chloro-1,2,2-trifluoro and 1,1,2-trichloro-2,3,3-trifluorocyclobutane the ring puckering barrier was ca. 6-7 kJ mol⁻¹, for the remaining compounds it was smaller than 5 kJ mol⁻¹.

INTRODUCTION

It is well known that in monohalogenated cyclobutanes the equilibrium is highly shifted towards the equatorial conformer and recent results give enthalpy differences (ΔH^0) between the axial and equatorial conformers of 5.2 and 5.7 (vapour) and 8.2 and 9.0 kJ mol⁻¹ (liquid) for chloro- and bromocyclobutane, respectively (ref. 1). Slightly smaller conformational enthalpy differences were observed in cyanocyclobutane (ref. 2) and methylcyclobutane (ref. 3).

We have now extended our studies of halogenated cyclobutanes to include two different series of polyhalogenated cyclobutanes:

(1) 1-chloro-2,2,3,3-tetrafluoro- (TFCLOB) and 1-cyano-2,2,3,3-tetrafluorocyclobutane (TFCNCB).. In these molecules the conformational equilibrium is presumably decided by the single substituent in the 1-position, giving a strongly preferred equatorial conformer like in the monosubstituted cyclobutanes.

(2) 1-chloro-1-fluoro- (CFCB), 1-chloro-1,2,2-trifluoro- (CTFCB) and 1,1,2-trichloro-2,3,3-trifluorocyclobutane (TCTFCB) in which the Cl and F atoms, attached to the same carbon will compete for the preferred equatorial position. Much smaller enthalpy difference between the conformers are expected in these molecules.

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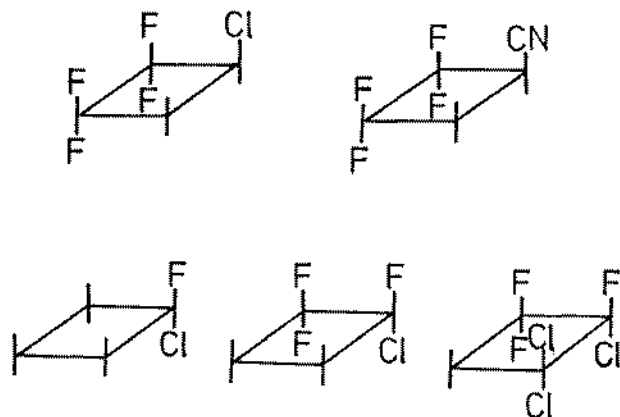


Fig. 1. Schematic structures of the halogenated (or pseudohalogenated) Cyclobutanes.

Our preliminary results for these 5 polyhalogenated cyclobutanes (Fig. 1) will be given in the present communication.

EXPERIMENTAL

The sample of CFCB was prepared in the laboratory of N. C. Craigh, Oberlin College, Ohio, USA; all the other compounds were commercial products. Whenever necessary the samples were purified by gas chromatography.

The IR spectra were recorded with Bruker FTIR spectrometers IFS-88(4000-400 cm^{-1}) and IFS-114c (700-50 cm^{-1}) and with a Perkin-Elmer model 225 dispersive spectrometer. Matrix isolation spectra in argon and nitrogen matrices with a ratio 1: 500 were obtained at 14 K with a closed cycle cryostat from Air Products. The vapour- matrix gas mixtures were heated to various temperatures between 313 and 900 K with a hot nozzle of quartz before being quenched on the cold window. IR spectra of the original deposits and of those obtained after annealing to 34-38 K were recorded. Conventional low temperature IR spectra of the amorphous and crystalline solids were recorded at 85 K, and high pressure crystal spectra were recorded at ambient temperature with a diamond anvil cell.

Raman spectra, including polarization measurements were recorded with a Dilor RTI 30 spectrometer, interfaced to the Aspect 2000 computer and the samples were excited by an argon ion laser from Spectra Physics. Spectra of the samples as liquids and as crystalline solids were recorded at different temperatures in a Miller-Harney cell (ref. 4), and additional low temperature spectra were measured with a solid deposited on a copper finger, cooled with liquid nitrogen.

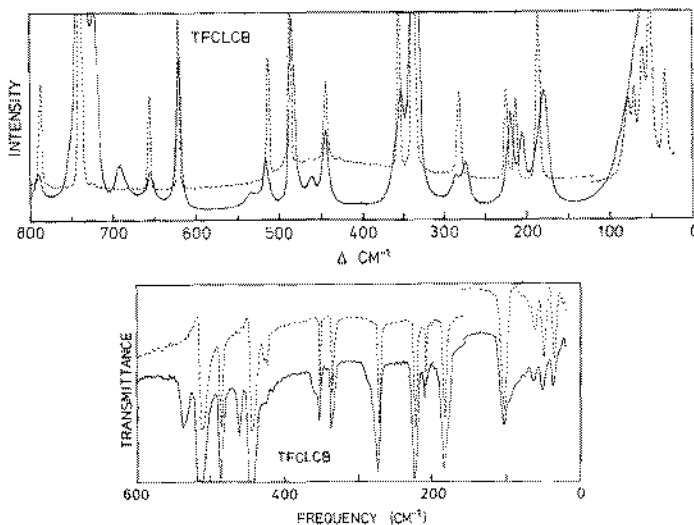


Fig. 2. (top) Raman spectra of 1-chloro-2,2,3,3-tetrafluorocyclobutane (TFCLCB) as a liquid (solid line) and as a crystalline solid at 85 K (dashed line).
 Fig. 3 (bottom) Far IR spectra of TFCLCB as a liquid (solid line) and as a crystal at 85 K (dashed line).

RESULTS

1-chloro-(TFCLCB) and 1-cyano-2,2,3,3-tetrafluorocyclobutane (TFCNCB)

As representative examples, Raman spectra of TFCLCB in the region 800-0 cm^{-1} as a liquid and as a crystalline solid are given in Fig. 2, whereas far IR spectra of the same phases are shown in Fig. 3. It is immediately apparent from these spectra that the IR and Raman bands: 1064, 940, 750, 723, 692, 537, 462, 402, 358, 285 and 187 cm^{-1} for TFCLCB vanish in the crystal. They are interpreted as belonging to the less stable axial conformer, while the bands present in the crystal belong to the equatorial conformer. Quite similar results were obtained for TFCNCB, and for this molecule bands belonging to the axial conformer were observed at: 1213, 863, 806, 715, 692, 560, 465 and 432 cm^{-1} . Even a quick glance at the spectra reveal that the axial conformer is more abundant than for the corresponding chloro- (ref. 1) and cyanocyclobutane (ref. 2) in which the axial conformer bands had very low intensities in the liquid state at ambient temperature.

Raman spectra of the liquids were recorded in the temperature range 339-193 K (TFCLCB) and 379-261 K (TFCNCB) and the enthalpy difference ΔH^0 (axial-equatorial) were calculated from van't Hoff plots. For this purpose several Raman lines assumed to be "pure" axial and equatorial bands were employed and the axial/equatorial ratio plotted against $1/T$. The preliminary ΔH^0 values (axial - equatorial) of 3.7 kJ mol^{-1} and 4.5 kJ mol^{-1} were obtained for TFCLCB and TFCNCB, respectively.

An IR spectrum of TFCNCB in an argon matrix is shown in Fig. 4, using a nozzle temperature of 313 K. None of the axial bands listed above were observed in the matrix spectra neither in argon nor in nitrogen. Also, if the nozzle temperature was increased to 450 or 700 K the matrix spectra contained only equatorial bands. The same was the case for TFCLCB. Apparently, the barrier to ring conversion must be so low that the less stable conformer (axial) converts to the more stable conformer at an appreciable rate at the temperature of the cold window (14 K), indicating a barrier of less than 5 kJ mol^{-1} . In the amorphous phase, however, obtained by condensing the pure vapour on a window at liquid nitrogen temperature (82 K) the axial bands were clearly visible, revealing a considerably higher barrier in the pure condensed state than in the matrices.

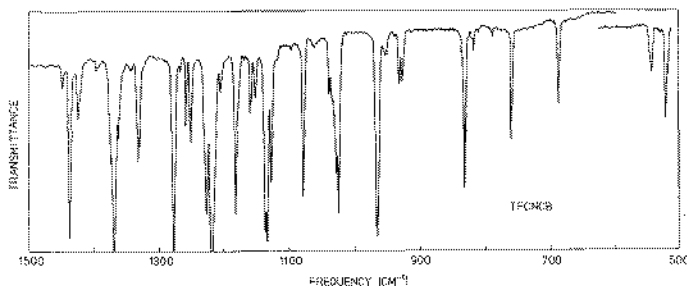


Fig. 4. IR spectrum of 1-cyano-2,2,3,3-tetrafluorocyclobutane (TFCNCB) in an argon matrix at 14 K, unannealed sample, nozzle temperature 313 K.

1-Chloro-1-fluorocyclobutane (CFCB)

The IR spectra of CFCB in the liquid state and in the crystal are shown in Figs. 5 and 6, respectively, while the Raman spectra of the two phases are reproduced in Fig. 7. From these spectra it can be concluded that the IR and/or Raman bands at: 1087, 921, 882, 831, 737, 710, 668, 483, 447, 376, 342 and 262 cm^{-1} vanish in the crystal spectra. Most of these bands are weak although the Raman bands at 921 and 483 cm^{-1} are medium or strong. Obviously, the disappearing bands belong to a less stable conformer in CFCB. From Raman spectra of the liquid, recorded at different temperatures, a ΔH° equal to 2.2 kJ mol^{-1} between the conformers was obtained.

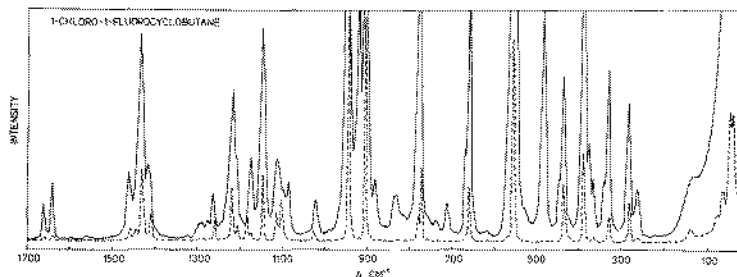


Fig. 5. Raman spectra of 1-chloro-1-fluorocyclobutane (CFCB) as a liquid (solid line) and as a crystal at 85 K (dashed line).

The matrix spectra of CFCB in argon and nitrogen matrices contained only the same bands as the crystal spectra. Thus, the bands listed above, belonging to the high energy conformer are absent in the matrix spectra. Apparently, the barrier to ring conversion is again smaller than 5 kJ mol^{-1} , resulting in a conversion to the more stable conformer in the matrices.

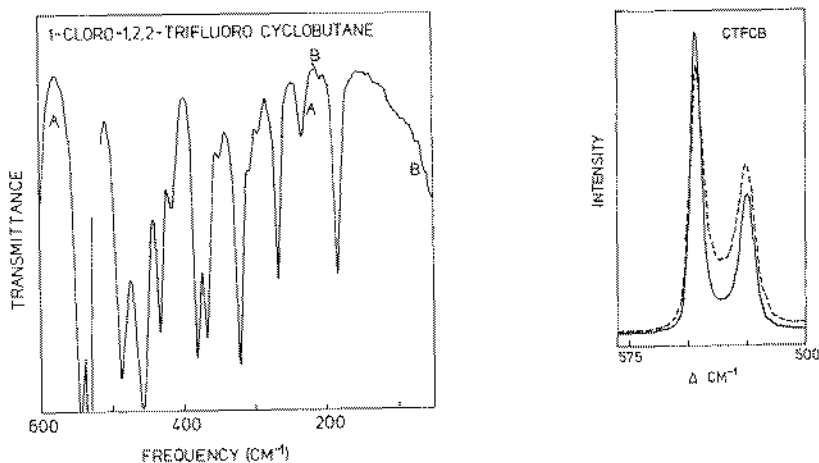


Fig. 6. (left) A far IR spectrum of 1-chloro-1,2,2-trifluorocyclobutane (CTFCB) as a liquid. Fig. 7. (right) Two Raman bands of CTFCB belonging to different conformers, recorded at 228 K (solid line) and 295 K (dashed line).

1-Chloro-1,2,2-trifluorocyclobutane (CTFCB)

A far IR spectrum of the liquid is given in Fig. 6 and a Raman spectrum of the liquid bands at 547 and 525 cm^{-1} , recorded at 295 and 228 K are given in Fig. 7. A matrix spectrum in nitrogen (nozzle temperature 313 K) is reproduced in Fig. 8 giving the unannealed spectrum (solid) and the spectrum recorded after annealing (dashed). For this molecule we can easily verify that the bands at: 990 , 882 , 695 , 615 , 613 , 522 , 490 and 417 cm^{-1} are present in the unannealed matrix, but vanish after annealing. They apparently belong to the high energy conformer since these bands are enhanced at higher temperatures in the liquid spectra. We never succeeded in crystallizing CTFCB by cooling or pressing, and the high energy conformer bands could therefore not be checked by their disappearance in the crystal. The enthalpy difference ΔH^0 was calculated from a number of band pairs similar to those in Fig. 7, giving values of 2.9 kJ mol^{-1} in the liquid and 2.7 kJ mol^{-1} in the vapour. No reliable ΔH^0 could be obtained from the hot nozzle experiments, indicating that the barrier between the conformers must be around 6 kJ mol^{-1} , making it possible to detect the unstable conformer but not to measure the equilibrium quantitatively.

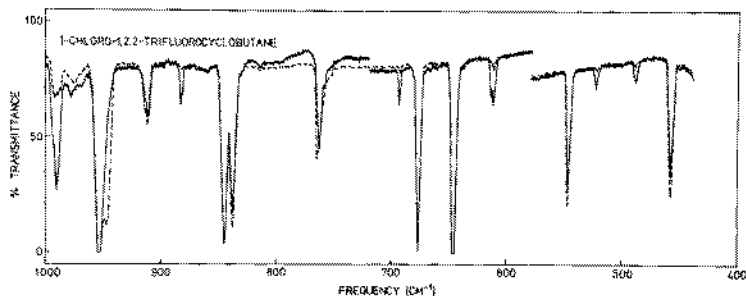


Fig. 8. IR spectrum of CTFCB in nitrogen matrices at 14 K, nozzle temperature 313 K, unannealed sample (solid line), sample annealed to 34 K (dashed line).

1,1,2-Trichloro-2,3,3-trifluorocyclobutane (TCTFCB)

The far IR spectra of the liquid and crystalline TCTFCB are given in Figs. 9 and 10 respectively, revealing that a number of prominent bands vanish in the crystal. From various sets of Raman bands of which one pair is shown in Fig. 11, the ΔH^0 was calculated to be 0.9 in the liquid and 0.4 kJ mol⁻¹ in the plastic phase, revealing nearly the same abundance of the two conformers. The plastic phase with both conformers in thermodynamic equilibrium was observed between 194 and 240 K. When TCTFCB was pressurized in a diamond anvil cell, a plastic phase was formed under a few kbar pressure, while an anisotropic crystal containing the most stable conformer was formed at ca. 30 kbar pressure.

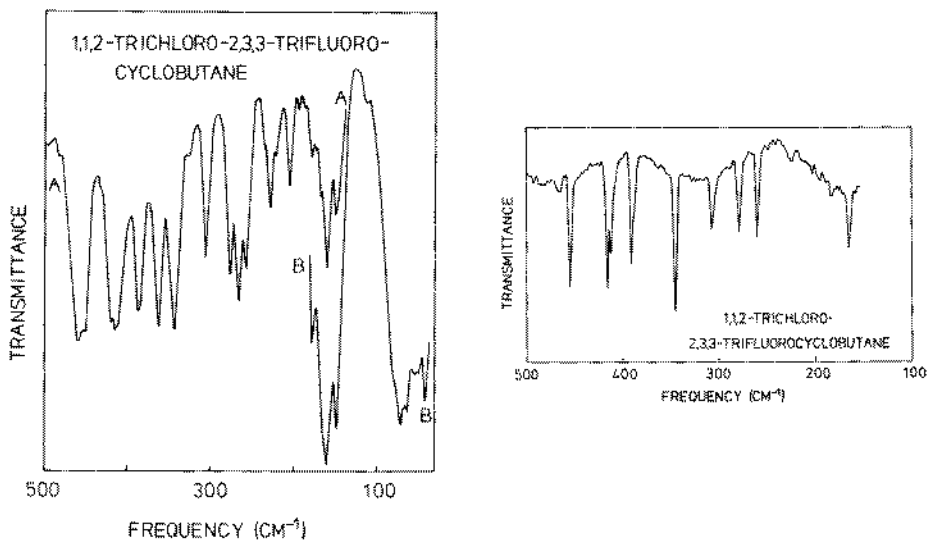


Fig. 9. (left) A far IR spectrum of 1,2,2-trichloro-2,3,3-trifluorocyclobutane (TCTFCB) as a liquid.

Fig. 10. (right) A far IR spectrum of TCTFCB as a crystal at 85 K.

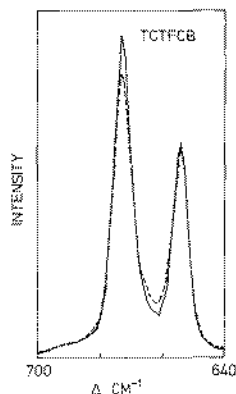


Fig. 11. Raman curves of liquid TCTFCB recorded at 257 K (solid line) and 296 K (dashed line).

The matrix spectra in argon and nitrogen are given in Figs. 12 and 13, respectively, demonstrating distinct intensity variations between the bands of the unannealed (solid) spectra, and opposite increases / decreases in the annealed (dashed) curves. It can be easily seen that the most stable conformer, present in the crystal, is favoured in the argon matrix, while the less stable conformer is preferred in the nitrogen matrix. Specific interactions between TCTFCB and the matrices take place immediately and are enhanced after the annealing is carried out. The quite even conformational equilibrium of the vapour is displaced in opposite directions to more one-sided equilibria in the matrices, having a difference in Gibbs free energy ΔG° equal to ca. 0.5 kJ mol^{-1} .

In the three cyclobutanes with geminal Cl and F substituents, it is not obvious from the vibrational spectra if the more stable conformer has Cl or F as the equatorial substituent (ref. 5). However, from the chloro- and bromocyclobutane spectra (ref. 1) it appears that the axial substituent has the C-X stretching mode at a higher wave number than the equatorial. In CFCB the C-Cl stretches are attributed to bands at 561 and 488 cm^{-1} , in CTFCB they are found at 645 and 616 cm^{-1} . Since the high wave number bands are present in the

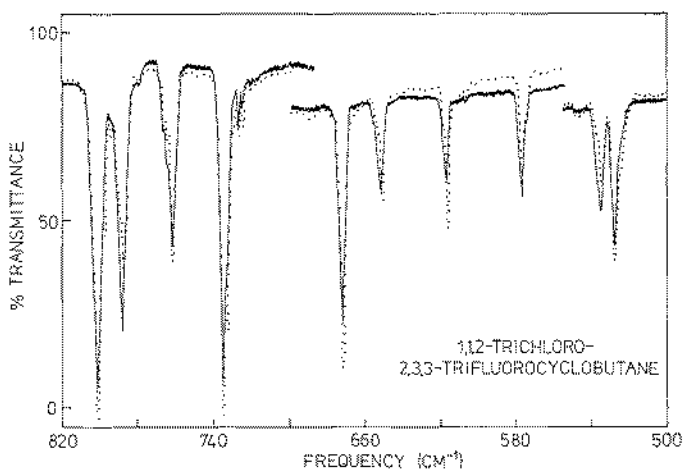


Fig. 12. IR spectra in argon matrix of TCTFCB at 14 K, nozzle temperature 313 K, unannealed sample (solid line), sample annealed 1/2 h at 36 K (dashed line).

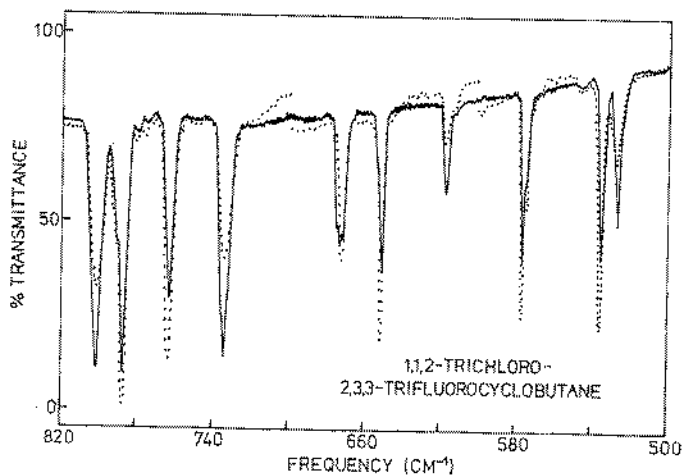


Fig. 13. IR spectra in nitrogen matrix of TCTFCB at 14 K, nozzle temperature 313 K, unannealed sample (solid line), sample annealed at 34 K (dashed line).

crystals, the stable conformers should accordingly be Cl(a)F(e) in both molecules. For TCTFCB, the corresponding bands are situated at 651 and 616 cm^{-1} of which the low wave number band remains in the crystal. Therefore, we have tentatively attributed the more stable conformer to Cl(e)F(a) in this compound.

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