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# 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 substituent 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 °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 $^{19}F$ NMR[8,9] 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 $\mu$m 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.[11] For three of the carbon atoms in this compound, where the

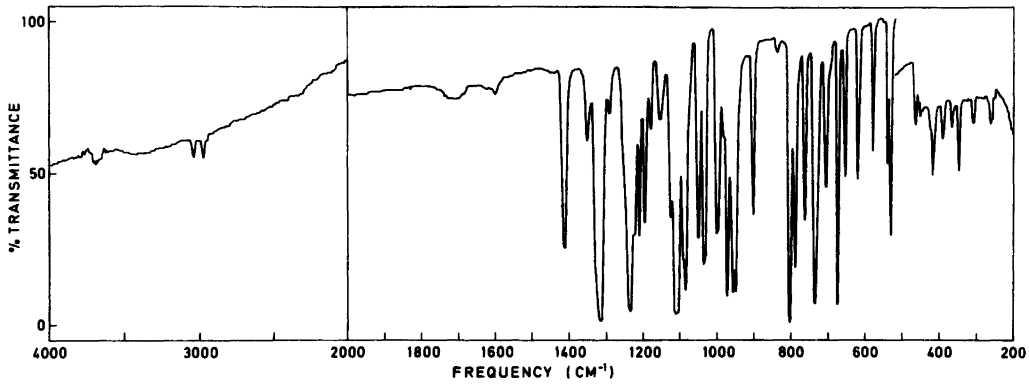


*Fig. 1.* The infrared spectrum of liquid 1,1,2-trichloro-2,3,3-trifluorocyclobutane (4000–200 $cm^{-1}$).

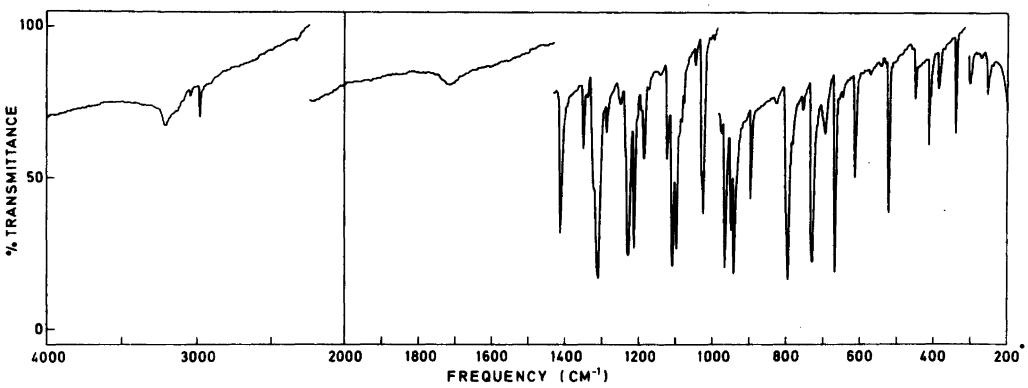


*Fig. 2.* The infrared spectrum of crystalline 1,1,2-trichloro-2,3,3-trifluorocyclobutane (4000–200 $cm^{-1}$) at −185 °C.

*Table 1.* Vibrational spectral data for 1,1,2-trichloro-2,3,3-trifluorocyclobutane.

| Infrared[a] | | | | Raman[a] | | | Interpretation | |
|---|---|---|---|---|---|---|---|---|
| Vapour | Liquid | Unannealed Solid | Crystal | Liquid | Unannealed Solid | Crystal | Conformer | Approx. motion |
| | 3048 w[b] | 3041 w | 3036 w | 3039 m | 3037 m | 3036 m | *a,e*[c] | $CH_2$ str |
| | 2975 w | 2974 m | 2975 m | 2975 s | 2971 s | 2970 s | *a,e* | $CH_2$ str |
| | | | | | 1429 vw | *?[d] | | |
| | | ~1420 vw | *? | | | | | |
| 1424 w | | | | | | | | |
| 1421 m | 1414 s | 1410 m | 1415 m | 1413 w | 1409 w | 1414 w | *a,e* | $CH_2$ def |
| 1417 w | | | | | | | | |
| ~1352 vw | 1350 w | 1350 w | 1353 w | | | | | |
| | | 1343 vw | 1343 vw | | | | | |
| | | 1327 w | 1325 w | | | | | |
| 1319 s | 1314 vs | 1314 s | 1313 s | 1315 vw | 1316 w | 1316 w | *e* | CF str |
| ~1290 vw | 1290 vw | 1290 vw | 1291 vw | | | | | |
| | | | | | 1275 vw | 1276 vvw | | |
| | | | 1255 w | | | | | |
| | | 1250 vw | * | | 1250 vw | * | *a* | $CH_2$ def |
| | | | 1241 vw | | | | | |
| 1248 m | | | | | | | | |
| 1242 s | 1236 vs | 1235 s | 1232 s | 1235 vw | | | *e* | CF str |
| | | | | | 1225 vw | 1224 vw | | |
| | | 1222 m | 1217 m | | | | | |
| 1214 w | | | | | | | | |
| 1210 m | 1208 s | 1209 m | * | 1210 vw | | * | *a* | CF str |
| 1205 w | | | | | | | | |
| 1197 vw | | | 1199 vw | | | | | |
| | 1193 m | 1194 m | 1191 mw | 1194 vw | 1192 vw | 1189 vw | *e* | $CH_2$ def |
| | 1178 w | 1178 w | 1178 w | | | | | |
| 1169 mw | | | | | | | | |
| | | 1153 w | * | | | | *a* | $CH_2$ def |
| | 1146 vw | | 1145 vw | | | | | |
| | 1122 w | 1125 m | 1128 m | 1122 w | 1122 vw | 1122 w | | |
| 1117 s | 1111 vs | 1112 s | 1112 s | 1112 w | 1108 w | 1109 w | *e* | CF str |
| | 1104 m | 1104 s | 1102 s | | 1102 mw | 1101 mw | | |
| | | | 1093 vw | | | | | |
| | 1090 m | 1092 w | 1088 w | | | | | |
| 1095 s | 1084 vs | 1084 s | 1081 w (*) | | | | *a* | CF str |
| 1054 m | 1047 s | 1050 m | 1052 w (*) | 1050 vw | 1050 vw | * | *a* | CF str |
| | | 1034 s | 1035 w | | | | | |
| 1036 ms | 1031 m | 1030 ms | 1033 m | 1030 vw | 1032 vw | 1030 vw | *e* | |
| 1032 ms | | | 1029 ms | | | | *e* | |
| | | | 1011 vvw | | | | | |
| 1003 m | 996 s | 1000 m | * | 1001 vw | | * | *a* | |
| 998 mw | | 995 mw | * | 993 vw | | * | *a* | |
| | | 980 vw | 980 vw | | 380 vw | 980 vw | | |
| | 968 s | 970 s | 970 s | | 970 mw | 968 mw | *e* | $CH_2$ def |
| | | | 963 vw | 965 vw | | | | |
| | | | | 955 w | 958 w | * | *a* | CC str |
| 960 s | | | | | | | | |
| 955 s | 953 s | 953 s | 953 ms | | | | *e* | |
| | 947 w | 947 s | 946 s | | | | *e* | |
| 904 mw | 900 m | 901 m | 900 m | 903 w | 901 w | 900 w | *e* | |
| 840 w | 830 vw | 840 w | 832 vvw(*) | | | | *a* | |

*Table 1. Continued.*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 806 ms<br>796 ms<br>790 ms | 800 s | 800 s | 797 s | ~800 vw | 800 vw | 804 vw | *e* | CCl str |
| | 787 s | 786 ms | 786 vvw (*) | 785 vw | | * | *a* | CCl str |
| 765 mw | 760 s | 760 ms | 759 vw (*) | 762 vw | 764 vw | * | *a* | CCl str |
| 738 m | 734 s | 732 s | 732 s | 734 w | 733 w | 732 mw | *e* | CCl str |
| 713 w<br>709 m | 703 vw | 703 m | * | | | | *a* | |
| | 688 vw | ~695 w | 697 w | | | | | |
| 672 mw | 671 s | 672 s | 672 s | 672 s | 674 s | 672 s | *e* | CCl str |
| | 667 m | 667 w | 667 w | | | | | |
| 653 w | 653 m | 652 m | 650 vw (*) | 654 s | 654 mw | * | *a* | CCl str |
| 619 w *e* | 616 m | 617 ms | 616 m | 615 w | 617 mw | 615 mw | *e* | |
| | | | | 610 vw | | | | |
| | | | | | 590 w | * | *a* | |
| 577 mw | 576 m | 577 m | 576 vw (*) | 578 s | 578 s | * | *a* | |
| | | 547 vw | 547 vw | | | ~550 vw? | | |
| 540 vw<br>536 mw | 534 m | 535 m | 533 vw (*) | 537 w | | * | *a* | |
| 531 mw<br>527 mw<br>520 vw | 527 m | 527 ms | 524 ms | 530 s | 527 s | 525 s | *e* | ring def |
| | | | | ~505 w | ~500 vw | * | *a* | |
| 458 w | 457 m | 461 mw | 461 vvw(*) | 460 s | 463 s | * | *a* | |
| | 452 m | 452 w | 453 w | | 454 mw | 453 mw | *e* | |
| | | ~385 vw | ~385 vw | | | | | |
| | 364 w | 363 w | * | 366 m | 365 w | * | *a* | |
| | 343 m | 344 m | 345 m | 347 m | 346 m | 346 m | *e* | |
| | 327 vw | | | 329 m | 328 w | * | *a* | |
| | 306 w | 306 w | 306 w | 308 m | 307 m | 308 m | *e* | $CF_2$ |
| | | 302 w | 302 w | | | | | $CCl_2$ |
| | 278 vw | 275 vw | 277 vw | 280 w | ~280 vw | 281 w | *e* | def |
| | 268 w | ~265 vw | * | 268 vw | 269 w | * | *a* | |
| | 258 w | 259 mw | 259 mv | 260 w | 261 w | 260 mw | *e* | |
| | 235 vw | | | 239 m | | * | *a* | |
| | 230 w | | | 226 mw | 225 mw | 226 mw | *e* | |
| | 205 vw | 205 vw | 204 vw | 208 w | 207 vw | 207 w | *e* | |
| | 180 vvw | | | 180 w | 185 vw | 184 w | *e* | |
| | ~167 vw | | | 167 w | 164 vw | 164 w | *e* | |
| | 160 w | | | | | | | |
| | 149 vw | | | 146 m | | | | |
| | | | | | 136 vw | 136 vw | | |

[a] Weak bands in the regions above 3100 $cm^{-1}$ and between 2800 and 1500 $cm^{-1}$ have been omitted. [b] Abbreviations: s, strong; m, medium; w, weak; v, very; C, C type contour. [c] *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. [d] An asterisk signifies that the band vanishes in the spectrum of the crystalline solid.

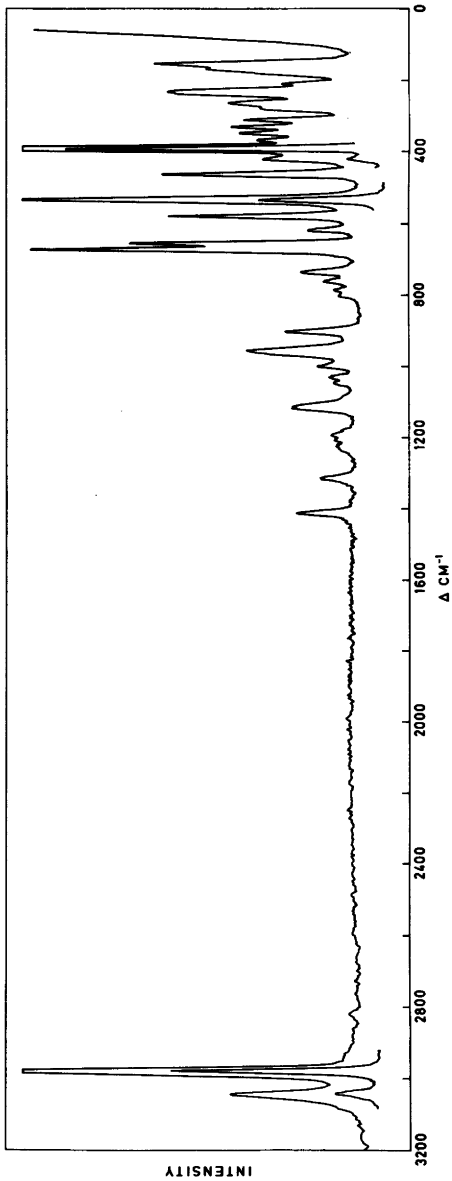


*Fig. 3.* The Raman spectrum of liquid 1,1,2-trichloro-2,3,3-trifluorocyclobutane.

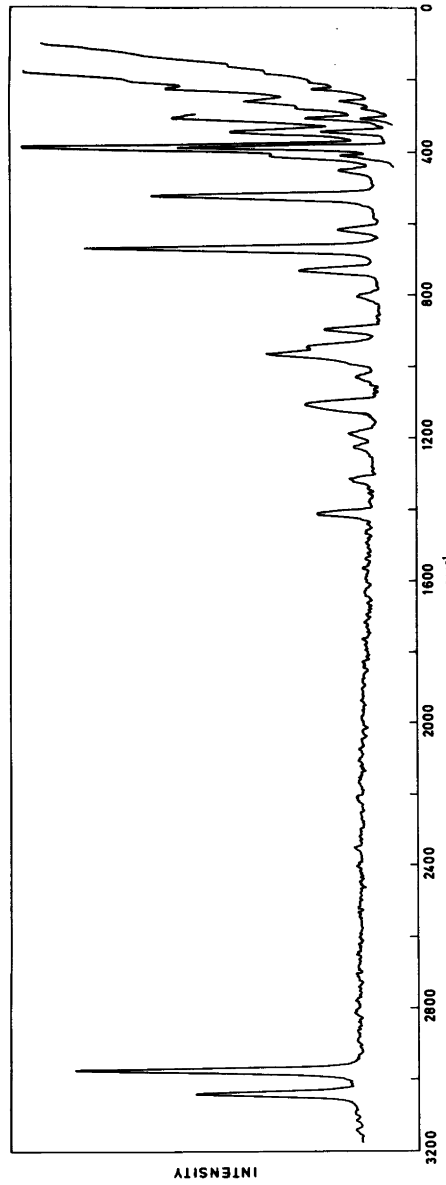


*Fig. 4.* The Raman spectrum of crystalline 1,1,2-trichloro-2,3,3-trifluorocyclobutane at −185 °C.

substituents are identical, this does not lead to different species. On the fourth, though, clearly the fluorine atom must be axial and the chlorine equatorial 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 crystallization 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; those 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 abundance 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-tetrafluorocyclobutane[12] and 1-chloro-2,2,3,3-tetrafluorocyclobutane,[13] introduction of fluorine atoms leads to higher than normal $CH_2$ 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 electronegative atoms tend to withdraw electrons from the ring and so weaken the band. In $C_4Cl_8$, 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 probably 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 frequency[15] 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-trichloropropane.[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 cyclobutane, we feel that we have cast doubt on an earlier report of the same effect.

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