

6. Akimoto, S., Nagata, T. and Katsura, T. *Nature* **179** (1957) 37.
7. Shirane, G., Cox, D. E. and Ruby, S. L. *Phys. Rev.* **125** (1962) 1158.
8. Haggerty, S. E. and Lindsley, D. H. *Carnegie Inst. Washington Yearb.* **68** (1970) P. 247.
9. Shannon, R. D. and Prewitt, C. T. *Acta Cryst. B* **25** (1969) 925.

Received March 17, 1971.

## The Vibrational Spectra of 1,1,2-Trichloropropionitrile

T. TORGRIMSEN and P. KLÆBOE

*Department of Chemistry, University of Oslo,  
Oslo 3, Norway*

In order to prepare trichloro acrylonitrile we synthesized 1,1,2-trichloropropionitrile  $\text{CH}_2\text{ClCCl}_2\text{CN}$  (later called TCPN) as an intermediate product. We have previously reported the vibrational spectra of the related molecules 2-chloro- and 2-bromopropionitrile<sup>1</sup> and found it of interest to study the conformational equilibrium of TCPN. The infrared, Raman and NMR data for this molecule will be reported in the present communication.

*Experimental.* The sample of TCPN (b.p.  $31^\circ$  at 7 torr) was prepared by chlorinating acrylonitrile<sup>2</sup> and the purity was checked by mass spectrometry and gas chromatography. The compound decomposed upon storage and was distilled immediately before the spectral recordings. However, a few impurity bands were detected in the low temperature infrared spectra.

The infrared and Raman spectrometers and the experimental technique have been described.<sup>3</sup> NMR spectra of TCPN dissolved in  $\text{CCl}_4$  and  $\text{CDCl}_3$  at  $25^\circ$ ,  $-30^\circ$  and  $-60^\circ$ , using TMS as an internal standard were recorded with a Varian A 60 spectrometer.

*Results.* The infrared spectra of TCPN as a liquid and as a crystalline solid at ca.  $-70^\circ$  are shown in Fig. 1. A complete list of the observed Raman shifts and all

except the weakest infrared bands are given in Table 1. Additional infrared spectra of TCPN dissolved in the unpolar  $\text{CCl}_4$  and the highly polar  $\text{CH}_3\text{CN}$  were recorded. Significant variations in the intensities of certain infrared bands were observed, those which increase or decrease in polar solvents are denoted *i* or *d* in Table 1, respectively. A corresponding variation in the Raman intensities was difficult to observe for this molecule, since most of the appropriate bands were rather weak.

The number of infrared and Raman bands observed for TCPN confirms that the molecule exists in different conformations in the liquid. These are undoubtedly the two staggered conformers having the symmetry  $C_s$  (pseudo *trans*) and  $C_1$  (pseudo *gauche*). At least six infrared bands present in the liquid disappeared in the crystalline state. Among them, the bands at 653, 725, and  $564\text{ cm}^{-1}$  definitely were reduced in intensities with polar solvents (*d*) whereas no corresponding conclusions could be made for those at 1298, 402, and  $276\text{ cm}^{-1}$  because of interfering solvent bands. The  $C_1$ -conformer has the higher dipole moment in TCPN and should therefore be stabilized in polar solvents. Accordingly, in agreement with succinonitrile<sup>4</sup> and the 2-halo propionitriles<sup>1,5</sup> TCPN crystallized in the  $C_1$ -conformer at low temperatures. Moreover, as roughly estimated from the relative infrared and Raman band intensities, the  $C_1$ -conformer is much more abundant in the liquid TCPN at room temperature than the  $C_s$ -conformer. For 2-chloro- and 2-bromopropionitrile<sup>1</sup> on the other hand, the abundance of the two conformers appeared close to the statistical  $C_1/C_s=2:1$  ratio in the liquid. Thus for TCPN as well as in the 1,1,2-trihaloethanes,<sup>6</sup> the steric repulsion between the halogens favours the  $C_1$ -conformer. Furthermore, a cyano group apparently favours orientation *gauche* to another cyano group<sup>4</sup> or to a halogen<sup>1,5</sup> in the crystal, also favouring the  $C_1$ -conformer in the crystalline TCPN.

The stronger infrared and Raman bands of TCPN are generally interpreted as fundamentals and are fitted with a description of the atomic motions in Table 1. Apart from the localized group frequencies:  $\text{CH}_2$  stretch,  $\text{CH}_2$  scissor, and  $\text{C}\equiv\text{N}$  stretch, most of these motions probably involve several atoms. The strong bands at 1214 and  $1000\text{ cm}^{-1}$  are interpreted as overtones in Fermi resonance

Table 1. Infrared and Raman spectral data of 1,1,2-trichloropropionitrile.

Liquid	Infrared <sup>a</sup> Solid	Raman Liquid	Conformer	Tentative interpretation
3022 s <sup>b</sup>	3017 s	3027 m D	I, II <sup>c</sup>	CH <sub>2</sub> asym stretch
2965 s	2959 s	2967 vs P	I, II	CH <sub>2</sub> sym stretch
2836 w		2838 w		
2250 s	2253 w	2255 vs P	I, II	C≡N stretch
1425 s	1427 s	1429 m D	I, II	CH <sub>2</sub> scissor
	1397 vw			
1298 m	* <sup>d</sup>	1300 vw	I	CH <sub>2</sub> wag
1281 s	1286 m	1286 w P	II	CH <sub>2</sub> wag
1224 s	1226 s	1225 m D	I, II	CH <sub>2</sub> twist
1214 s	1215 s	1215 m		2 × 611 = 1222
	1110 m	1113 m, sh		
1100 s, sh	1099 m			
1087 s	1087 s	1092 w D	I, II	CH <sub>2</sub> rock
1065 w, sh	1065 vw			
1040 vw	1048 w	1049 vw?		
1011 m, sh	1023 vw	1015 vw		
1000 s	1000 s	1003 m P		2 × 496 = 992
986 s <sup>i e</sup>	987 s	991 m P	II	C—C—C asym stretch
975 m, sh	975 m			
953 s <sup>d</sup>	*	955 vw	I	C—C—C asym stretch
877 s	879 s	881 s P	I, II	C—C—C sym stretch
819 m	824 w	826 vw	I	CCl <sub>2</sub> asym stretch
	800 m sh			
788 vs <sup>i</sup>	782 s	791 vs P	II	CCl <sub>2</sub> asym stretch
750 vs <sup>i</sup>	744 s	754 m P	II	C—Cl stretch
725 s <sup>d</sup>	*	729 vw D	I	C—Cl stretch
657 w	662 w	664 vw		
611 s	613 s	614 s P	II	CCl <sub>2</sub> sym stretch
564 m <sup>d</sup>	*	568 m P	I	CCl <sub>2</sub> sym stretch
	513 vw			
496 s	497 s	499 m, sh	I, II	C—C—C def
487 s	487 s	489 vs P	I, II	C—C—Cl def
430 vw				
402 w	*	406 w P	I	C—C≡N def
340 s	345 s	343 m P	II	C—C≡N def
319 m	321 m	322 vs P	II	CCl <sub>2</sub> def
276 w	*	278 vw P	I	CCl <sub>2</sub> def
255 s	256 s	259 m D	I, II	CCl <sub>2</sub> def
208 s	207 s	212 m D	I, II	CCl <sub>2</sub> def
		190 vw	I, II	CCl <sub>2</sub> def
		172 s D	I, II	C—C≡N def
		144 s D	I?	torsion
		113 s D	II?	torsion

<sup>a</sup> The weakest infrared bands are omitted.

<sup>b</sup> The following abbreviations have been used: s, strong; m, medium; w, weak; sh, shoulder; v, very; P, polarized and D, depolarized.

<sup>c</sup> The conformers are denoted: I = *trans* (C<sub>s</sub>-symmetry) II = *gauche* (C<sub>1</sub>-symmetry).

<sup>d</sup> Bands marked with *i* and *d* increase and decrease in polar solvents, respectively.

<sup>e</sup> Bands marked with an asterisk are absent in the solid.

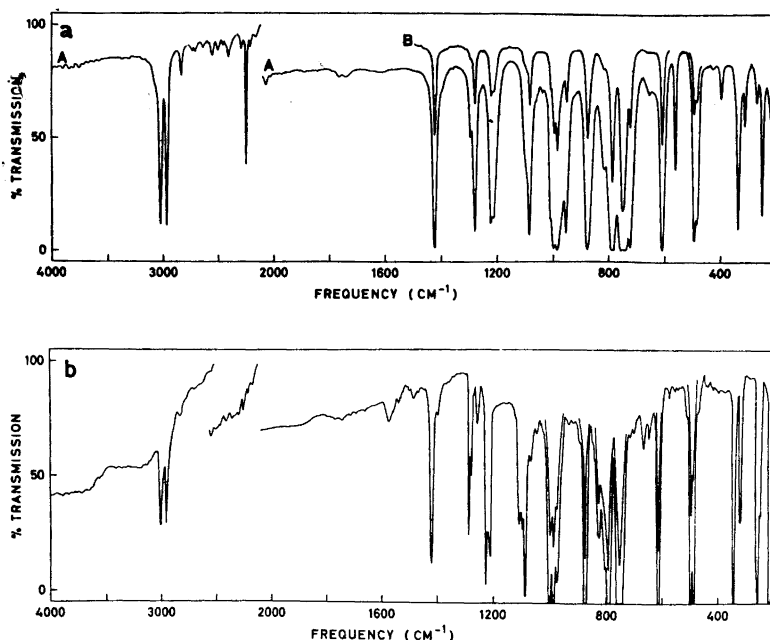


Fig. 1. The infrared spectra of 1,1,2-trichloropropionitrile; upper curve: liquid, cell thickness A: 0.1 mm, B: capillary; lower curve: polycrystalline solid at  $-70^{\circ}$ , cell thickness 0.1 mm. (The bands at 1575, 1258, 839, 642, and  $573\text{ cm}^{-1}$  in the lower curve are due to an ethylene compound impurity.)

with the fundamentals at 1224 and  $986\text{ cm}^{-1}$ .

As observed for the 2-halo propionitriles<sup>1</sup> the majority of infrared and Raman bands of TCPN have been assigned to both conformers. Obviously, the bands disappearing in the crystalline state are assigned to the  $C_2$ -conformation only, whereas the corresponding  $C_1$  bands are more uncertain. We have no infrared or Raman data of the crystalline TCPN below  $200\text{ cm}^{-1}$ , but the Raman bands at 113 and  $144\text{ cm}^{-1}$  are tentatively assigned to torsional modes for the  $C_1$  and  $C_2$  conformers, respectively, in agreement with the results<sup>7</sup> for various halo ethanes.

The NMR spectra displayed one single proton shift ( $\delta = 4.17\text{ ppm}$ ) in  $\text{CCl}_4$  at  $25^{\circ}$ . Lowering the temperature and changing to the more polar solvent  $\text{CDCl}_3$ , raised the chemical shift ( $\delta = 4.30\text{ ppm}$  at  $-60^{\circ}$  in  $\text{CDCl}_3$ ). These data reveal that the conformational equilibrium is shifted to

the more polar conformer ( $C_1$ ) in polar solvents and at lower temperatures.

We are indebted to K. Ruzicka for preparing and purifying the compound.

1. Klæboe, P. and Grundnes, J. *Spectrochim. Acta A* **24** (1968) 1905.
2. Brintzinger, H., Pfannstiel, K. and Koddebusch, H. *Angew. Chem.* **A 60** (1948) 311.
3. Klæboe, P. *Acta Chem. Scand.* **25** (1971) 695.
4. Fitzgerald, W. E. and Janz, G. J. *J. Mol. Spectry.* **1** (1957) 49.
5. Wyn-Jones, E. and Orville-Thomas, W. J. *J. Chem. Soc. A* **1966** 101.
6. Torgrimsen, T. and Klæboe, P. *Acta Chem. Scand.* **24** (1970) 1145.
7. Allen, G., Brier, P. N. and Lane, G. *Trans. Faraday Soc.* **63** (1967) 824.

Received March 16, 1971.