

VIBRATIONAL SPECTRA AND CONFORMATIONS OF  
1-CHLORO-4-FLUOROBUT-2-YNE

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ABSTRACT

IR and Raman spectra of liquid 1-chloro-4-fluorobut-2-yne do not agree with an expected nearly free internal rotation in the molecules. The conformational state in the solid and in Ar and N<sub>2</sub> matrices has also been studied. Comparisons are made with the results of 1,4-difluoro, dichloro and dibromobut-2-ynes. Preliminary IR and Raman results on 1,4-diiodobut-2-yne, indicate an anti conformation in the solid state.

INTRODUCTION

It has been assumed that but-2-yne and its 1,4-dihalogenated derivatives have very low barriers to internal rotation. Contrary to the ethanes, the long distance between the tetrahedral end groups (Fig. 1) causes only weak interactions through space and the dominating forces may be due to polarization of the triple bond. Accordingly, the barrier of but-2-yne has been determined to be less than 0.4 kJ/mol, the molecules exhibiting free internal rotation even in the solid state. It has been concluded from the vibrational spectra and electron diffraction results that 1,4-dibromobut-2-yne (DBB) (ref. 1) and 1,4-dichlorobut-2-yne (DCB) (refs. 2,3,4) have nearly free internal rotation in the vapour and in the liquid states. In contrast, a surprisingly high barrier (4.1 kJ/mol) was found in 1,4-difluorobut-2-yne (DFB) (refs. 5,6). In the present communication we want to present our preliminary spectroscopic results for the hybrid molecule 1-chloro-4-fluorobut-2-yne (FCB) and compare these data with those recently obtained for DFB (ref. 6), DCB (ref. 4) and DBB (ref. 1). Some tentative results for 1,4-diiodobut-2-yne (DIB) (which is highly unstable and rearranges to 2,3-diiodo-1,3-butadiene) will also be presented. To our knowledge no structural data have been published on FCB or DIB thus far.

## EXPERIMENTAL

Raman spectra of FCB as a liquid, supercooled liquid and as a solid at various temperatures were recorded with a Dilor RT 30 triple monochromator. A Spectra Physics model 2000 argon ion laser was used for excitation. IR spectra of the vapour, liquid and solid and of isolated molecules in Ar and  $N_2$  matrices deposited on a cold window at different temperatures and subsequently annealed were recorded using a Perkin-Elmer model 225 spectrometer, a Bruker model 114C FTIR spectrometer and a Displex unit from Air Products. Raman and incomplete IR spectra of solid DIB cooled to 90K to avoid reactions were also recorded. For further description of experimental details and equipment, see recent papers (refs. 4,6).

## RESULTS

The Raman spectra of FCB as a liquid and supercooled liquid are shown in Figs. 2.b and 3. (upper three curves), and the Raman spectrum below  $600\text{ cm}^{-1}$  of one crystal modification is also given in Fig. 3. FCB melts at ca. 205K, but a considerable supercooling was observed (down to 120K). Some temperature dependence in the band shapes in the low frequency part of the spectrum was detected (Fig. 3). On cooling, the background scattering intensity was drastically reduced and a band appeared at ca.  $\pm 28\text{ cm}^{-1}$  for temperatures below 160 K (Fig. 4).

At least three genuine crystal modifications were detected depending on the cooling conditions. We have so far not succeeded

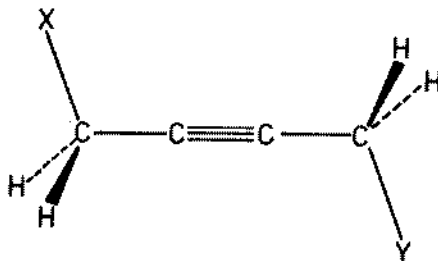
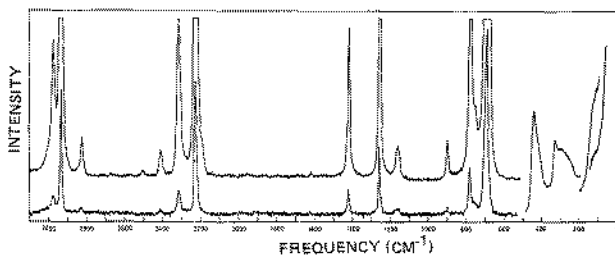
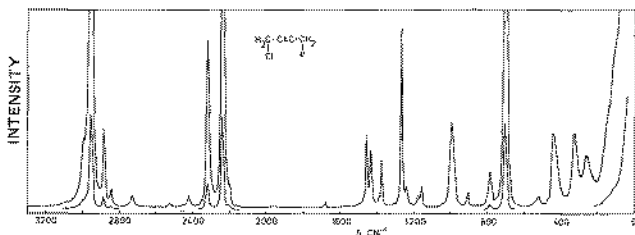
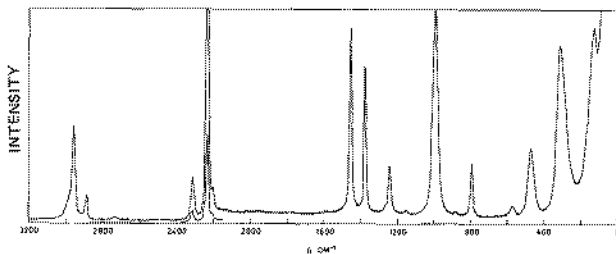


Fig. 1. Structure of 1-X-4-Y-but-2-yne in anti conformation. A rotation of one end group through  $120^\circ$  gives the gauche conformation. With X,Y = Cl the minimum distance between the X and Y substituents (syn) is ca. 5.3 Å, while the van der Waals distance is ca. 3.6 Å, resulting in a very weak interaction through space.

in crystallizing FCB under high pressures (up to 50 kbar). IR spectra of FCB isolated in Ar and  $N_2$  matrices showed splittings into two components of most bands below  $600\text{ cm}^{-1}$ . These doublets were separated as much as  $8\text{ cm}^{-1}$  and our incomplete data indicate that the intensity ratios are dependent on the deposition temperature and annealing of the matrices. The relative intensity pattern of the band pairs was reversed on going from Ar to  $N_2$  matrices, indicating specific interaction with the matrices.

DIB is quite unstable and isomerizes quickly to 2,4-diiodo-



- Fig. 2a. Raman spectrum of liquid 1,4-difluorobut-2-yne (DFB).  
 Fig. 2b. Raman spectrum of liquid 1-chloro-4-fluorobut-2-yne (FCB).  
 Fig. 2c. Raman spectrum of liquid 1,4-dichlorobut-2-yne (DCB).

1,3-butadiene at room temperature, a process which is accelerated in the presence of light. The butadiene reacts further to an insoluble polymer. It was observed that when DIB was exposed to the 5145Å Argon ion laser, a vastly increased scattering occurred. Apparently a decomposition product gave a resonance enhanced signal and the process occurred even at 90K. No abnormal scattering intensities were detected at very low laser powers (below 50 mW) or if the 6328Å line of a He-Ne laser was employed.

DFB, DIB and the diiodobutadiene will be discussed in detail in forthcoming papers.

## DISCUSSION

### The torsional barrier

For comparison, Raman spectra of liquid DFB, FCB and DCB are displayed in Figs. 2 a, b, c, respectively. In the broad asym-

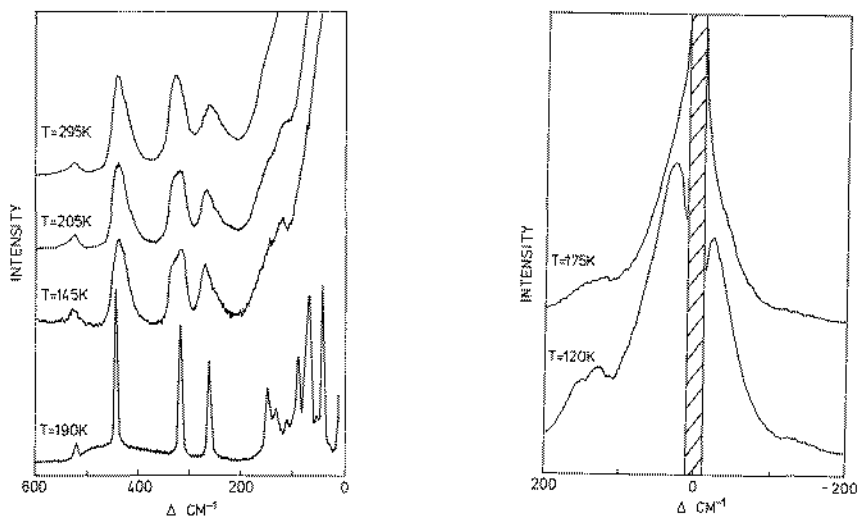


Fig 3. (left) Raman spectrum of liquid FCB at temperatures 295 K and 205 K, supercooled liquid at 145 K and of one crystal modification at 190 K.

Fig. 4. (right) Stokes and anti Stokes spectra of supercooled liquid FCB. Upper curve above and lower curve below temperatures of 140-160 K, where the bands at  $\pm 28 \text{ cm}^{-1}$  appear. The area marked with diagonal lines is the protection zone for the photomultiplier.

metric bands in the spectrum of DCB below  $600\text{ cm}^{-1}$ , features characteristic of a nearly free internal rotation in the molecule are easily recognized. In the spectrum of DFB, which is known to have one stable conformation with a dihedral angle of 99 degrees from syn (ref. 6), we have quite symmetric bands, and they do not have the spectral band width expected for molecules with no restriction on the dihedral angle. A comparison of the spectra of DFB and DCB with that of FCB reveals that in spite of some asymmetry present in the latter (below  $600\text{ cm}^{-1}$ ) (Fig. 3), it is rather similar to that of DFB, indicating a higher barrier in FCB than in DCB. Furthermore, the band appearing at ca.  $28\text{ cm}^{-1}$  in both the Stokes and anti Stokes Raman spectra of supercooled liquid DFB (Fig. 4) is a likely candidate to the torsional mode (observed at  $42\text{ cm}^{-1}$  in gaseous DFB (ref. 6)). If this interpretation is correct, a nearly free internal rotation in liquid FCB seems improbable, at least below 160 K. Alternatively, the bands at  $\pm 28\text{ cm}^{-1}$  may be associated with the dynamics of the gradually more viscous liquid at these low temperatures.

#### Conformations

Possible conformers of FCB are gauche ( $C_1$  symmetry), anti ( $C_s$  symmetry) and syn ( $C_s$  symmetry). All fundamentals are active both in IR and Raman for all structures, although a certain pseudo symmetry might be observed for anti (pseudo  $C_{2h}$ ) and syn (pseudo  $C_{2v}$ ). Accidental degeneracy has been observed in DBB, DCB and DFB for most vibrations of the two halomethyl groups as there is only weak mechanical coupling across the molecular framework. For the same reason, the spectrum of liquid FCB is almost a superposition of the spectra of liquid DFB and DCB in the  $4000\text{--}600\text{ cm}^{-1}$  region. The bands that show conformational dependency (the six skeletal bending modes) are all situated in the region below  $600\text{ cm}^{-1}$ . Consequently, the temperature dependence of the band shapes in this region, although not very pronounced (Fig. 3), is interpreted as a change in the equilibrium mixture ratio. The small variations in the spectrum, taking the broad temperature range into account, must reflect a very small enthalpy difference between the conformers.

On crystallization the bands sharpen considerably and lines are shifted (Fig. 3), due to a selection of one specific conformer in the crystal lattice. The differences in the spectra of the various crystal modifications are probably too small to

represent different conformers. The observed frequencies for the gauche conformations of DCB and DFB are given in Fig. 5 together with the observed frequencies of solid FCB. The frequencies of liquid DBB are also given. Although DBB are supposed to have nearly free internal rotation in the liquid state, the authors (ref. 1) assume that the maxima of the broad bands shapes coincide roughly with frequencies of a hypothetical gauche conformer. The frequencies fit well in the correlation diagram and allow us to assign a gauche conformation to the molecules of FCB in the crystal lattice. From Fig. 3 it seems obvious that we have a gauche conformer in the liquid equilibrium mixture. The second conformer has not yet been determined, but normal coordinate calculations indicate an anti conformation.

The results from the Ar and N<sub>2</sub> matrices have not yet been interpreted in detail. The splittings of ca. 8 cm<sup>-1</sup> seem too small to represent two conformers in these molecules, but are unusually large for ordinary matrix splittings. With small barriers the actual structure can be strongly dependent on the surroundings. The splitting might be due to different sites in the matrices, resulting in slightly different dihedral angles in the molecules. The conformation would then be gauche in the matrices as well.

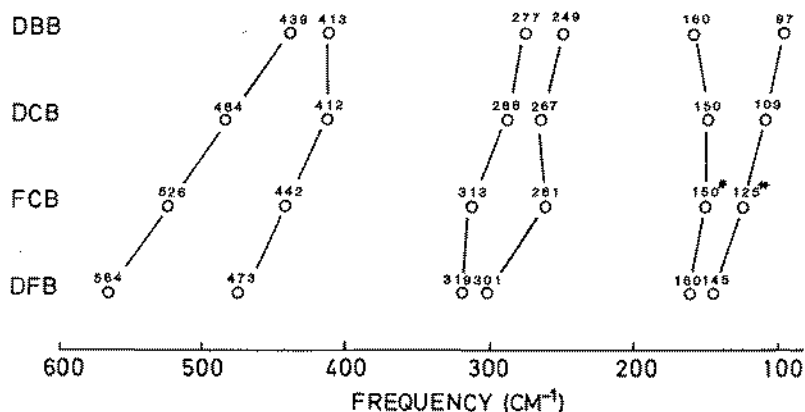


Fig. 5. Correlation diagram of the observed gauche frequencies for solid DCB, FCB and DFB and from liquid DBB (nearly free internal rotation). The frequencies of FCB marked with asterisks are selected from one of the crystal modifications.

### 1,4-Diiodobut-2-yne

Like DBB, DCB and DFB, DIB has a very simple spectrum in the IR and Raman, which implies accidental degeneracy for several in-phase and out-of-phase modes in the iodomethyl groups (Fig.6). Furthermore, some bands in the Raman spectra do not have counterparts in the IR spectra and vice versa, indicating a center of symmetry in the molecule and the presence of an anti conformation ( $C_{2h}$  symmetry).

### CONCLUSION

Examining the conformers of the molecules in the series DIB, DBB, DCB, FCB and DFB, a distinct tendency seems to be apparent. In the cases of the more bulky halogen substituents, iodine and bromine, the conformation in the solid state is anti. For DCB, two different crystal modifications have been found (refs. 4,7,8); one with the molecules in the anti conformation, the other with the molecules in the gauche conformation. The former of these is the more stable at high pressures, but metastable at low temperature/normal pressure, where the "gauche crystal" is the more stable. With one fluorine and one chlorine, only one conformation (gauche) has so far been observed in the crystal lattices, and with two fluorines the preference for gauche conformation is pronounced (ref. 6). This scheme has obvious similarities to that for the ethanes. Further, the insertion of fluorine(s) (or small strongly electronegative substituents) increases the torsional barrier.

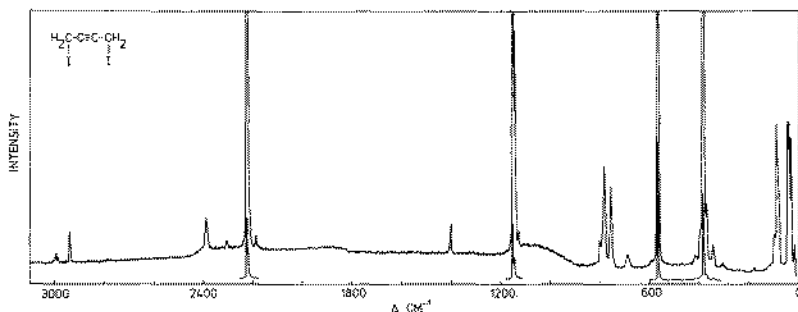


Fig. 6. Raman spectrum of solid 1,4-diiodobut-2-yne (DIB).

## ACKNOWLEDGEMENT

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