

Short Communication

Rotational isomerism in fluorinated ketones: $\text{CF}_3\text{COCF}_2\text{Cl}$ and $\text{CF}_2\text{ClCOCF}_2\text{Cl}$

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Rotational isomerism has been shown to exist in several fluorinated acetones including $\text{CH}_3\text{COCH}_2\text{F}$ [1, 2], $\text{CH}_2\text{FCOCH}_2\text{F}$ [3, 4] and $\text{CF}_3\text{COCH}_2\text{Br}$ [5]. These three compounds each have two conformers present in appreciable concentration, but in each case the difference in configuration results from rotation of one or two CH_2X groups, *i.e.*, a group that contains only one halogen bonded to the rotating carbon atom. The present work was undertaken to check for rotational isomerism in compounds in which interconversion of the conformers would involve rotation of completely halogenated groups.

Chloropentafluoroacetone

Solid-state and solution spectra of $\text{CF}_3\text{COCF}_2\text{Cl}$ are shown in Figure 1. The compound exists as a gas at room temperature and for this reason solutions of unknown concentration were made by bubbling the gas into carbon disulfide. The solid compound was obtained by spraying the gas on to a cooled KBr plate.

Comparison of the solution and solid-state spectra shows that disappearance or near-disappearance of several bands accompanies crystallization of the sample. This behavior indicates the presence of rotational isomers. There should be only two conformers present, as is the case for the mono-haloacetones [1, 2, 6, 7] and $\text{CF}_3\text{COCH}_2\text{Br}$ [5]. The number of bands present in the $1100 - 1300 \text{ cm}^{-1}$ region of the solid-state spectrum must therefore result in part from solid-state splittings. This is also assumed to be the case for the solid-state pairs of bands at $884, 903$ and $718, 728 \text{ cm}^{-1}$, whose counterparts in solution are 890 and 722 cm^{-1} .

The solution spectrum (Fig. 1) shows a strong band at 1014 cm^{-1} . The 722 cm^{-1} band is more intense than the one at 740 cm^{-1} and the 890 cm^{-1} band is stronger than the one at 830 cm^{-1} . In a solution of different concentration, the 1014 cm^{-1} band became very weak and stronger bands at 1000 and 1025 cm^{-1} appeared. These two bands actually appeared as

shoulders on either side of the 1014 cm^{-1} band depicted in Figure 1. Also in this second solution, the relative intensities of the 722 , 740 and 830 , 890 cm^{-1} pairs were reversed from those of the first solution. The two bands in the solid-state spectrum observed at 1005 and 1026 cm^{-1} must be equivalent to the two solution bands rather than to crystal-field splitting.

Both conformers are present in comparable amounts in the vapor state. The bands at 1024 and 1076 cm^{-1} have about equal intensities at room temperature, but at $80\text{ }^\circ\text{C}$ the 1076 cm^{-1} band is much less intense than the other. The band observed at 1000 cm^{-1} for the solution must shift in the vapor so as to overlap the 1025 cm^{-1} band since only one vapor-state band was observed in this region. Such a liquid-vapor frequency shift is quite common for C-F stretching vibrations.

The dependence of intensity of the 1076 cm^{-1} vapor-state band on temperature shows that this band is due to the low-energy conformer, and that this is the one that is absent in the solid.

1,3-Dichlorotetrafluoroacetone

Liquid- and solid-state spectra for this compound are shown in Figure 2. The absence of several strong liquid-state bands from the spectrum of the solid verifies the presence of rotational isomerism. Although there are a

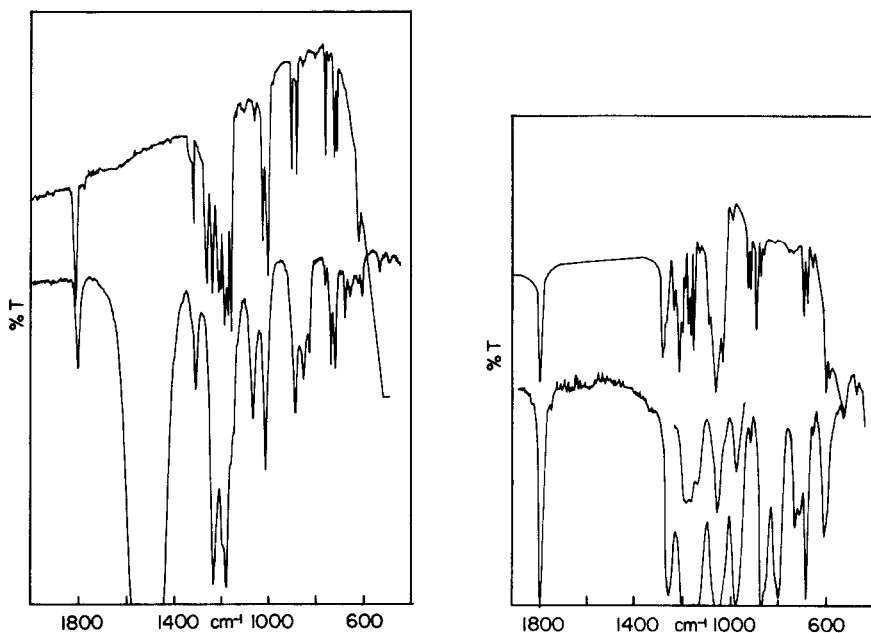


Fig. 1. Infrared spectra of $\text{CF}_3\text{COCF}_2\text{Cl}$. Top curve, solid film at about $-190\text{ }^\circ\text{C}$; bottom curve, solution in CS_2 , concentration unknown.

Fig. 2. Infrared spectra of $\text{CF}_2\text{ClCOCF}_2\text{Cl}$. Top curve, solid film at about $-190\text{ }^\circ\text{C}$; bottom curve, neat liquid, 0.015 mm or film.

fairly large number of bands present in the 1000 - 1300 cm^{-1} region of the solid-state spectrum, where only five fundamentals are expected, some of these must result from the crystalline state of the sample. The presence of only one conformer in the solid state is concluded from examination of the spectra in the lower region.

Of the liquid-state bands at 693, 719 and 739 cm^{-1} , only the 693 cm^{-1} band is present in the solid-state spectrum, where it shows up as a doublet at 688, 698 cm^{-1} . The 719 and 739 cm^{-1} bands are due to different conformers, which means that 1,3-dichlorotetrafluoroacetone exists as three rotational isomers as does 1,3-dichloroacetone [7, 8]. Assignment of the 719 and 739 cm^{-1} bands to two separate conformers was made by comparison of the relative intensities of these bands in the liquid-, solution- and vapor-state spectra. In the liquid-state spectrum, these two bands have about equal intensities, but each band is considerably less intense than the 693 cm^{-1} band. In the spectrum of a 10% solution of the compound in CS_2 , the 739 cm^{-1} band is more intense than either of the other two bands. In the vapor-state spectrum the 739 cm^{-1} band appears as a weak shoulder on the side of the 724 cm^{-1} band, which has about the same intensity as the one at 694 cm^{-1} . These variations in the intensities of these three bands lead to the conclusion that they are due to three separate conformers. These bands are probably due to a vibrational mode analogous to that which gives rise to the two bands observed at 722 and 740 cm^{-1} in the solution spectra of $\text{CF}_3\text{COCF}_2\text{Cl}$. The most likely vibration is the symmetric C—C—C stretch, whose frequency is 779 cm^{-1} in both acetone [9] and hexafluoroacetone [10]. This would be the region in which the C—Cl stretch would normally be expected, but the presence of the fluorines attached to the same carbon atom as the chlorine should increase the C—Cl frequency [11]. This would probably result in considerable mixing of the C—F and C—Cl stretching modes.

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