Vibrational analysis of propiolyl chloride and tetrolyl chloride

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Abstract—The i.r. and Raman spectra of propiolyl chloride H—C=C—COCl and tetrolyl chloride CH₃—C=C—COCl were examined in the region 4000–40 cm⁻¹. The i.r. spectra were recorded in the gas phase and solution, whereas the Raman spectra were obtained from the pure liquids. The fundamental frequencies have been assigned and the low frequency vibrations of the COCl group have been discussed. Relatively free rotation of the CH₃ group is evident from the i.r. spectrum. The syntheses of the compounds are reported.

INTRODUCTION

IN EXTENSION of vibrational studies on strictly linear haloacetylenes a vibrational analysis of the planar halopropynals X—C=C—CHO (X = Cl, Br, I) was recently published [1]. These molecules and earlier work on propynal [2] arose our interest in acetylenic acyl halides and we succeeded in the preparation of propiolyl chloride H-C=C-COCl (PC) and tetrolyl chloride $CH_3-C=COCl$ (TC). Although acyl chlorides have been extensively studied by i.r. spectroscopic methods, complete vibrational analyses are limited to carbonyl chloride [3], oxalyl chloride [4] and acetyl chlorides [5-7]. It was hoped that the present work would contribute to the understanding of the low frequency vibrations of the COCl group which have received relatively little attention. Also TC would be an interesting molecule on account of the relatively free internal rotation of the methyl group.

EXPERIMENTAL

Chemicals

The acetylenic acid chlorides were prepared from the corresponding carboxylic acids by halogenation with 1,1-dichlorodimethyl ether [8].

1,1-Dichlorodimethyl ether. This was prepared by an alternative procedure from catechyl phosphorus trichloride and methyl formate. The former was produced from catechol and phosphorus pentachloride according to literature [9].

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Catechyl phosphorus trichloride was added dropwise to an equivalent amount of methyl formate under an atmosphere of nitrogen with stirring at 0°C. After heating to 60°C under reflux and stirring during 1 hr fractional distillation *in vacuo* on a 50 cm spinning band column yielded 1,1-dichlorodimethyl ether b.p. 82-85° [8] in 87 per cent yield.

The gas chromatographic separations were performed on an Aerograph A700 and a Beckman GC 2A instrument using helium as a carrier gas. Columns of 3 m length and 8 mm internal diameter were filled with 20% Apiezon on Chromosorb W HMDS 60/80 mesh. The samples were collected in traps fitted with vacuum stopcocks and glass joints and cooled in dry ice. Collected colourless material was sublimed into vacuum tubes. Products of 99 per cent purity were thus obtained, apparent from a second GLC.

Tetrolyl chloride. Tetrolic acid was produced [10] from sodium methylacetylide and gaseous carbon dioxide in abs. tetrahydrofurane/ether. The former was prepared from methylacetylene and sodium amide in liquid ammonia.

1,1-dichlorodimethyl ether (1.37 g) was added dropwise to tetrolic acid (1.0 g)and a few grains of anhydrous zinc chloride at 0°C under an atmosphere of nitrogen over a period of 30 min. The flask was shaken now and then. Spontaneously formed hydrogen chloride was allowed to disappear through a drying tube filled with magnesium perchlorate. After half an hour the stream of nitrogen was disconnected, and most of the residual volatiles were removed by repeated expansion into an evacuated trap cooled in dry ice. The reaction mixture was subject to GLC at 65°C. 0.89 g of pure tetrolyl chloride (73%) was isolated as a colourless liquid. Vapour pressure 9.5 torr/19°C.

Propiolyl chloride [11]. Propiolic acid was obtained from acetylene dicarboxylic acid monopotassium salt by decarboxylation and acidification [12].

Propiolic acid (3.0 g) and a few grains of zine chloride were treated with 1,1dichlorodimethylether (6.5 g) as above. The reaction mixture was left for 2 hr, purified *in vacuo* as above and gas chromatographed at 55°C. 1.42 g propiolyl chloride (37.4%) was isolated as a colourless liquid.

Instrumental

The instruments and experimental technique have been described [1]. For the i.r. studies of TC in the vapour phase a 1 m cell with KRS-5 windows was also employed. Gradual decomposition was taking place in this cell resulting in over-all reduced intensities and the appearance of new bands in some parts of the spectrum. The compound appeared quite stable in a Pyrex cell (9 cm, CsI-windows).

Solutions were prepared by evaporating a small sample *in vacuo* into a cooled tube containing the solvent. For the Raman recordings the sample was *vacuum* transferred into a cooled Pyrex capillary and sealed off.

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Symmetry

PC has almost certainly a planar structure with C_{\bullet} symmetry. In TC a methyl group is attached to the same heavy-atom skeleton. A recent study on tetrolaldehyde $CH_3-C\equiv C-CHO$ indicated a barrier $< 20 \text{ cm}^{-1}$ for the internal rotation of the methyl top relative to the rest of the molecule, which was regarded as a rigid planar framework [13]. Nearly free internal rotation is assumed also for TC.

If the internal rotation of the methyl group is completely free the vibrations can be classified according to a molecular symmetry group of order 6, isomorphous with the point group C_{3v} [14, 15], or the vibrations of the rigid-C=C-C(O)Cl frame can be classified by the species of its point group C_s and those of the methyl group by the species of C_{3v} [16]. There are in all 3N-7 fundamentals since one internal rotational degree of freedom replaces the torsional motion of the methyl group.

In PC the fundamentals are divided into those in the plane a' and those perpendicular to the plane a'', of which the former should exhibit A, B or A/B hybrid type infrared vapour phase contours. The latter vibrations should appear as pure C-type bands. The same considerations should apply to the vibrational motions of TC, except for the perpendicular bands of the methyl group, which would be expected to show fine structure due to the free internal rotation of the methyl top. All the fundamentals in each molecule are allowed in the i.r. and Raman spectrum. In the latter the a' fundamentals are polarized and the a'' are depolarized.

RESULTS AND DISCUSSION

Propiolyl chloride (PC)

The vibrational modes of PC give the irreducible representation: $\Gamma_{vlb} = 9a' + 3a''$. The principal moments of inertia are calculated using the following parameters [17, 18]: r(C-H) = 1.085, $r(C\equiv C) = 1.211$, r(C-C) = 1.445, r(C=O) = 1.192, r(C-C) = 1.789 Å, $\angle CCO = 125.0$ and $\angle CCCl = 112.6^{\circ}$. The calculation gives $I_A = 71.2$, $I_B = 164.6$ and $I_C = 235.8$ a.m.u. Å² and 27° for the angle formed by the A-axis and the C=C-C axis. The *PR*-separations calculated according to SETH-PAUL and DLIKSTRA [19] are 15.3, 12.2 and 22.9 cm⁻¹ for the *A*, *B* and *C* bands, respectively, at 40°C.

Tables 1 and 3 contain the observed frequencies and the proposed assignments. The vibrational spectra are shown in Figs. 1 and 2.

Assignment of the fundamentals associated with stretching of the C—H, C=C, C=O and C—C bands is straight forward. The C=C band shows a very complex vapour-phase contour arising from overlap with a series of narrow weak bands with

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a spacing of ca. 2 cm^{-1} . Similar fine structure observed in other acetylenes [20] has been ascribed to hot bands of the type $v_i + (nv_k - nv_k)(n = 1, 2 \cdots)$, where v_i is the C=C fundamental and v_k a low frequency bending mode. The band is shown in Fig. 3.

Infrared			D	Interpretation *	
Gas		Solution (CCl ₄)		Interpretation +	
4010 vw		3993 vw		$v_1 + v_{10} = 4029 \; A''$	
3956 vw		3934 vw		$v_1 + v_6 = 3981 \ A'$	
³⁵¹⁶ 3505} ^w	B	3481 w		$2\nu_{3}=3534~A'$	
3333 3326 3317)	A/B	3301 s		$v_1(a')$ fund	
3300 w, sh		0110			
3130 VW 27685		3118 VW		$v_2 + v_4 = 3134 A$	
2755 vw		2743 vw		$\nu_3 + \nu_4 = 2770 \ A'$	
		2335 w		$v_2 + v_{12} = 2355 A''$	
2136 2131·4 vs		2120 s	2116 vs P	$\nu_2(a')$ fund	
2128·2 2126·2 2122·7				${\left\{ { m Hot \ bands} ight.}$	
2120.07		2079 yrm eb			
20075		2072 VW, 81		a ana 1/	
1993} ^{vw}		1988 vw		$2\nu_4 = 2006 A^2$	
		1921 vw		$\nu_3 + \nu_9 = 1924 \; A'$	
1773 1761 vs	B	1753 vs	1742 m P	v_3 (a') fund	
1701) 1722 w. sh		1715 w. sh			
~1650 vw 1590 w				$v_4 + v_5 = 1658 A'$ Impurity ?	
1409 1394 W		1412 w		$2\nu_{10} = 1406 A'$	
1359 1347 VW	В			$v_5 + v_8 = 1351 A'$	
1313 vw, sh 1300 w, sh 1294 w		1315 vw, sh 1302 w 1290 w, sh			
1281 w, sh 1145 vw, sh 1120 w		1155 vw 1115 w		$\nu_4+\nu_9=1160~A'$	
1075 1065}m	В	1070 w, sh		$\nu_{8} + \nu_{8} = 1069 \; A'$	
1054 1048 1045 1041	Ø	1056 m		$2\nu_8 + \nu_{12} = 1052 \ A''$ {Hot bands	
1010 1003 996	A/B	998 vs	∼1005 w, bd	$v_4(a')$ fund	

Table 1. Infrared and Raman spectral data for propiolyl chloride (PC).

* Combination frequencies and overtones are cale. from gas data.

s,m,w, = strong, medium, weak, v = very, bd = broad, sh = shoulder, P,D = polarized, depolarized.

† CS₂ solution.

1 Heptane solution.

+ <u>1</u>

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Table	1 (*	Contd)	1
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		Infrared		Raman	Tutamentation\$	
-	Gas	·····	$Solution(CCl_4)$	Liquid		
	965					
	958 m	A/B	953 m	\sim 950 vw	$2\nu_7 = 964 \ A^2$	
	950				,	
	948				{Hot bands	
	938 w. sh					
	885)					
	877 w	A/B	876 w		$v_{11} + v_{12} = 889 A'$	
	870)					
	810 _{2vw}		810 w†	810 w. bd	$v_1 + v_2 = 812 A'$	
	7955		010 11		· · · · · · · · · · · · · · · · · · ·	
	\sim_{703}^{720} s	a			$(\nu_{10}(a''))$ fund	
	699)		709 s	\sim 720 w. bd	{	
	696 m	A/B?			$(v_5(a'))$ fund	
	689)	,				
	669 s, sh		668 m, sh		(* (a*) fund	
	665 vs		661 vs	653 s P	$v_{11}(a')$ fund	
	655 vs		653 s, sh		() (a) rand	
			580 vw, sh†	\sim 585 w, sh		
	486	4170		450 B		
	482 m	А/В	475 m	47881	$\mathcal{P}_{7}(\boldsymbol{\alpha})$ rung.	
	470				Hot band	
	420)					
	414 w	A/B	414 w	413 m P?	$v_{a}(a')$ fund	
	405	,				
	232)					
	224 vw	C	226 vwt	227 s D	$v_{12}(a'')$ fund	
	213)					
	$163 \\ 150 $ vw	B	165 vw‡	167 vs P	$\nu_{\mathfrak{g}}(a')$ fund	

Table 2. Infrared and Raman spectral data for tetrolyl chloride (TC)*

Infrared			Raman	To do a serie de la serie S	
Gas	Solution (CCl ₄)		Liquid	Interpretation§	
		4400 v w		$2\nu_2 = 4450 A_1$	
		4341 v₩		$\begin{cases} v_1 + v_{16} = 4352 \ E \\ v_2 + v_{22} = 4339 \ E \end{cases}$	
		4074 vw		$v_1 + v_5 = 4082 A_1$	
		3980 vw		$v_2 + v_3 = 3983 A_1$	
$3532 \\ 3522 \end{bmatrix}^{w}$	В	3490 w		$2\nu_3 = 3516 A_1$	
		3438 vw		$\nu_{\rm B} + \nu_{15} = 3433 \ E$	
3166 vw		3157 vw		$v_3 + v_{16} = 3189 E$	
3082 w		3060 w		$v_2 + v_6 = 3067 A_1$	
2987 2945)		2961 vw	2977 w D	ν_{15} (e) fund	
2940 w	A/B	2921 w	2925 s P	$\nu_1(a_1)$ fund	
2934)	•				
		2911 вh		$v_3 + v_5 = 2919 A_1$	
2868 vw		2846 vw	2842 w P	$2v_{16} = 2862 A_1 + E$	
		2819 vw		$v_{\rm B} + v_{\rm 7} = 2825 A_{\rm 1}$	
		2724 vw	2727 w P	$2\nu_4 = 2756 A_1$	
		2603 vw		$v_3 + v_6 = 2600 A_1$	
		2531 vw		$v_4 + v_5 = 2539 A_1$	

* Footnotes: See Table 1. § Combination frequencies and overtones are calc. from solution data. [] v_0 calc.

Table 2 (Contd)

	Infrared		Raman	T 1
Gas		Solution (CCl_4)	Liquid	Interpretation§
		2459 vw		$v_{15} - v_8 = 2489 E$
		2380 sh		$v_4 + v_{17} = 2394 E$
		2347 sh		$v_3 + v_7 = 2358 A_1$
~2327 m		2325 s	2328 w P	$2p_1 = 2322 A_1$ Fermi resonance
2243 sh		2249 sh	2260 vw	$v_6 + v_{16} = 2273 E$
2233 s		2225 vs	2224 vs P	$v_{g}(a_{1})$ fund
		2186 w	2186 sh P	$v_4 + v_6 = 2220 A_1$
		2155 sh		$v_3 + v_9 = 2153 A_1$
		2036 w		$2v_{17} = 2032 A_1 + E$
$2009 \\ 2001 \}^{w}$		1996 w	1991 vw	$v_{\sharp}+v_{\sharp}=2003\ A_1$
1050		~1950 vw bd		$v_4 + v_7 = 1978 A_1$
1870 W		\sim 1850 vw bd		$v_{*} + v_{17} = 1858 E$
10001		-		V AF T
1778	415	1760	1761 - 75	. In Sound
174 178	АјБ	1708 VH	1701 8 1	ν_3 (a_1) runa
1708)		_ 1715 -1	1710 -1	
1729 8h		~1/10 Sh	1/19 80	$v_{10} + v_{16} = 1/24 M$
1091 W		1000 m	1494 m D	$\Delta \nu_6 \simeq 1034 A_1$
		1401 III 1979 m	1434 W D	v_{16} (c) fund
		1970 W	-1375 mm	$v_4 (a_1)$ mu $v_5 - v_5 - 1363$
1314 1				$v_3 - v_1 - 1000 A_1$
1304·5}w		1305 m	1306 vw	$2\nu_{12} = 1304 A_1$
1257		1260 w		$v_5 + v_{11} = 1265 A_1$
1248)				• • •
1165.5	4 / D	1101	1105 - D	
1161.0 Vs	АјБ	1101 VS	1100 W P	$\boldsymbol{\nu}_{5}$ (\boldsymbol{a}_{1}) rund
1155-5)		1000		1 1079 /
1060 80		1000 VW		$\nu_7 + \nu_8 = 10/2 A_1$
1049		1049 -5	1020 -1	a a 1047 d
1040}W		1042 80	1038 BH	$\nu_0 + \nu_{12} \equiv 1027 M_2$
1042)		1016 m	1099 m D	a (a) fund
1014 VW		075 mm	1023 W 17	$p_{17} (e)$ rund $m \perp m \rightarrow 0.77 A$
		913 VW		$p_6 + p_{14} \rightarrow p_{11} + n_2$
~ 859.5)		010 W		$2\nu_{8} = 044 n_{1}$
0.02.0	4/18	849 100	836 m P	v (a) forad
843	21,20	UTA VB		all (all tange
020 J 7871	_			
780 m	B	793 w, sh†	795 sh P	$2\nu_g = 790 A_2$
731)				
$\frac{1}{721}$ w		729 m†	736 w P	$2\nu_{13} = 730 A_1$
~666)				
654 m	С	652 s	653 w D	\boldsymbol{v}_{12} (\boldsymbol{a}_2) fund
645	-			- 14 1 27
602)	n	<u> 200 -</u>	800 - T	
592 ^m	В	000 s	602 s P	ν_7 (a_1) runa
568 sh		581 s	586 s P	$2v_{10} = 586 A_1$ Fermi resonance $(v_{14} + v_{19} = 500 A_1)$
492 sh		\sim 500 w, sh		$v_{1} + v_{1} = 499 A_{1}$
481	a	479	474 ava D	u (a) fund
470} ^m	a	9128	4/4 VN L'	P_8 (σ_1) rand
390 w		395 m‡	396 m D(?)	v_{9} (a_{1}) fund
371	C	365 m t	369 a D	$v_{\rm ex}$ (a) fund
361 } **	v	909 mt		-13 (w2) I unit
		293 w‡	299 m P	ν_{10} (a ₁) fund
		135 w, sh‡		$\boldsymbol{v_{14}}(\boldsymbol{a_2})$ fund

PC			тс			Approx.	
Species	Infrared gas	Raman liquid	Species	Infrared solution	Raman liquid	motion	
a' v1	3326					v (CH)	
-			$a_1(a') v_1$	2921	2925	$v_{s}(CH_{3})$	
v ₂	2131	2116	v2	2225	2224	ν(C==C)	
v_3	1767	1742	¥3	1758	1751	v(C==O)	
			ν ₄	1378	1375	$\delta_{s}(CH_{3})$	
٣d	1003	1005	ν_5	1161	1165	v (CC)	
			νe	842	836	v(CC)	
^v 5	696	~ 720				$\delta(CH)$	
ve	655	653	ν_7	600	602	v(CCl)	
¥7	482	478	ν_8	472	474	$\delta(\text{COC1})$	
v 8	414	413	r ₉	395	396	$\delta(\text{COCl})$	
v ₉	157	167	^{<i>v</i>} 10	293	299	$\delta(CC \equiv C)$	
			<i>v</i> 11	104	105	δ(CC =C)	
$a'' v_{10}$	703	~720	_			$\gamma(CH)$	
v11	665		$a_2(a'')r_{12}$	652	653	γ(C==0)	
v_{12}	224	227	^v 18	365	369	$\gamma(CC \equiv C)$	
			v_{14}	135		γ(CC══C)	
			e v ₁₅	2961	2977	$\nu_{a}(CH_{3})$	
			v_{16}	1431	1434	$\delta_a(CH_3)$	
			^ν 17	1016	1023	ω(CH ₃)	

Table 3. Observed fundamental vibrations of propiolyl and tetrolyl chloride



Fig. 1. The i.r. spectrum of propiolyl chloride (PC), vapour, path length 9 cm, pressures (A) 60, (B) \sim 20 and (C) \sim 10 torr.

Monosubstituted acetylenes with axial symmetry are known to show a single strong band in the region 600-700 cm⁻¹ arising from the CH deformation. Attachment of a planar group may result in splitting of the degeneracy and the occurrence of two bands corresponding to out-of- and in-plane motions. The strong C-type vapour band at 703 cm⁻¹ is undoubtedly connected with the former and the medium strong hybrid band near 696 cm⁻¹ is tentatively assigned to the latter vibration. The strong i.r. solution band at 709 cm⁻¹ and the weak diffuse Raman band at ca. 720 cm⁻¹ in the pure liquid are most likely connected with these fundamentals. An alternative assignment for the in-plane vibration would be the strong vapour band at 669 cm⁻¹, which would give better agreement with the observed splitting of 41 cm⁻¹ in propynal H—C=C—CHO [2]. However, this assignment would imply a separation of less than 20 cm⁻¹ between two fundamentals of the same species. If associated with a CH vibration the band at 669 cm⁻¹ most likely would be shifted by the change of phase, in contrast to observations.



Fig. 2. The Raman spectrum of propiolyl chloride (PC), liquid.



Fig. 3. The C=C stretching band, v_2 of propiolyl chloride, vapour.

Of the remaining six fundamentals two should belong to species a'', e.g. the C==O out-of-plane wag and a low frequency skeletal deformation. The latter appears as a distinct *C*-type vapour band at 224 cm⁻¹, observed at 260 cm⁻¹ in propynal [2]. The former is probably overlapped by the strong C--Cl stretching band near 655 cm⁻¹. Three bands occur in the region 655-670 cm⁻¹ in the vapour and the very strong i.r. solution band at 661 cm⁻¹ shows inflections at 653 and 668 cm⁻¹ which are not readily explained as overtone or combination bands. The observation of a medium strong *C*-type band at 654 cm⁻¹ with a weak Raman counterpart in TC supports this assignment.

The three remaining skeletal deformations of species a' are easily recognized from their vapour phase contours, *PR*-separations and partly from polarization measurements. The two vibrations at 482 cm⁻¹ and 414 cm⁻¹ are mainly located in the COCl group, while the frequency at 157 cm⁻¹ most likely is a deformation of the C=C-C skeleton, observed at 205 cm⁻¹ in propynal [2].

Tetrolyl chloride (TC)

The vibrational representation of TC emerges as $\Gamma_{vib} = 11a_1 + 3a_2 + 3e(C_{3v})$. For convenience the vibrations of the heavy-atom skeleton and the parallel type vibrations of the methyl group are also classified according to C_s symmetry as shown in Table 3.

By transferring bond angles and distances from geometries of structurally related molecules [13, 18] the following principal moments of inertia are calculated: $I_A = 83.6$, $I_B = 355.5$ and $I_C = 435.8$ a.m.u. Å². The asymmetry parameter (κ) is estimated to be -0.89, suggesting that TC is a prolate asymmetric top. The angle formed by the A-axis and the C=C-C axis is 36°. From calculations the *PR*-separations were estimated to 10.2, 8.5 and 15.2 cm⁻¹ for A, B and C-type bands, respectively, at 40°C [19]. The i.r. spectrum is shown in Fig. 4, and the vibrational frequencies and proposed assignments are presented in Tables 2 and 3.

The e-type CH_3 bands v_{15} and v_{16} show a clearly resolved fine structure in the vapour caused by the relatively free rotation of this group with respect to the rest



Fig. 4. The i.r. spectrum of tetrolyl chloride (TC), vapour, path length 9 cm, pressure (A) ~ 10 torr.

of the molecule. The spacing of the Q-branches of ca. 10 and 15 cm^{-1} for v_{15} and v_{16} , respectively, are in good agreement with observations for related molecules [13, 21, 22]. Owing to the low vapour pressure of TC the v_{15} band appears rather weakly even at a path length of 1 m. Interfering bands produced by decomposition in the 1 m cell prevented examination of the v_{16} band at this path length.

The r_{15} band (Fig. 5) shows clearly the strong, weak, weak intensity alternation characteristic of the Q-branches in symmetric top molecules. The $K_1 = 0$ Q branch is located at 2992 or possibly at 2962 cm⁻¹ apparent from the observed solution frequency at 2961 cm⁻¹. The data are listed in Table 4 together with the approximate values calculated for Coriolis interaction constant ζ_i and the band origin r_0 . These parameters are obtained from the equation given by MoLACHLAN [21], neglecting the quadratic terms in K and assuming identical rotational constants in the upper and lower vibrational levels. The employed value of 0.0872 cm⁻¹ for B + C is obtained from a microwave broad band spectrum.



Fig. 5. The CH₃ stretching bands, v_{15} and v_1 of tetrolyl chloride (TC), vapour, path length 1 m, pressure ~10 torr. Spectral slit width 0.7 cm⁻¹.

A closer examination of the r_{15} band reveals a splitting of the Q-branch at 2992 cm⁻¹ and a separation of ca. 2 cm⁻¹ for this doublet. In the perpendicular bands of the rotating group the effect of lifting the vibrational degeneracy will be observed first in the $K_1 = 0$ subband, which suggests $r_{156} - r_{155} = 2$ cm⁻¹. Tetrolaldehyde showed no splitting or broadening of the $K_1 = 0$ g branch under

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		^v 16		
	$\overline{K_1^{\dagger}}$		$^{P}Q_{H_{1}}$	Q^{\ddagger}
	0	2992 §		1369
	1	3002	2982	1383
	2	3011	2971·5	1398
	3	3020.5	2962.5	1413
	4	3030.5		1427
	5	3040		1441.5
	6	3050 §		1456
				1468
ro cale.		2987		_
ζ,		0.05		-0.38
ζ_1 (tetrolaidehyde)		0.06		-0.41

Table 4. Spectral data and ζ_i values for v_{15} and v_{16} in tetrolyl chloride*

* Frequency readings not better than ± 0.5 cm⁻¹.

† Quantum number for the internal rotation of the CH₃ group.

‡ Bands too weak for assignment (9 cm cell).

§ Central minimum of doublet.

comparable resolution [13]. This observation may indicate a somewhat larger internal rotational barrier in TC. The value of the term V_6 of the six-fold potential barrier [23] may be estimated from the magnitude of the splitting in the $K_1 = 3$ Q branches [13]. Appearance of a shoulder or weak asymmetry in these bands indicate a value $\geq 4 \text{ cm}^{-1}$ for V_6 in TC. No splitting or broadening was observed in the corresponding bands in tetrolaldehyde, where V_6 was estimated to $< 4 \text{ cm}^{-1}$.

The C=C stretching vibration at 2225 cm⁻¹ is apparently in Fermi resonance with $2r_5$. In contrast to the observation for PC this band shows a smooth vapour phase contour. The strong bands at 1161 and 842 cm⁻¹ having A-type gas contours are attributed to the two C—C stretching modes. Also the two stretching vibrations characteristic of the COCl group are easily identified.

Of the seven skeletal deformations the two in-plane vibrations involving bending of the COCl angles are assigned to bands at 472 and 395 cm⁻¹. The two in-plane C—C=C bending vibrations are located at 293 and 104 cm⁻¹. Prominent *C*-type contours are shown by the bands at 652 and 365 cm⁻¹, suggesting out-of-plane sketetal modes. The former must be associated mainly with the C=C wag, r_{12} and the latter with the C--C=C deformation, r_{13} . Also the 135 cm⁻¹ band is attributed to a non-planar skeletal mode, r_{14} , involving bending of the C--C=C group. The assignment of the four C--C=C deformations is based on force constant calculations [24] and analogous assignments reported for tetrolaldehyde and 1-halo-2butynes in the region 360-100 cm⁻¹ [13, 21]. These vibrations are rather localized according to the potential energy distribution. In tetrolaldehyde the two planar modes were observed at 334 and 128 cm⁻¹, whereas one non-planar mode was observed at 368 cm⁻¹.

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In the far i.r. region we observed a broad absorption band at ca. 52 cm⁻¹ in the heptane solution of TC. The far i.r. absorptions of several polar and nonpolar liquids have been studied in the region 5–70 cm⁻¹ by JAIN and WALKER [25]. These bands arise from the molecular environmental conditions. For polar molecules this phenomenon has been considered partly as a librational motion and partly as a rotational-translational motion [26, 27].

The COCl bending vibrations

A comparison of the COCl in-plane deformations in PC and TC with the corresponding vibrations in CH₃COCl [5] reveals shifts of 40-70 cm⁻¹ toward higher frequencies in the former molecules. These frequencies fall outside the region 420-440 cm⁻¹ reported for complex saturated acyl chlorides [28]. Still greater shifts occur for C=O wag from ca. 500 cm⁻¹ in CH₃COCl to ca. 650 cm⁻¹ in PC and TC. Good agreement with observed frequencies was obtained from calculations using the same force constant for this mode in PC and TC [24]. The vibration is fairly well localized as shown by the potential energy distribution.

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