Conformation and Vibrational Spectra of 1,1,2-Trichloro-2,3,3-trifluorocyclobutane

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Infrared spectra in vapour, liquid, and crystalline states and Raman spectra in the liquid and crystalline states have been obtained for 1,1,2-trichloro-2,3,3-trifluorocyclobutane. Based on the disappearance upon crystallization of a total of 22 different bands, the results are interpreted in terms of two conformers being present in the vapour and liquid but only one in the crystal.

When the ring in a cyclobutane is non-planar, one substituent on each carbon atom can be described as axial and the second as equatorial in a way completely analogous to the notation used in cyclohexanes.1 Earlier work has shown that the more stable configuration for a compound with a single halogen substitutent on a cyclobutane ring is that in which the halogen assumes the equatorial position.1

Several years ago Rothschild claimed, on the evidence of the disappearance upon crystallization of one band each in the spectra of cyclobutyl chloride and cyclobutyl bromide, the presence of two conformers in each of these compounds.2 Durig et al. in their further study of these compounds and various deuterated derivatives treated this interpretation with some skepticism but eventually concluded that their results supported this interpretation.3,4 In the case of the bromo compound this is somewhat surprising since the results of a far infrared investigation indicated that that compound possessed only a single minimum in the puckering potential and hence only a single conformer.5 Only the conformer with the chlorine equatorial was found in a microwave investigation of cyclobutyl chloride, but it must be noted that this study was carried out at $-70\,^\circ\text{C}$.6

In trans-1,3-bromochlorocyclobutane, in which both halogen substitutents cannot simultaneously assume the equatorial position, the electron diffraction data for the vapour have been interpreted in terms of a nearly 50:50 mixture of the two conformers.7 Several 1,1-difluorocyclobutanes have been studied by $^{19}$F NMR8,9 and in some cases the spectra have been interpreted in terms of an equilibrium between two conformers. In the only one of these compounds in which all substituents are monatomic and in which a definite conclusion was reached, 1,1-difluoro-2,2,3-trichlorocyclobutane, the ratio between the two conformers at room temperature was approximately 3:1.8 In a separate study, the title compound among others was investigated, but no conclusions about conformation were reached.10

EXPERIMENTAL

The sample used was purchased from PCR, Inc. and purified by distillation before use. Its identity was confirmed by mass spectrometry.

Infrared spectra were recorded of the vapour, liquid, and solid on a Perkin-Elmer Model 225 Infrared Spectrophotometer. For the solid, spectra were taken both of the unannealed material and of the crystal after prolonged annealing. Even after careful annealing, approximately 5% amorphous material remained.

Far infrared spectra of the pure liquid were recorded on a Bruker Model 114C Fourier transform spectrometer over the range 400–40 cm$^{-1}$ using 6, 12, and 23 μm beamsplitters.

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Raman spectra were run on a Cary Model 81 Raman spectrometer, modified for 90° illumination and equipped with a CRL model 52G argon ion laser, for the liquid and for the solid deposited on a cold copper block cooled with liquid nitrogen. Even the first spectrum taken immediately after deposition of the solid showed a weakening of those bands eventually shown to be due to the non-dominant conformer. Disappearance of the minor conformer, as shown by the complete disappearance of several bands, occurred spontaneously, and only very minor changes were then observed during several annealings. For the liquid, polarization measurements were made and proved useful as a means of resolving several bands. Even though without symmetry all bands are polarized, the bands of course may be polarized in varying degrees.

RESULTS

The experimental results obtained are shown in Table 1. Infrared spectra of the unannealed and annealed solid and Raman spectra of the liquid and crystalline solid are shown in Figs. 1–4.

In Table 1 it can be seen that, in general, bands marked as disappearing in the infrared spectrum of the crystal were still weakly present indicating that all material was not crystalline. In contrast, completely crystalline material was obtained in the Raman cryostat.

DISCUSSION

A cyclobutane of this sort can be expected to possess a non-planar cyclobutane ring. For three of the carbon atoms in this compound, where the
Table 1. Vibrational spectral data for 1,1,2-trichloro-2,3,3-trifluorocyclobutane.

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* Weak bands in the regions above 3100 cm⁻¹ and between 2800 and 1500 cm⁻¹ have been omitted. ** Abbreviations: s, strong; m, medium; w, weak; v, very; C, C type contour. * a refers to the conformer which disappears upon crystallization; e in most cases refers to the stable conformer or both conformers. Bands denoted, e, a or e,a are considered as fundamentals. An asterisk signifies that the band vanishes in the spectrum of the crystalline solid.
Fig. 3. The Raman spectrum of liquid 1,1,2-trichloro-2,3,3-trifluorocyclobutane.

Fig. 4. The Raman spectrum of crystalline 1,1,2-trichloro-2,3,3-trifluorocyclobutane at −18.5 °C.
substituents are identical, this does not lead to
different species. On the fourth, though, clearly the
fluorine atom must be axial and the chlorine equa-
torial in one conformer — or vice versa in the
other.

In 1,1,2-trichloro-2,3,3-trifluorocyclobutane there
is in effect a competition between the chlorine and
fluorine atoms for the favoured equatorial position.
Since the effectiveness of each in minimizing the
energy of the system in the equatorial position will
be roughly the same, substantial amounts of each
conformer should be present in the liquid.

Our conclusion is that this expectation is borne
out by the experimental results. Upon crystalliza-
tion four infrared bands, five Raman bands, and 13
bands common to both effects may definitely be
classed as disappearing, or a total of 22 different
bands. The spectra of the crystal which remains can
well be interpreted in terms of a single conformer;
these bands which disappear are quite reasonable
for a second conformer. To our knowledge, this
study is the first in which a cyclobutane, existing in
more than one conformer in the vapour and liquid,
is shown conclusively to exist in only one conformer
in the crystalline solid.

In order to obtain some approximate idea of the
relative abundance of the two conformers in the
liquid phase, we can note that, very roughly, each
disappearing band is about half as intense as some
near-lying counterpart, or that the ratio of abun-
dance must be somewhere near 1:2, with the
conformer present in the crystal being the more
stable.

For each conformer of this 12 atom compound a
total of 30 normal modes is expected, all but three
lying below 1400 cm⁻¹, and all potentially active in
both the infrared and Raman. In the spectra of the
crystalline solid, a total of about 30 bands which are
strong in one or both effects is readily found. Those
which we think are fundamentals in the dominant
conformer appear in Table 1 labelled with an e (or
with a.e if we think they are common to both), and
those we think are fundamentals in the other
conformer are labelled with an a. Because no possible
conformer in this compound, even the unlikely one
with the ring planar, possesses any symmetry at all,
the normal modes should be highly mixed and the
atomic motions suggested in Table 1 should be
considered highly approximate.

A few general observations can be made, though.
As in 1,1,2,2-tetrafluorocyclobutane¹² and 1-chloro-
2,2,3,3-tetrafluorocyclobutane,¹³ introduction of
fluorine atoms leads to higher than normal CH₂
stretching frequencies. As is usual, modes with a
high degree of CF stretching character give strong
infrared and very weak or invisible Raman bands,
*e.g* those bands at 1319, 1246, and 1117 cm⁻¹ of the
dominant conformer and 1210, 1095, and 1054 cm⁻¹
of the disappearing conformer.

Often, but not always, the symmetric stretching
of a ring gives rise to a strong Raman band, near
1000 cm⁻¹ in the case of cyclobutane rings. Such a
band is not obvious here; perhaps the many elec-
tronegative atoms tend to withdraw electrons from the
ring and so weaken the band. In C₄Cl₈, for
example, a band which was not especially strong
was assigned to this motion.¹⁴

Several bands of appreciable intensity in both
infrared and Raman can be noted which are prob-
ably associated with C—Cl stretching. In the
dominant conformer these bands occur at 796, 738,
and 672 cm⁻¹ and in the other conformer at 787,
765, and 653 cm⁻¹.

We located no band which we could ascribe to
the ring puckering mode.

However, the most interesting question is which
form is which. Placing the compound in solvents of
varying polarity would not give useful information
as both conformers should have nearly the same
dipole moment.

Correlations have been suggested between
conformation and carbon-halogen stretching fre-
quency¹⁵ except for fluorine where the conclusion
was that such correlation does not exist.¹⁶ The
situation would be complicated here, in utilizing
the C—Cl frequencies, by the three chlorine atoms
in the molecule. Thus each conformer should give
rise to 3 C—Cl stretching frequencies, in the one
case two axial and one equatorial and in the other
one axial and two equatorial. Further complications,
even if modes richest in C—Cl stretching character
could be unequivocally identified, result from the
question of whether such correlations can be
extended to the case of a cyclobutane and from their
known shortcomings in the case of compounds
containing several chlorine atoms, *e.g.* 1,2,3-tri-
chloropropene.¹⁷,¹⁸

Lacking at the present time any experimental
evidence one way or the other, we are still willing
to hazard the guess that the more stable form is
that in which the more bulky atom, in this case the
chlorine, occupies the equatorial position (*cf.* for
example Ref. 8 and references cited therein). Thus
we feel those bands marked with e in Table 1 belong
to the conformer with two chlorine atoms in equatorial positions.

The implications of this work on the simpler cyclobutyl chloride and cyclobutyl bromide must also be explored. The comments of Durig et al. with reference to the two conformer interpretation are reminiscent of the principle that when all which is impossible has been eliminated, then whatever remains, however unlikely, must be the truth.19

If a total of 22 bands disappear in our compound, then obviously some of these must be associated with modes other than carbon-halogen stretching frequencies. In the related monohalocyclohexanes, at least 10 bands per compound show substantial conformation dependence.20 It then seems extremely unlikely than only the C—Cl or C—Br stretches should be conformation-sensitive in the cyclobutyl halides. At the very least, the two C—X bending frequencies and probably also some of the ring modes should depend upon conformation. Thus, somewhat paradoxically, in showing what we think is a clear case of conformations in a cyclo-

butane, we feel that we have cast doubt on an earlier report of the same effect.

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REFERENCES


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