

CONFORMATIONAL BEHAVIOUR OF FIVE CYCLOBUTANE DERIVATIVES

D.L. POWELL,¹ A. GATIAL,¹ P. KLAEBOE,¹ C.J. NIELSEN,¹ and
A.J. KONDOW²

¹Department of Chemistry, University of Oslo

²Department of Chemistry, College of Wooster, Wooster, Ohio, USA

ABSTRACT

Chloro-, bromo-, and cyano cyclobutane, 1-chloro-1,2,2-trifluorocyclobutane (CTFCB), and 1,1,2-trichloro-2,3,3-trifluorocyclobutane (TCTFC) have been crystallized in the Raman at low temperature and in the infrared at high pressure and deposited in inert gas matrices to obtain information on the presence of a second conformer and on the size of the barriers between the two conformers.

INTRODUCTION

For many years it has been thought that chloro- and bromo-cyclobutane may have two conformers, although the evidence in favour of this was admittedly rather weak. Quite recently, electron diffraction results for these two compounds and for methylcyclobutane have been interpreted in terms of 2 conformers with, respectively, 10, 4, and 11% of the axial conformer at room temperature (ref. 1). Microwave investigations on chloro- and bromocyclobutane (refs. 2,3) as well as on cyanocyclobutane (refs. 4,5) found only one conformer, that in which the lone substituent is equatorial. However, in an investigation which has just appeared, a second, axial conformer has been shown to exist in cyanocyclobutane by microwave spectroscopy (ref. 6). Several years ago 1,1,2-trichloro-2,3,3-trifluorocyclobutane (TCTFC) was shown by infrared and Raman techniques to have two conformers (ref. 7). Methylcyclobutane was also recently shown by infrared and Raman spectroscopy to have two conformers (ref. 8).

DLP on leave from the College of Wooster, Wooster, Ohio, USA.
AG on leave from Department of Physical Chemistry, Slovak
Technical University, 81237, Bratislava, Czechoslovakia.

EXPERIMENTAL

Infrared spectra were recorded using a Perkin-Elmer model 225 and a Bruker model 114C FT-IR. The diamond anvil cell was from High-Pressure Diamond Optics, Inc. and the matrix work was performed using an Air Products Displex cryostat.

Raman spectra were taken using a Dilor RT 30 triple monochromator Raman spectrometer equipped with a Spectra-Physics model 2000 argon ion laser.

RESULTS AND DISCUSSION

Drawings of the compounds in this study are shown in Figure 1.

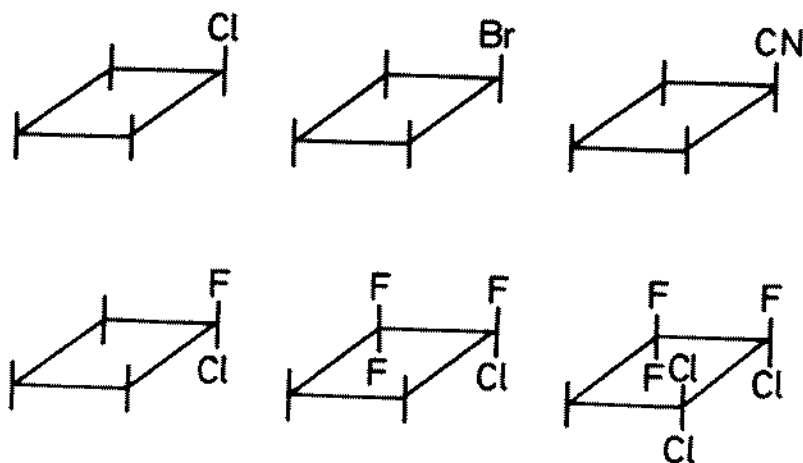


Fig. 1. Schematic representation of the cyclobutanes.

Crystallization in Raman

The low temperature Raman results will be discussed only for the three mono-substituted compounds inasmuch as TCTFC was discussed earlier (ref. 7) and no anisotropic crystal has yet been obtained for 1-chloro-1,2,2-trifluorocyclobutane (CTFCB). The crystallization of these compounds has also been studied by infrared spectroscopy, but, for reasons not clear to us, the Raman results are so much more convincing that only they will be given.

We have always found untenable the suggestion given earlier (ref. 9) that only one mode in chloro- and bromocyclobutane is conformation dependent in light of the many differences in the spectra of axial and equatorial monohalocyclohexanes (ref. 10) and in 1,1,2-trichloro-2,3,3-trifluorocyclobutane (ref. 7). When the three mono-substituted compounds were crystallized from the liquid, several weak bands disappeared in the spectra of each one (see for example Figure 2 where two small portions of the Raman spectra of chlorocyclobutane are shown.) The disappearance of

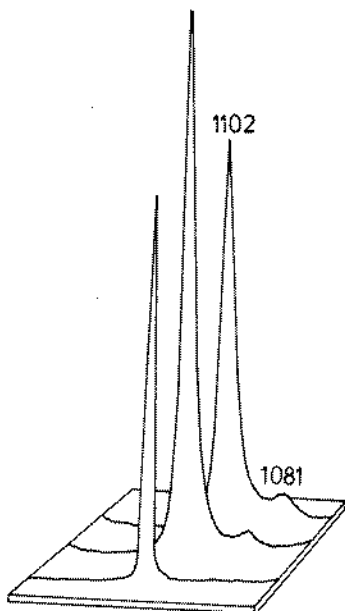


Fig. 2. Raman spectra of chlorocyclobutane. The trace behind is of the liquid at 295 K, the middle trace is of the liquid at 205 K, and the front trace is of the crystalline solid at 150 K.

several bands each in the spectra of chloro-, bromo- and cyanocyclobutane, even though they are quite weak, does two things: (i), it allows the postulation of a second conformer based on the observation of several bands rather than just one, and (ii), it helps to explain why the second conformer has been so elusive. It

is plain from the the relative intensities of the bands that the two bands identified by Rothschild as belonging to the C-X stretch of the axial conformer are easily the most intense of the axial bands which are not overlapped by equatorial bands. Given this, there is probably less than 5% of the axial conformer in the liquid phase of any of these compounds at room temperature.

High pressure crystallization

The crystals of chloro- and bromocyclobutane obtained at both low temperature and high pressure are much the same showing that the same conformer is present in both of these crystals. This is not the case with cyanocyclobutane. For this compound a small portion of the experimental frequencies is shown in Table 1 and

TABLE 1
Infrared Spectral Data for
Cyanocyclobutane
(1100-500 cm^{-1})

Liquid	Low Temperature Crystal	High Pressure Crystal
1106 s	1101 ms	1105 ms 1094 ms
1065 vw	1073 m	
1047 vw	1049 w 1040 vw	1049 w
1032 vw	1036 vw	1033 mw
1014 vw	1015 m	
		960 m
938 m	940 m	941 m 932 s
921s	927 m 903 w 885 vvw	
887 w	874 m	
		848 w
815 vw	813 vw	
785 w	784 m 781 w	
		772 m
	754 mw	
747 s	747 ms	
		733 mw
	596 mw	
589 m	590 w 580 w	
		549 w
	532 w	
518 m	520 m	523 mw

abbreviations: s, strong;
m, medium; w, weak; v, very.

portions of the infrared spectra of the liquid and of both the low temperature and high pressure crystals are shown in Figures 3 and 4. The bands of the high pressure crystal differ so greatly from those of the liquid that it is apparent that the conformer more stable at high pressure must be present in only very small abundance in the liquid. This is consistent with the results of the crystallization in the Raman in which only very weak bands disappear.

That the high pressure crystal of cyanocyclobutane should contain the axial conformer is not totally unexpected. In both the low temperature and high pressure crystals of cyanocyclohexane, the

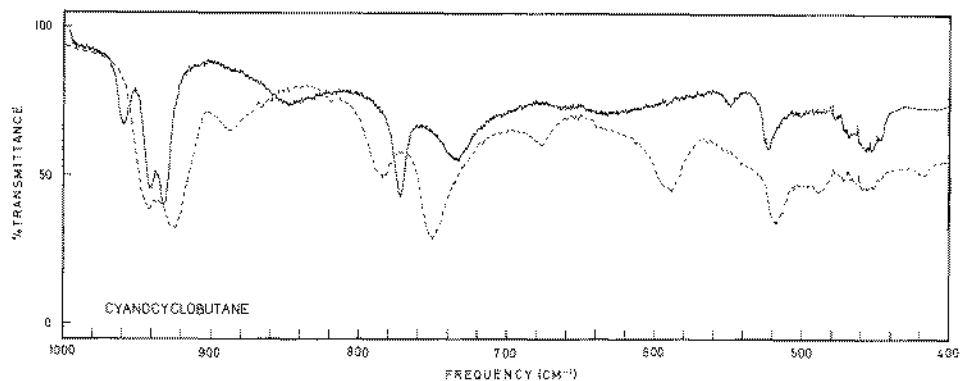


Fig. 3. Infrared spectra of the liquid (dashed curve) and high pressure crystal (solid curve) of cyanocyclobutane.

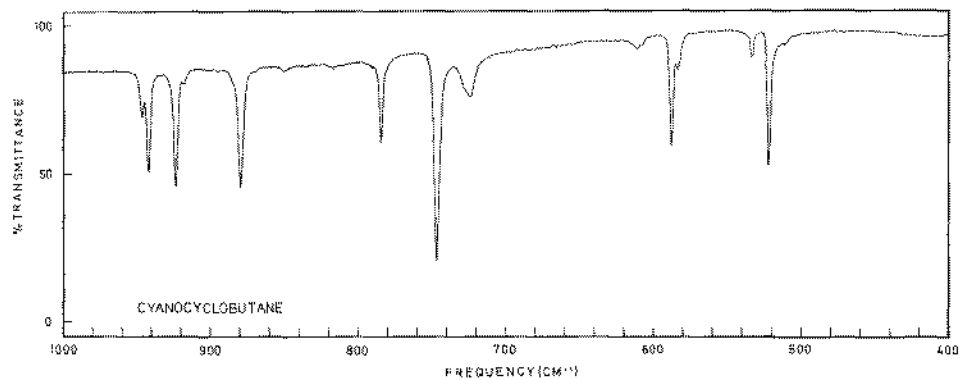


Fig. 4. Infrared spectrum of the low temperature crystal of cyanocyclobutane.

cyano group is axial (ref. 11). Isocyanatoatocyclohexane, in which there are substantial amounts of both conformers in the liquid phase, crystallizes at low temperature in the equatorial conformation but in the axial conformation at high pressure (ref. 12). However, our result is truly unusual as a conformer, present

initially at less than 5% abundance at atmospheric pressure, is able to be crystallized in a pure form. Apparently the volume change ΔV between the equatorial and axial conformer of cyanocyclobutane must be considerable, leading to a substantial displacement of the equilibrium between the conformers, according to the expression $d \ln K/dP = -\Delta V/RT$, toward the axial conformer before crystallization occurs.

MATRIX

Mono-substituted cyclobutanes

Results on the three mono-substituted cyclobutanes are quite straightforward. In each case, when deposition in either argon or nitrogen matrices was made even at temperatures up to 900 K (at which temperature there will be much more of the less stable conformer than at room temperature), the spectra show only the more stable conformer. Bands due to the less stable conformer are completely absent, implying that in each case the barrier between the conformers is less than 5 kJ/mole.

Multiply-substituted cyclobutanes

The ratio of conformational abundance in the matrices of CTFCB and TCTFC is not the same as in the vapours from which they were deposited implying a "cooling of the conformational equilibrium" (ref. 13). (See Figure 5.)

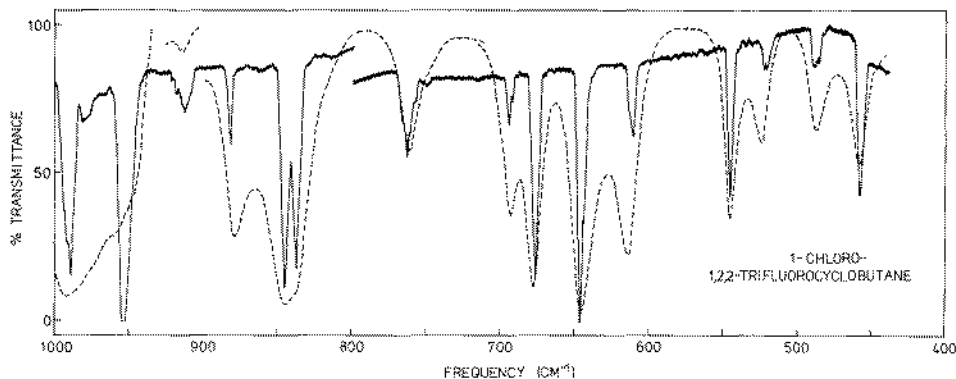


Fig. 5. Infrared spectra of CTFCB as a liquid (dashed curve) and isolated in an argon matrix (solid curve).

1-Chloro-1,2,2-trifluorocyclobutane

In CTFCB the amount of the less stable conformer is substantially reduced from that which was present in the vapour in both argon and nitrogen matrices; this less stable conformer is further reduced upon annealing. This implies a barrier between the two conformers of the order of 7 kJ/mol.

1,1,2-Trichloro-2,3,3-trifluorocyclobutane

That there is a "cooling of the conformational equilibrium" in TCTFC again implies a barrier near 7 kJ/mol. At first glance this "cooling" does not seem as great as in CTFCB, but this is not quite accurate. The energy difference between the conformer is less, leading to an equilibrium constant closer to unity. In argon, the amount of the less stable conformer is smaller and this is further diminished upon annealing just as with CTFCB. However, in nitrogen the exact opposite occurs. The amount of the less stable conformer is enhanced compared with the vapour; annealing leads to even more of the less stable conformer. Annealing of the matrices quickly leads to equilibrium in each case as witnessed by no further change.

This apparently peculiar behaviour can be rationalized as follows. The energy difference between the conformers is small. Even a small change in ΔH may be sufficient to change its sign, so that the formerly less stable conformer is now the more stable conformer. Using the intensities of bands at equilibrium to calculate apparent equilibrium constants and assuming $\Delta S = 0$, the change in ΔH is found to be 0.7 kJ/mol. A ΔH of - 0.5 kJ/mol in argon would then become + 0.2 kJ/mol in nitrogen.

In a matrix composed of 97% argon and 3% nitrogen, while the behaviour on deposition and annealing more closely resembled that in an argon matrix, the apparent point of equilibrium is shifted about 30% of the way from what it was in pure argon toward what it was in nitrogen. If some sort of weak complex with the matrix material is occurring, it is with the nitrogen and not the argon (ref. 14).

1-Chloro-1-fluorocyclobutane

Our preliminary results of this compound are that bands of the less stable conformer are absent in the matrix spectra

implying a barrier like these of the monosubstituted compounds rather than those in the highly substituted molecules.

CONCLUSION

In summary, we feel that we have demonstrated that small amounts of axial conformers are present in mono-substituted cyclobutanes, separated from the dominant equatorial conformers by rather small barriers. The barriers are higher in the two multiply substituted compounds which we have studied, high enough that both conformers are trappable in the matrix but not high enough to preserve the equilibrium in the vapour phase.

ACKNOWLEDGEMENTS

We would like to thank the Norwegian Marshall Fund, NAVF, NTNF, and Research Corporation for financial support of this work.

REFERENCES

1. T. Jonvik, to be published.
2. H. Kim and W.D. Gwinn, *J. Chem. Phys.* 44 (1966) 865.
3. W.G. Rothschild and B.P. Dailey, *J. Chem. Phys.* 36 (1982) 2931.
4. M.Y. Fong and M.D. Harmony, *J. Chem. Phys.* 58 (1973) 4260.
5. J.R. Durig, L.A. Carreira and W.J. Laffety, *J. Mol. Spectrosc.* 46 (1973) 187.
6. W. Caminati, B. Velino, M. Dakkouri, L. Schäfer, K. Siam and J.D. Ewbank, *J. Mol. Spectrosc.* 123 (1987) 469.
7. D.L. Powell and P. Klaeboe, *Acta Chem. Scand.* A32 (1978) 71.
8. J.R. Durig, T.J. Geyer, T.S. Little and V.F. Kalasinsky, *J. Phys. Chem.* 86 (1987) 545.
9. W.G. Rothschild, *J. Chem. Phys.* 45 (1967) 1214, 3599.
10. T. Woldbaek, *Acta Chem. Scand.* A36 (1982) 641.
11. T. Woldbaek, A. Berkessel, A. Horn and P. Klaeboe, *Acta Chem. Scand.* A36 (1982) 719.
12. C.E. Sjøgren and P. Klaeboe, *J. Mol. Struct.* 100 (1983) 433.
13. P. Huber-Wälchli and Hs. H. Günthard, *Spectrochim. Acta* 37A (1981) 285.
14. J. Murto, A. Kivinen and I. Mutikainen, *Chem. Phys. Lett.* 36 (1975) 369.