IR SPECTRA, METHYLENE CHAIN VIBRATIONS AND ROTATIONAL ISOMERISM OF n-ALKYL TRICHLOROACETATES

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ABSTRACT

IR spectra of ten n-alkyl trichloroacetates $CCl_3COO(CH_2)_nCH_3$ (R'-TCA) in the crystalline state (R'-TCAs with n = 4, 5 in the glassy state) have been studied. End-group (CCl_3COO-) vibrations have been assigned by referring to the previous results for methyl and ethyl analogs and four methylene band progressions have been analyzed. Interaction between methylene and end-group vibrations is discussed. It is suggested that in the crystalline state the nP-TCA (n = 2) molecule takes a gauche conformation only in O-CH₂-CH₂CH₃ group and the other R'-TCA molecules adopt the all-trans extended form relative to skeletal rotational axes.

INTRODUCTION

This is one of a series of studies on the rotational isomerism, molecular conformation and polymorphism of simple chloroacetates by means of IR, Raman and 35 Cl NQR spectroscopy [1-4]. In the systematic study of such serial compounds, two approaches will be considered to examine vibrational spectra and elucidate isomerism and conformational problems.

One approach is to examine the effect of successive α -chlorination upon the vibrational spectra. Successive chlorination causes certain vibrations to shift regularly and their intensity to change due to the inductive and mass effect [2].

The other approach is to study the effect upon spectra of stepwise substitution of an n-alkyl group for the methyl group in methyl esters. This approach makes it possible to distinguish between alkyl- and ester-group absorptions observed in the spectra, and to complete the band assignment. Also, another interest for this approach lies in clarifying the presence of interaction between a methylene vibration originating from an n-alkyl group and another CH_a vibration from a CH_aCl_bCOO- group, for example between the

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two kinds of CH_2 twisting modes of $CH_2ClCOO(CH_2)_nCH_3$. Therefore, both approaches are valuable for establishing vibrational properties of esters.

In this paper, a series of n-alkyl trichloroacetates, R'-TCAs, are examined as a continuation of previous work on methyl- and ethyl-analogs (abbreviated as M-TCA and E-TCA, respectively) [3, 4] and as a part of our studies on alkyl haloacetates [1-7].

EXPERIMENTAL

R'-TCA, CCl₃COO(CH₂)_nCH₃ (n = 2-9) compounds were prepared from trichloroacetic acid and the corresponding alcohol in benzene. Crude samples were purified by vacuum distillation. The purified sample was checked by elemental analysis and gas chromatography (above 98.4%). The melting point, crystallization temperature and glass transition temperature, have already been determined by thermal analysis [8].

The IR and Raman spectrometers, low temperature cryostats used in Kobe University, their spectral resolution and accuracy, and experimental conditions were as described previously [1]. The IR spectra were recorded on a Perkin-Elmer 580 IR spectrometer (2.1 cm⁻¹ in maximum resolution). The crystalline data were obtained by a deposition method (slow spraying of a sample on a cooling KBr plate and annealing) using an RIIC VLT-2 cell. The R'—TCA spectral data recorded in Kobe University were in essential agreement with those made in Universidad Complutense de Madrid.

RESULTS AND DISCUSSION

Spectral changes due to change of state and isomerism

The glassy state of the esters was obtained by rapidly cooling the liquid sample in a cryostat using liquid nitrogen coolant. The crystalline state was obtained by annealing the glassy state taking account of the results of thermal analysis [8]. Only n-decyl ester (R'-TCA with n = 9) was immediately transformed from the liquid state to the crystalline state by cooling. The crystalline states of R'-TCAs with n = 4 and 5 could not be obtained in the cryostat.

The crystalline state thus obtained, when measured at various temperatures, gave no changes in the IR spectra except for the n-nonyl ester (R'-TCA with n = 8), for which the presence of polymorphism has been suggested [9]. The spectral bands in the crystalline state are sharper than those in the liquid and glassy states because of crystal formation and a cooling effect.

For esters with a shorter chain such as n-propyl and n-butyl esters (nP-TCA and nB-TCA; R'-TCAs with n = 2 and 3), as well as E-TCA [4], the spectra exhibited disappearance of some bands due to the change from the liquid and glassy state to the crystalline state (Figs. 4-7 and Tables 1 and 2). This indicates the existence of conformational isomerism, only one conformer being stable in the crystalline state.



Fig. 1. IR spectra of nP-TCA in the crystalline state at ca. 80 K, glassy state at ca. 80 K and liquid state at room temperature. Marked bands are absent in the crystal.



Fig. 2. Raman spectra of nP-TCA in the crystalline state at ca. 80 K, glassy state at ca. 80 K and liquid state at room temperature. Marked bands are absent in the crystal.

For esters with a longer chain, such as n-heptyl ester (\mathbb{R}' -TCA with n = 6), however, such disappearance of spectral bands could not be clearly detected on change of state. On the contrary, for longer chain esters the number of bands in the crystalline-state spectra was greater than that in the liquid-state



Fig. 3. IR spectra of nB-TCA in the crystalline state at ca. 80 K, glassy state at ca. 80 K and liquid state at room temperature. Marked bands are absent in the crystal.



Fig. 4. Raman spectra of nB–TCA in the crystalline state at ca. 80 K, glassy state at ca. 80 K and liquid state at room temperature. Marked bands are absent in the crystal.

spectra because of the resolution of overlapping bands by crystallization and cooling effects. Moreover, the liquid-state spectra become more similar to each other as the n-alkyl chain of R'-TCAs becomes longer.

Therefore, our attention should be focused on the crystalline-state spectra,

where all the spectra of the esters can be studied and compared. In addition, the results of thermal analysis and ³⁵Cl NQR measurements for the esters [8] are available for the preparation of crystalline R'-TCAs with physically defined properties. It is very important to prepare defined crystals and represent the spectra of the crystals as well as to examine the reproducibility of spectra.

IR spectra of crystalline R'-TCAs

The observed IR spectra $(1500-650 \text{ cm}^{-1})$ of the crystalline esters (the glassy-state data for R'-TCAs with n = 4 and 5) are schematically illustrated by vertical lines in Fig. 5. In this figure are seen some methylene band progressions characterized by series of almost equally spaced absorptions whose wavenumbers are dependent on methylene number n: CH₂ wagging (ν_3) and CH₂ twisting-rocking (ν_7) 1380-1175 cm⁻¹, C-C stretching (ν_4) 1135-970 cm⁻¹ and CH₂ rocking-twisting (ν_8) 1040-720 cm⁻¹. They can be reasonably interpreted by using the complied results of vibrational analysis on solid n-alkanes and polymethylene [10-12]. Some bands in the region between 1468 and 1427 cm⁻¹ are assigned to the CH₂ scissoring (ν_2) and CH₃ asymmetric bending modes, and a band near 1390 cm⁻¹ to the CH₃ symmetric bending mode.

Some strong absorptions of nearly constant wavenumber, independent of methylene number *n*, are found to be characteristic of the CCl₃COOgroup. They can be assigned as follows: ν C=O 1760 cm⁻¹, ν C-O ca. 1260 cm⁻¹, ν O-C' ca. 980 cm⁻¹, ν C'-C/ δ rCH₃ near 890 cm⁻¹ [13], two ν aC-Cl 840 and 830 cm⁻¹, ν sC-Cl 434 cm⁻¹ (Fig. 8), δ C=O 755 cm⁻¹ and π C=O 683 cm⁻¹.

It is well known that the ν C—O and ν O—C' vibrations interact with each other [14, 15]. In the case of R'—TCAs, in addition to the mutual interaction, they also couple with neighboring in-plane vibrations such as the ν_3 , ν_4 , ν C'—C/ δ rCH₃ and ν CCl—C modes. Since such an interaction causes changes in band position and intensity, and as bands are crowded in a narrow region with increasing methylene number n, it is difficult to distinguish the ν C—O band from the members of the ν_3 and ν_7 band progressions, and especially the ν O—C', ν C'—C/ δ rCH₃ and ν CCl—C band from the members of ν_4 and ν_8 band progressions.

The difficulty can be overcome by determining all members of CH₂ band progressions and taking them into account. Thus, three bands observed in the 850–1020 cm⁻¹ region are associated with the ν O–C', ν C'–C/ δ rCH₃ and ν CCl–C modes, which are indicated in Fig. 7. The ν C'–C/ δ rCH₃ band is known to converge characteristically at 890 cm⁻¹ with increasing methylene number *n* [11, 16–19]. For crystalline E–TCA the band at 969 cm⁻¹ was assigned to the ν C'–C/ δ rCH₃ vibration for the following reasons:

(1) the band does not appear in the spectra of M-TCA;



Fig. 5. Illustrated IR spectra of $CCl_3COO(CH_2)_nCH_3$ (n = 0-9), R'-TCA, in the crystalline state at ca. 80 K (the glassy data for R'-TCAs with n = 4, 5).

(2) it appears as a band pair, as do other ethyl group vibrations, in the liquid-state spectra of E-TCA;

(3) from the results of a normal coordinate calculation [4] the band pair was interpreted to be from the vibrational mode of the *trans/(gauche)* model, the isomer in parentheses being absent in the crystal. For nP-TCA the lowest wavenumber band of the three (981, 901 and 860 cm⁻¹) may be associated with the $\nu C'$ - $C/\delta rCH_3$ vibration because of the fact that the band exists with a partner in the liquid state.

Methylene band progressions in IR spectra of crystalline R'-TCAs

Interestingly, the introduction of polar groups at the end of an n-alkane chain often gives rise to intensity change in some band-progression members, as well as shifting and disturbance, due to couplings between methylene and polar group vibrations [16–19], in both k arrays of a band progression and in a constant frequency array for a polar end-group vibration. The k integer is characterized by a phase difference δ in the coupled oscillator model for an infinite polymethylene chain [11, 12, 16–19].

The intensities of some ν_3 and ν_4 band-progression members are very noticeably enhanced, most strongly near 1260 cm⁻¹, but also strongly in the 1020–960 cm⁻¹ region, compared with the intensities of corresponding bands in solid n-alkanes [11]. This means that the coupled ν C–O and ν O–C' (in another sense, ν aC–O–C and ν sC–O–C) vibrations absorb near 1260 cm⁻¹ and in the 1020–960 cm⁻¹ region, respectively.

For the methylene band progressions detected, the observed wavenumbers ν are plotted against methylene number n. The k arrays, which are drawn in the $\nu-n$ plots on the basis of an excellent guide containing very complete studies on the extended zigzag n-alkanes [11, 12], are well-shaped, as seen in Figs. 6 and 7.



Fig. 6. $n-\nu$ plots for methylene wagging (ν_3, left) , twisting—rocking (ν_7, right) band progression, and W_k and T_k arrays: $\circ R'$ —TCAs; \times solid n-alkanes [11, 12]; \circ strongest ν C—O band in band progressions.



Fig. 7. n- ν plots for methylene C-C stretching (ν_4 , left), rocking-twisting (ν_8 , right) band progression, and R_k and P_k arrays: \circ R'-TCAs; \times solid n-alkanes [11, 12]; \circ R'-TCA end group vibrations; \bullet , \bullet liquid nP-TCA.

The CH₂ wagging band progression (ν_3 ; 1380–1205 cm⁻¹, W_k array) is overlaid with the CH₂ twisting—rocking band progression (ν_7 ; 1310–1180 cm⁻¹, T_k array), but here they are exhibited separately in Fig. 6. The coupling of the ν C-O vibration with the ν_3 mode not only brings about the enhancement in IR band intensities of some ν_3 members but also causes the intrinsic ν C-O position to deviate slightly from a constant frequency array. This deviation contrasts with the large deviation near 1260 cm⁻¹ which occurs between the amide III (δ N-H) and ν_3 arrays of N-methyl-N'-n-alkyl ureas [19]. In the ν_3 band progression shown in Fig. 6, the W_1 array line runs through drawn on the liquid-data point (1287 cm⁻¹) not through the crystalline-data point of nP-TCA, for reasons which will be stated later. No interpretation could be made of the shift of T_1 array from that of solid n-alkanes.

Figure 7 displays the methylene C—C stretching and CH₂ rocking-twisting band progression (ν_8 ; 1040—720 cm⁻¹). For the ν_4 band progression not all R_k arrays could be clarified since the so-called *B* region members were arranged in a complex-fashion set within the 1060—970 cm⁻¹ region [11]. The shift of the R_1 and R_2 (R_3) arrays to low wavenumber compared to the corresponding array of solid n-alkanes contrasts with the large shift to high wavenumber of those for n-alkyltrimethylammonium bromides (R'—TMAB) [17].

From these results, the direction and extent of shift from the corresponding solid n-alkane array are considered to be qualitatively dependent on whether polar-group vibrations absorb on the high or on the low wavenumber side of the P_k arrays and on the degree of the group polarity, respectively.

Judging from preliminary results, the ν C—O vibration of R'—TCAs (near 1260 cm⁻¹) and the in-plane ν C—N vibrations of R'—TMAB (below 1000 cm⁻¹) affect their R_1 , R_2 (R_3) arrays, and the coupling with the ν C—O vibration is estimated to be less than that with the ν C—N vibrations of R'—TMAB. However, the R_n array seems to be unaffected in every case, probably because the value of its phase difference, which is expressed as $\delta = \pi k/n$ or $\pi k/(n + 1)$ [11, 12, 16—19], is π , or approaches π , as n (= k for the R_n array) becomes larger.

For the ν_8 band progression most of the P_k arrays could be drawn. However, the P_1 members in the higher wavenumber region are weak, often undetectable. This is because no P_k band-progression members are enhanced in intensity, suggesting that in the ν_8 band-progression region there are no out-of-plane vibrations to affect the mode. This contrasts with the case of R'-TMAB where principally a ν C-N mode of the a'' species is coupled with the out-of-plane ν_8 band progression mode, disturbing a few ν_8 arrays near 980 cm⁻¹ [17].

Such an analysis of arrays in a band progression is very useful for the assignment of the remaining absorptions to CCl₃COO—group vibrations. Moreover, the greater the number of derivatives, the more reliable the assignments.

Rotational isomerism and conformation of nP-TCA

For nP-TCA and nB-TCA (R'-TCAs with n = 2 and 3), as well as E-TCA [4], the crystalline-state spectra show disappearance of some bands which

TABLE 1

Observed wavenumbers, in cm^{-1} , for n-propyl trichloroacetate $(nP-TCA)^{a,b}$

Liquid			Glass		Crystal		Assignment	
IR	Raman	DR¢	IR	Raman	IR	Raman		
1763 vs	1766 s	р	1763 vs	1762 s	1760 vs	1763 s	νC=0	
					1722 w		$860 \times 2 = 1720$ 901 + 824 = 1725	
1464 s			1464 s		1467 m	ר 1463 sh	501 + 524 - 1125	
					1458 m		δ dCH.	
	1452 s	dp		1452 s	1451 m	1449 m (δCH,	
1437 w	1439 m	dp	1438 w	1438 m	1438 w	$1438 \mathrm{m}$)	1	
1389 m	1394 vw	-	1391 m	1392 vw	1390 m	1395 vw	δ sCH ₃	
1381 m			1381 m	1380 w	1377 vw	1378 vw	$W_1(T,G)$	
1348 w	1347 vw		1350 w	1350 vw	1355 w	1351 vw	$680 \times 2 = 1360?$	
1312 w			1312 m				$W_{1}(T)$	
1284 sh	1281 m		1281 sh	1279 m	1287 m	1286 m	$W_{1}(G), T_{2}(T, G)$	
1260 sh			1264 vs		1265 s	1264 m	$\nu C - O(T, G)$	
1256 sh					1256 sh		433 + 824 = 1257	
1238 vs	1242 w		1243 vs	1242 w	1244 s	1240 m	$T_1(T, G)$	
1154 vw	1153 w		1157 w	1154 w	1160 w	1162 w	$\delta r CH_3(G)$	
	1135 w			1135 w			$\delta r CH_3(T)$	
1119 vw	1119 w		1118 vw	1119 w			$R_1(T)$	
1097 vw	1095 w		1096 vw	1097 w	1096 w	1097 w	$R_1(G)$	
1050 m	1051 m		1051 m	1051 m	1046 m	1045 m	$R_2(G)$	
1034 wsh	1034 m		1037 wsh	1040 m			$R_2(T)$	
991 s	990 vw		996 sh	995 vw			$\nu O - C(T)$	
981 s	986 vw		985 s	990 wb	981 s	983 w	$\nu O - C(G)$	
972 sh			973 m					
928 m	928 m	р	921 m	922 m	916 m	919 m	$P_1(T, G)$	
910 sh	909 m	р	909 m	911 m	901 m	905 s	ν CCI–C (T, G)	
881 w	882 s	р	881 w	885 s		(883 vw)	$\nu C' - C(T)$	
870 w	876 sh		869 w		860 m	860 m	$\nu C' - C(G)$	
838 sh	840 sh		839 sh		839 sh	831 sh	ν aC—Cl (T, G)	
828 vs	831 s	dp	826 s	829 s	824 vs	824 s	ν aC—Cl (T, G)	
763 msh	766 m	р	764 m	766 m	769 m	773 m	$P_2(G)$	
747 m	747 m	р	750 s	750 m			$P_{2}(T), \delta C=O(T)$	
(747 m	747 m	p)		740 sh	733 m	735 m	$\delta C=O(G)$	
682 vs	683 m	dp	682 vs	685 m	680 s	680 m	$\pi \mathbf{C} = \mathbf{O}(T, G)$	
500 w	502 vw		502 vw	502 vw	497 m	498 w	$\delta \operatorname{CCO} (G)$	
480 sh	480 vw		483 vw	481 vw			$\delta \operatorname{CCO}(T)$	
433 w	434 vs	р	1	435 vs		433 vs	ν sC—Cl (T, G)	
406 sh				412 sh	Į	410 vw		
399 w	396 m	р		398 s		388 s	$\delta \operatorname{CCC}/\operatorname{OC'C}(G)$	
	369 w	р		371 vw	[$\delta \operatorname{CCC}/\operatorname{OC'C}(T)$	
343 w	349 w	р	1	347 m		357 m	δ CCC (G) or (T, G)	
325 vw			1	322 w	ļ	324 vw ($\delta \operatorname{COC} (G)$	
300 w			not		not	306 w ∫	?	
292 sh	287 m	dp	measured	288 s	measured	288 s	$\delta \operatorname{CCl}_{\mathfrak{z}}(T, G)$	
280 sh				278 w		273 s	$\delta \operatorname{CCl}_3(T, G)$	

Liquid			Glass		Crystal		Assignment
IR	Raman	DR ^c	IR	Raman	IR	Raman	
260 w	263 m	p	1	261 m	1		$\delta \operatorname{COC}(T)?$
I	243 vw	•	1	244 w	ţ	245 s	δ CCl
1	230 m			225 w	e e e e e e e e e e e e e e e e e e e	223 vw	δrCCl ₃
not				196 w	1	201 m	\ \
measured	184 w			184 w	1		Torsion
í	150 w			164 w			
	138 vw			152 w	1	$142 extbf{w}$,

TABLE 1 (continued)

^a Wavenumbers above 2000 cm⁻¹ and combinationtone wavenumbers are omitted. ^bAbbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad; ν , stretching; δ , deformation, δ r, rocking; δ w, wagging; δ t, twisting; π , out-of-plane bending; s, symmetric; a, asymmetric; T, trans-trans-trans-trans and G, trans-trans-trans-gauche form in relation to the skeletal rotational axes of CCl-CO-O-CH₂-CH₂CH₃. ^cRaman depolarization: p. polarized and dp, depolarized line.

are present in the liquid- and glassy-state spectra, as mentioned above and as seen in Figs. 1-4 and Tables 1 and 2. Such disappearance is detected more clearly in the Raman spectrum than in the IR spectrum of the compound, and better in the spectra of nP-TCA than in those of nB-TCA.

We now discuss possible rotational axes which cause isomerism. The conformation for the first ClC—COR' rotational axis is concluded to be *trans* just as in M—TCA and E—TCA [3, 4], since in R'—TCAs three ν C—Cl bands appear at constant positions (830, 820 and 434 cm⁻¹) despite change of physical state. The most likely conformation for the second CCl₃—OR' rotational axis is also restricted to *trans*, in the light of the results obtained from many studies on esters [20—22].

Therefore, the isomerism of R'-TCAs is concluded to arise from rotational axes in the n-alkyl group. The rotational axes increase in number with increasing n in the alkyl group, being one $(O-CH_2CH_3)$ for E-TCA, two $(O-CH_2-CH_2CH_3)$ for nP-TCA, three $(O-CH_2-CH_2-CH_2CH_3)$ for nB-TCA, and so on. Indeed, as the number of rotational axes increases, the number of possible isomers increases exponentially although the probability of many of them existing is very low, even in the liquid state. Generally, the crystalline-state spectra are much simpler and one single molecular form is assumed to exist [23]. Accordingly, it is important to trace the positions of those methylene band-progression members directly affected by isomerism.

In the $\nu-n$ plot diagrams (Figs. 6 and 7) only some crystalline-data points of nP-TCA (n = 2) are displayed from methylene band-progression arrays and are replaced by the corresponding liquid-data points giving smooth arrays like those of the extended zigzag n-alkanes [11, 12]. This suggests that in the crystalline state only the nP-TCA molecule exists in a different form from the other R'-TCAs, whose molecular forms are all *trans* relative to the skeletal axes, as in the solid n-alkanes.

TABLE 2

Observed wavenumbers, in cm⁻¹, for n-butyl trichloroacetate (nB-TCA)^{a,b}

-	Assignment
IR Raman DR ^c IR Raman IR Raman	
1765 vs 1766 s p 1766 s 1759 m 1760 vs 1754 s	νC=0
1715 sh 1714 w	
1462 m 1468 m 1466 m 1466 s	
1456 sh 1451 s dp 1461 sh 1455 m 1461 s	(δdCH₃
1446 m 1451 m 1451 m	δCH ₂
1433 w $1435 m$ dp? $1432 w$ $1431 m$ $1427 w$ $1432 m$. J
1385 w 1390 vw 1384 w 1388 m 1390 vv	ν δsCH,
1378 vw 1380 m 1382 v	N
1376 w 1372 v	$W W_3$
1356 vw 1354 vw	
1339 vw 1341 vw	W_2
1309 m 1306 m 1308 m 1311 m	T_3
1298 w 1300 m dp 1298 sh 1299 m 1291 m 1304 m	T_2
1272 sh 1264 wsh 1270 sh 1267 s	W_1
1247 s 1246 w 1258 s 1252 w 1260 s 1256 w	ν C O
1227 s 1299 w 1233 s 1229 w 1230 m 1232 w	T_1
1153 vw 1149 w p 1154 w 1152 w 1153 w 1152 w	δrCH ₃
1120 vw 1121 m / 1122 w 1122 w 1121 m 1121 w	R_{i}
1068 sh 1065 sh 1068 sh	
1058 m 1058 m dp 1057 m 1053 w 1058 s 1057 w	R_{2}
1019 m 1019 w p 1022 m 1020 w 1021 s 1022 m	R_{3}
1007 m 1003 vw 1007 sh	
984 m ** sh 980 m 976 vw 976 s 977 v	v vO—C
957 m ** sh 956 m ** sh 960 w 963 v	$\mathbf{v} P_1$
936 w 938 m p 935 m 932 m 935 s 940 s	{ νCCl−C
908 w 909 m p 905 w 906 w	\$
897 sh ** sh 896 sh ** sh	$\nu C - C/\delta CH_3$
859 m 860 m 860 s 860 m 856 s 859 m	
834 sh 837 s	′ vaC−Cl
826 s 830 s dp 828 s 828 s 828 s 831 vs	vaC—Cl
815 sh ** sh 814 s 813 sh 814 s 816 w	P_2
753 m 752 m p 757 m 754 m 756 m 758 m	δC=O
738 w ** sh 736 m 737 vw 736 w 735 vv	v P ₃
** sh 689 m	
681 s 682 m dp 682 s 682 m 679 s 681 m	∫ πC=O
511 w 520 vw 512 w 522 vw 511 m 516 vv	δCCO
487 487 vw 487 vw 488 w	
473 473 vw 472 vw 471 vw	
432 433 vs p 432 vs 438 vs	vsC—Cl
416 417 s p 414 s 417 s	
348 w p 353 w	(δCCC/OCC
337 333 w	δ CCC
320 318 w p 316 w 318 m)
293 286 m dp not 288 s not 295 s	δCCl ₃
measured measured 274 w	δCCl_3
247 250 m p 248 m 253 m	δCOC
221 w 227 m	δrCCl ₃
not 210 m 209 m 215 m	> δrCCl ₃
measured 158 w 149 w 151 w	Torsion
141 sh 135 w 122 w)

^{a,b,c}See footnotes to Table 1.

The bands corresponding to the crystalline-data points appear as band pairs in the liquid-state spectrum, as seen in the spectra of E—TCA [4]; (1309)/ 1287: W_1 ; (1119)/1096: R_1 ; 1050/(1034): R_2 ; (881)/860: ν C'—C/ δ rCH₃; 769/(747): P_2 ; 388/(369): δ C'CC/ δ OC'C; (747)/733: δ C=O and 497/(480) cm⁻¹: δ CCO, the band in parentheses being absent in crystal. The band pairs (1119)/1096, (881)/860, 388/(369), (747)/733 and 497/(480) cm⁻¹ seem to correspond to those at 1116/(1095), 969/(952), (380)/368, 757/(745) and (461)/449 cm⁻¹ in E—TCA, originating from the *trans/(gauche)* form, but in nP—TCA parentheses are reserved. Band pairs in nP—TCA are suggested to arise from *trans—gauche/(trans—trans)* conformations for two O—CH₂—CH₂CH₃ axes.

This discussion concerning conformations leads to the conclusion that in the crystalline state, although only the nP-TCA molecule exhibits the gauche conformation, probably in the terminal OCH_2 -CH₂CH₃ axis, the other R'-TCA molecules take on the all-trans extended form relative to all skeletal rotational axes.

Considering that in solid n-propyl acetate there are two polymorphic phases resulting from the *trans-trans* and *trans-gauche* conformations for the same axes [24], and that in the solid n-propyl monochloro analog four similar phases are found [25], the n-propyl group of acetates may have favorable factors for stabilizing the *gauche* conformation in the crystal.

Liquid-state spectra of R'-TCAs

As the n-alkyl chain of R'-TCAs is lengthened, the liquid-state spectra become similar to each other. However, as Fig. 8 shows, the IR band corres-



Fig. 8. Schematic IR and Raman (vertical lines) spectra (550–250 cm⁻¹) of liquid R'–TCAs.

ponding to the δ CCO deformations of M-TCA (407 cm⁻¹) at the left and close to the ν_5 (δ CCC) members with the highest wave-number for each R'-TCA, approaches (changing its position) the theoretical upper limit of ν_5 bands in an infinite polymethylene chain [16]. This suggests that the δ CCO vibration interacts with the ν_5 mode.

In addition, the Raman band corresponding to M-TCA and E-TCA appears as a strong band near the strongest vsC-Cl band at 434 cm⁻¹ but that of nP-TCA and nB-TCA is seen as a very weak band at a position far from the vsC-Cl band and that of R'-TCAs with longer R' groups could not be detected. This suggests that considerable vibrational coupling with the vsC-Cl mode occurs in the δ CCO band appearing near the vsC-Cl band and the coupling is weakened as the δ CCO band moves further from the vsC-Cl band. This is supported by the normal coordinate analyses for M-TCA and E-TCA molecule [3, 4].

In conclusion, the δ CCO vibration couples with the ν_5 (δ CCC) and ν sCCl₃ modes. Its band position is affected mainly by the ν_5 and its Raman intensity by the ν sCCl₃ mode.

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