

Conformation and Vibrational Spectra of 1,1,2-Tricyanoethane

D. L. POWELL,^a P. KLÆBOE,^b
R. SCHOCHET^{a*} and K. RUZICKA^b

^aDepartment of Chemistry, College of Wooster, Wooster, Ohio, USA, ^bDepartment of Chemistry, University of Oslo, Oslo 3, Norway

In connection with our work on 1,1,2,2-tetracyanoethane and 1,2-dichlorotetracyanoethane¹ we thought it of interest to study also 1,1,2-tricyanoethane thus filling in the gap between dicyanoethane^{2,3} and tetracyanoethane. Tricyanoethane is expected to exist as an equilibrium mixture of a less polar form having no symmetry (C_1) and of a more polar form having symmetry C_s in liquid phases but to crystallize in one or the other of these conformations. Earlier work on related compounds which may be noted includes that on 1,1,2-trichloroethane⁴ and 1,1,2-tribromoethane⁵ in both of which the pre-

ferred conformation in the crystal was the less polar C_1 form.

Experimental. The compound was prepared by a three step synthesis⁶ starting from ethyl cyanoacetate making ethyl-2,3-dicyanopropionate, 2,3-dicyanopropionamide, and finally 1,1,2-tricyanoethane. It was dried over P_2O_5 and purified by sublimation at 80–90°/0.02 torr.

IR spectra were recorded in the region 5000–200 cm^{-1} of Nujol and C_4Cl_8 mulls, of KBr and KI pellets, of CH_3CN , CD_3CN , and acetone solutions contained in KBr cavity cells, and of the melt between CsI plates employing a Perkin-Elmer Model 225 spectrometer. Far IR spectra of an adamantane disk from 400 to 40 cm^{-1} were recorded on a Hitachi Perkin-Elmer FIS-3 spectrometer. Raman spectra of the solid and of saturated solutions in CH_3CN and CD_3CN were recorded on a Cary Model 81 equipped with a Spectra Physics Model 125A He-Ne laser.

Results and discussion. Our spectral results along with our tentative assignments are given in Table 1; the Raman spectrum of the solid appears in Fig. 1. Since the results in the various solvents in the IR are of necessity less complete than those of the melt they have been omitted from the table. No expected bands failed

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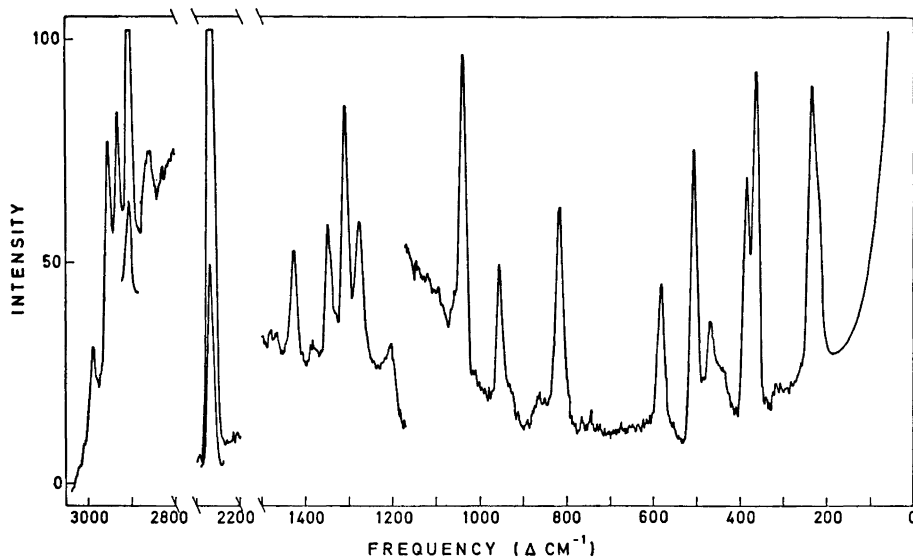


Fig. 1. Raman spectra of crystalline 1,1,2-tricyanoethane.

Table 1. Infrared and Raman spectral data for 1,1,2-tricyanoethane.

Infrared ^a		Raman			Interpreta- tion
Liquid ^b	Mull	CH ₃ CN and/or CD ₃ CN solution	Solid	Conformer	
2984 m ^c	2983 m	2990 vw ?	2987 w		CH str
2957 m	2947 m	2957 m	2950 m		CH str
2920 ms	2922 ms	2920 w 2907 w	2930 w		CH str
			2858 vw		
2664 w	2673 w		2680 vw		
	2267 ms		2267 vs		C≡N str
2262 s	2252 s		2255 w		C≡N str
1420 m	1419 m	1427 mw	1426 mw		CH ₂ scissor
~ 1385 w,sh	1390 w				
1338 w	1337 w	~ 1340 w	1348 mw		CH ₂ bend
	1330 vw				
1307 m	1305 m	1305 m ?	1309 ms		CH ₂ bend
1267 w	1272 m	1275 w ? 1260 w ?	1275 mw	I ^d	CH bend
1215 m	* ^e	~ 1215 m	*	II	CH bend
1197 mw,sh	1196 m		1203 w	II	CH ₂ bend
	1157 w		~ 1160 vw ?	I	CH ₂ bend
~ 1055 w,sh	1052 mw				
1032 m	1030 m	1040 s	1038 s		CC str
952 m	948 m	955 m	953 m		CC str
928 s	932 m				CH ₂ bend
~ 918 m,sh	923 m			I	CC str
873 w	*		858 vw ?	II	CC str
801 mw	810 mw	~ 805 vw	815 ms	I	CC str
780 mw	*	783 s	*	II	CC str
748 vw	*	753 w	*	II	
~ 725 vw	737 mw				
~ 705 w					
686 m	698 w	~ 690 w			
~ 580 vw,sh	~ 581 w,sh	577 s	579 m		skeletal bend
570 m	573 m				skeletal bend
498 w		498 s	507 s		skeletal bend
476 m	*			II	skeletal bend
459 m	461 m	462 s	468 w	I	skeletal bend
372 w	378 m		383 m		skeletal bend
352 m	357 w		361 s		skeletal bend
	312 w ^f	~ 315 vw ?			
~ 286 vw					
~ 275 vw					
245 s			238 s		skeletal bend
225 s	226 s ^f	228 s			skeletal bend
221 ms,sh			222 w		
212 m					
	165 s ^f	~ 175 vw ?	~ 177 vw		skeletal bend
	148 s ^f	~ 155 m			skeletal bend
	105 w ^f		110 w		
	90 m ^f		~ 98 vw		torsion

^a The weaker infrared bands are omitted. ^b Infrared solution data have been omitted from this table. ^c The following abbreviations were used: s, strong; m, medium; w, weak, sh, shoulder; and v, very. ^d Bands due only to the conformer, stable in the crystal are designated as I and those due only to the conformer not stable in the crystal are designated as II. ^e An asterisk signifies a band definitely absent in the solid. ^f Bands were determined from an adamantane pellet.

to appear in solution nor did any unexpected bands appear. The weaker IR bands especially in regions where there can be no fundamentals have also been omitted from the table; in a molecule of this complexity with this low symmetry any agreements based on overtone or combination bands would be quite unconvincing.

It is apparent from Table I that several bands, not present in the spectra from the crystalline state, appear in the spectra of the solutions and the melt. We take these as evidence that, as expected, only one conformer exists in the crystal but that two conformers are present in the liquid phases. We have designated those bands we feel are due to the conformer which persists in the crystal with a I and those due to the less stable form with a II. Many bands, of course must be ascribed to both conformers; these are not labelled.

From the "gauche effect"⁷ one could predict that the C_s isomer would be more abundant in the liquid. However, in the cases where one can designate the bands due to similar modes in the different conformers, the bands have approximately equal intensity implying that both forms are present in substantial amounts.

Unfortunately we are not able to tell which is the form stable in the crystal. In principle, good evidence can be provided by the use of solvents of differing dielectric constant. The more polar conformation (C_s) is favoured in solvents of high dielectric constant.⁷ However, tricyanoethane is so nearly insoluble in non-polar or weakly polar solvents such as CHCl_3 and CH_2Cl_2 that this effect could not be observed. Relative intensities of bands known to belong to the two different conformers showed no real change in the acetonitrile and acetone solutions or in the melt. This is not surprising because, although the dielectric constants in these three cases are certainly different, the position of equilibrium is rather insensitive to changes in an already large dielectric constant. Although contours could be roughly predicted for the vapour phase IR bands of both conformers, the very low volatility of tricyanoethane coupled with

its instability at elevated temperatures immediately discouraged such an attempt.

Finally, study of the melt at several temperatures could give information which would enable a calculation of the energy difference between the two forms to be made. However, decomposition was occurring even just above the melting point and it was obvious that any attempt at a higher temperature would not be worthwhile.

If one had available for comparison only the data on dicyanoethane^{2,3} in which the *gauche* conformation (C_s) is the stable form in the crystal, one would be tempted to assume that this is the situation also in tricyanoethane and that the C_s conformation is the more stable. However, in tetracyanoethane¹ the more stable form is the *trans* (C_{2h}) and we are left with no desire to make rash predictions.

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