

Conformation and Vibrational Spectra of 1,1,2,2-Tetracyanoethane and 1,2-Dichlorotetracyanoethane

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1,1,2,2-Tetracyanoethane and 1,2-dichlorotetracyanoethane have been studied by IR and Raman spectroscopy. Both have been shown to possess C_{2h} symmetry in the crystal and evidence is presented for their retention of this conformation in solution. Partial vibrational assignments have been made.

Many halogenated ethanes have been studied by vibrational spectroscopy. It is well known that in the liquid and vapour states ethanes of the type CX_2Y-CX_2Y exist in general as a mixture of *trans* (C_{2h}) and *gauche* conformers (C_2), but that in the solid state the ethane will usually crystallize preferentially in only one conformation.

In 1,1,2,2-tetrafluoroethane, this more favoured conformation in the crystal is the C_{2h} ,¹ in 1,1,2,2-tetrachloroethane it is the C_2 ,² and in 1,1,2,2-tetrabromoethane it may be either, depending upon the conditions during crystallization.² The situation is more straightforward in the 1,2-dihaloethanes as three of the four crystallize in the C_{2h} conformation,³ the data are not conclusive for difluoroethane⁴ which may crystallize in both forms, although the samples may have been amorphous rather than truly crystalline. Warning against the easy assumption that a cyano group will behave as a pseudo halogen is provided by the observation that 1,2-dicyanoethane crystallizes in the C_2 conformation.^{5,6} The cyano group is much more polar, with its lone pair of electrons directed outward, and, with its cylindrical shape, very different sterically. Furthermore, in the halocycanoethanes^{7,8} and in 1,1,2-trichloropropionitrile,⁹ the favoured conformations are those in which the cyano group is *gauche* to a halogen atom. Thus it is not at all clear which form of these compounds one could expect to be present in the crystal.

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In solution, these compounds present an interesting test of the "gauche effect",¹⁰ the tendency of a compound "to adopt that structure which has the maximum number of gauche interactions between the adjacent electron pairs and/or polar bonds". The gauche form (C_2) could be predicted to predominate in the case of tetracyanoethane. The case of dichlorotetracyanoethane, with its six polar substituents, is less obvious. In any case, use of a polar solvent would be expected to favour the form having the higher dipole moment, in these cases, the gauche forms.¹¹

It is of interest to see how well these expectations are fulfilled. Neither of these compounds has been studied spectroscopically before nor has to our knowledge any study been made of their conformational behaviour.

EXPERIMENTAL

Tetracyanoethylene served as a starting material for both compounds. Tetracyanoethane is the less stable of the two, the solid darkening in a few days time after preparation.¹² Accordingly the spectral work, especially the Raman, was done as soon as possible after preparation and purification by recrystallization.

No evidence of decomposition was observed for dichlorotetracyanoethane even after several months standing at room temperature after preparation¹³ and purification by sublimation under reduced pressure.

IR spectra in the region $5000 - 200 \text{ cm}^{-1}$ were recorded of mulls, KBr pellets, and of CH_3CN solutions on a Perkin-Elmer Model 225 and of adamantane disks in the region $400 - 40 \text{ cm}^{-1}$ on a Hitachi Perkin-Elmer Model FIS-3. Raman spectra of the solids and of CH_3CN solutions in standard Cary capillary cells or in melting point capillaries with polished ends were recorded on a Cary Model 81 equipped with a Spectra-Physics Model 125A He-Ne laser.

The solution work was restricted to the use of CH_3CN since both compounds are completely insoluble in non-polar solvents such as CCl_4 or CS_2 and in such slightly polar solvents as CHCl_3 or CH_2Cl_2 and are either insoluble or react with such other polar solvents as dimethyl sulfoxide or dimethylformamide. Even in CH_3CN the solubility was not very great.

The cavity cells were employed because of an apparent reaction of these compounds of the normal IR cells presumably caused by contact with metal. Even then, the solution of tetracyanoethane rapidly darkened and the solution of dichlorotetracyanoethane turned yellow during the recording of the spectra. Although the dichlorotetracyanoethane was more stable, it obviously reacted quickly with CsI and somewhat more slowly with KBr.

Neither compound was stable enough to be run as a melt (although an attempt was made to do so with dichlorotetracyanoethane) or stable and volatile enough to be run as a vapour.

In both compounds, the possibility of reversion to the very stable tetracyanoethylene had to be kept in mind. A rather pure sample of tetracyanoethane, when sublimed under reduced pressure in an attempt to remove some objectionable fluorescent impurities, gave a fine white crystalline sample which was, from the Raman spectrum, 25 to 50 % tetracyanoethylene. The solid phase IR spectra of dichlorotetracyanoethane show traces of tetracyanoethylene; in the solution spectra contamination has progressed so far that tetracyanoethylene is responsible for one of the strongest bands in the spectrum.

RESULTS AND DISCUSSION

The results in the IR and Raman for tetracyanoethane are shown in Tables 1 and 2. Similarly, the results for dichlorotetracyanoethane are shown in Tables 3 and 4. For purposes of illustration, the IR spectrum of tetracyanoethane and the Raman spectrum and far IR spectrum of dichlorotetracyanoethane are shown in Figs. 1 and 2.

Table 1. Infrared spectral data for 1,1,2,2-tetracyanoethane.^a

Mull	CH ₃ CN solution	Interpretation
4096 w ^b		1302 + 2859 = 4161
~ 2960, w, sh		115 + 2859 = 2974
2918 vs	2911 s	C-H str
	~ 2900 m, sh	
~ 2856 m, sh		
2604 m		1302 + 1302 = 2604
	2508 w, br	
2484 m		224 + 2273 = 2497
2360 w		
2273 m		C≡N str
2210 m		911 + 1302 = 2213
2186 w		911 + 1282 = 2193
1971 w		889 + 911 = 1800
1718 w	1722 m	437 + 1282 = 1719
~ 1660 vw	1678 w	362 + 1302 = 1664
1602 w	1595 mw	719 + 889 = 1608
	1372 s, sh	
1302 w		CH bend
1278 vw		575 + 719 = 1294
1260 vw	1256 m	355 + 911 = 1266
1197 vs	1203 s	CH bend
1168 vw		
1159 w	1153 vw	136 + 1034 = 1170
~ 1142 vw		115 + 1034 = 1149
1075 w		195 + 889 = 1084
1011 m		136 + 889 = 1025
997 s	998 vs	C-C str.
936 m	~ 935 m	437 + 513 = 950
911 s	906 vs	C-C str
905 m, sh		416 + 491 = 907
850 vw		362 + 491 = 853
797 w		
	780 m	
754 vw		355 + 416 = 771
719 m	728 s	160 + 575 = 735
	686 w	
600 vw		115 + 491 = 606
570 m		155 + 416 = 571
562 s	568 w	skeletal bend
	558 mw	
438 w	445 mw	skeletal bend
364 m		skeletal bend
314 w ^c		155 + 160 = 315
254 w ^c		skeletal bend
~ 195 m sh ^c		skeletal bend
183 m ^c		skeletal bend
160 m ^c		skeletal bend
136 w ^c		
115 w ^c		torsion

^a Weaker infrared bands in regions where there can be no fundamentals have been omitted.

^b The following abbreviations have been used: s, strong; m, medium; w, weak; sh, shoulder and v, very. ^c Bands are from an adamantane pellet.

Table 2. Raman spectral data for 1,1,2-tetracyanoethane.

Solid	CH ₃ CN solution	Interpretation
	3002 m	
2943 w ^a		680 + 2271 = 2951
2859 m	2845 w	C-H str
2672 w		416 + 2273 = 2689
2271 vs		C≡N str
1302 s		CH bend
1282 w		CH bend
	1210 m	
	1084 m	
	1070 m	
1034 s		C-C str
889 s		C-C str
680 w		C-C str
	660 w	
575 m	573 m	skeletal bend
513 m		skeletal bend
491 s	493 m	skeletal bend
	472 w	
	~ 443 m	
355 vs		skeletal bend
233 m		skeletal bend
224 m		skeletal bend
155 m		skeletal bend

^a Abbreviations as in Table 1.

The first question to be answered is which staggered conformation exists in the crystal, the *trans* with a centre of symmetry (C_{2h}) in which 15 fundamentals would be active in the IR and 15 in the Raman, or the *gauche* with symmetry C_2 in which all 30 fundamentals would be active in both effects. In both cases, the results are definite; both have a centre of symmetry. The IR and Raman spectra of both are quite simple, considering the size of these

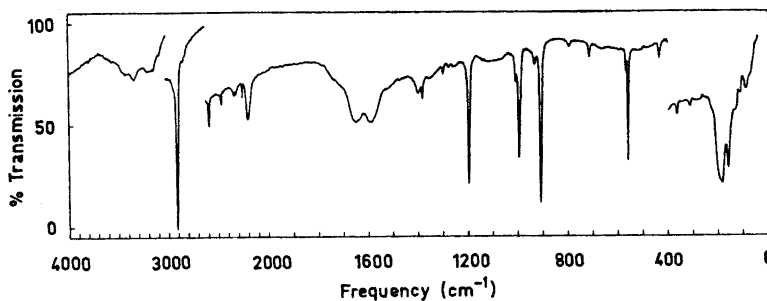


Fig. 1. IR spectrum of 1,1,2-tetracyanoethane, KBr pellet (4000–400), adamantane pellet (400–40 cm⁻¹).

Table 3. Infrared spectral data for 1,2-dichlorotetracyanoethane.^a

Mull	CH ₃ CN solution	Interpretation
2710 w ^b		455 + 2262 = 2717
2673 w		416 + 2265 = 2681
2502 w		245 + 2262 = 2507
2471 w		225 + 2256 = 2481
2458 w		197 + 2265 = 2462
2400 w		154 + 2256 = 2410
2262 s		C≡N str
2235 vw		
2219 w		
1706 w		
1407 w		478 + 935 = 1413
1382 vw		455 + 935 = 1390
1352 w		283 + 1067 = 1350
1312 vw		416 + 902 = 1318
~ 1215 vw		455 + 768 = 1223
1168 vw		245 + 935 = 1180
1154 mw	1153 s	imp. ^c
1146 vw		88 + 1062 = 1150
1113 w	~ 1110 m	imp.
1067 m		C-C str
1048 mw		
1004 w		
1000 m		
972 w		500 + 501 = 1001
958 vw	957 m	imp.
935 m	~ 935 m	C-C str
915 w		imp.
904 m		
867 w		416 + 500 = 916
832 w	832 vw	283 + 552 = 835
	802 mw	imp.
785 mw		245 + 552 = 797
~ 768 m		C-Cl str
724 w	~ 720 w, sh	225 + 500 = 725
703 vw	700 w	154 + 560 = 714
	~ 690 w	
660 w		245 + 416 = 661
618 vw		154 + 478 = 632
587 vw		88 + 500 = 588
579 vw	574 mw	imp.
552 m	553 m	skeletal bend
501 m		skeletal bend
~ 490 w sh		225 + 283 = 508
455 w		225 + 245 = 470
416 mw		skeletal bend
225 m ^d		skeletal bend
197 w ^d		skeletal bend
154 ms ^d		skeletal bend
132 ms ^d		skeletal bend
88 w br ^d		torsion

^a Weaker infrared bands in regions where there can be no fundamentals have been omitted.
^b Abbreviations as in Table 1. ^c Impurity is tetracyanoethylene. ^d Bands are from an adamantane pellet.

Table 4. Raman spectral data for 1,2-dichlorotetracyanoethane.

Solid	CH ₃ CN solution	Interpretation
~ 2945 vw ^a		455 + 2256 = 2711
~ 2675 vvw		416 + 2262 = 2678
~ 2635 vvw		
2315 vw		C≡N str
2265 m		C≡N str
2256 vs		245 + 1052 = 1297
~ 1283 vw		C - C str
1062 w		C - C str
1052 mw	~ 1050 w	2 × 500 = 1000
~ 995 vw?		C - C str
902 vs		C - C str
560 m	560 w	skeletal bend
	540 w?	
	500 m	C - Cl str
500 vs		
478 w		
455 w		skeletal bend
283 m	285 w	skeletal bend
245 m	250 w	skeletal bend
172 s		skeletal bend
164 s		skeletal bend
140 m		skeletal bend
137 s		skeletal bend
78 w		skeletal bend

^a Abbreviations as in Table 1.

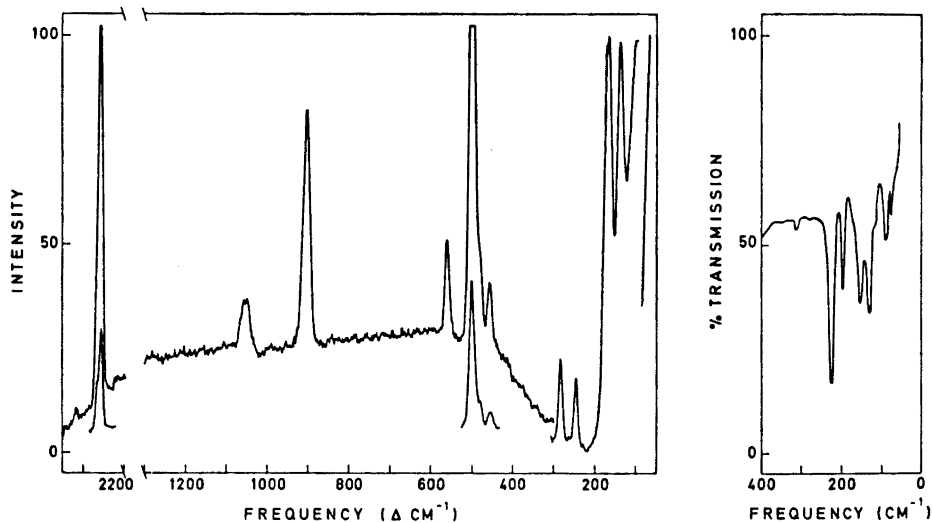


Fig. 2. Raman and far IR spectra of 1,2-dichlorotetracyanoethane.

molecules. Although coincidences may be easily pointed out, many bands, especially in the low frequency regions, may be noted which have no counterpart in the other effect.

The next question is which form predominates in solution. Here our answer is more surprising as we find no convincing evidence for any form but the *trans* in solution. Our unwillingness to make a stronger statement is closely connected with the various experimental difficulties mentioned earlier. The effect of these difficulties on our experiments can be summarized in this way. In the Raman, even though fairly wide "windows" are present, the limited solubility and availability only of a He-Ne laser make us reluctant to say that we could detect less than 10 or 20 % of the *gauche* conformer. In the IR, not only does CH_3CN have a more complex spectrum with extremely strong absorption bands than in the Raman, thus limiting our region of observation considerably, but reaction with CsI and the unsuitability of CH_3CN as a solvent in the far IR restricted us to the region above 400 cm^{-1} . This was especially unfortunate because the more interesting fundamentals (those which would be expected to be more sensitive to a change in conformation) lie in the low frequency region.

Tetracyanoethane does show some new bands in solution. However, its obvious decomposition during the course of our experiments made us very hesitant to assign these to a *gauche* conformer. We become even more cautious when we note that those new bands appearing in IR have no counterparts in Raman and *vice versa*. Since the *gauche* conformer would have no centre of symmetry, it is difficult to ascribe these sets of bands to it.

With dichlorotetracyanoethane we are a little more confident. Only one new weak, questionable band appears in solution in the Raman and no new bands appear in the IR with the exception of a set of bands which can be shown to be due to tetracyanoethylene.

To summarize, then, unless the energy difference is unusually large, at least small amounts of the C_2 conformers must exist in solution for each compound. We have no confidence that we have detected them, but we do feel that we can assert confidently that it is the *trans* form which predominates in solution. This must be looked upon as somewhat surprising. Statistically the C_2 conformer should predominate 2 : 1. The presence of the very polar solvent CH_3CN should stabilize the C_2 form to the extent of 1–2 kcal/mol compared to non-polar solvents. Finally, at least in the case of tetracyanoethane, one would predict¹⁰ that the preferred conformation would be *gauche*.

VIBRATIONAL ASSIGNMENTS

For various reasons, only a partial assignment can be attempted, in spite of the fact that for each compound we are able rather easily to pick out about 15 bands in both the IR and Raman and to designate them as fundamentals. Neither compound was soluble enough in CH_3CN for us to be able to determine polarization in the Raman and hence distinguish the A_g from the B_g modes. Nor was either compound stable enough at elevated temperatures for us to obtain a vapour phase spectrum in the IR and distinguish the A_u from the B_u modes. In the higher frequency region this is not too great a handicap and we can, guided by some group frequency correlations, assign with some con-

confidence. In the lower frequency region these relationships are not as helpful and we have also richer spectra forcing us to designate many bands as skeletal bends. The unsuitability of CH_3CN as a solvent in the far IR hindered us in attempting to distinguish unequivocally the torsional frequencies from the lattice modes. We will only note those details of the assignment which gave us especial difficulty or where we have been arbitrary.

Tetracyanoethane. The strong IR band at 2917 cm^{-1} is the only possibility for the IR-active C-H stretch. In the Raman, because the peak at 2859 cm^{-1} is twice as intense as that at 2943 cm^{-1} , we choose the former as the C-H stretch. In the $\text{C}\equiv\text{N}$ region, we find only one strong peak in each effect and conclude that both the A_g and B_g and the A_u and B_u modes are accidentally degenerate.

In the C_{2h} form of dicyanoethane the C-C stretches were assigned at 1023 cm^{-1} and 809 cm^{-1} in the Raman and 917 cm^{-1} in the IR.⁵ Thus our choices seem quite reasonable.

Dichlorotetracyanoethane. Although the two IR-active $\text{C}\equiv\text{N}$ stretches are accidentally degenerate, two bands do appear in the Raman. Picking out the C-C stretches is fairly easy. The C-Cl stretches are also fairly obvious, in particular the very strong Raman band at 500 cm^{-1} .

In the Raman we have two bands too few to assign as skeletal bands. Our assumption is not that the missing bands are too weak to be observed but that our resolution is inadequate to show which peaks actually possess two components.

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