13C NMR, 1H NMR AND IR SPECTRA OF A SERIES OF MONOCHLOROESTERS OF ALIPHATIC SHORT CHAIN CARBOXYLIC ACIDS

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Abstract—13C chemical shifts for 14 isomeric monochloroesters of aliphatic carboxylic acids from propanoic acid to hexanoic acid have been determined. Comparisons are made with the literature values for methyl monochloro-octanoate isomers. Substituent effects for all positions are given. Characteristic IR absorption bands are presented and comparisons are made with regard to the isomeric structure. Connections are suggested between observed trends in IR absorption frequencies and some "abnormal" chlorine substituent effects on 13C chemical shifts. 1H NMR spectra of these compounds are considered.

13C NMR spectroscopy has proved its utility in structural and stereochemical elucidations largely due to consistent trends exhibited by the shielding of carbon nuclei in similar environments. Since a thorough theoretical account for the observed trends is not yet available, signal assignments rely on the empirical knowledge of the shielding effects in closely related model systems.

In this paper we report the 13C chemical shifts for the methyl esters of isomeric monochlorocarboxylic acids. The unambiguous assignment of carbon resonances is, in general, greatly facilitated by comparison with the 13C NMR spectra of closely related compounds containing similarly substituted carbon atoms. The substituent effects of chlorine have been the subject of intensive study ever since the early years of 13C spectroscopy. The constancy of the effects within families of compounds have been established.

The values of α, β and γ effects determined in this study for aliphatic straight chain esters seem to be quite constant except for a few cases where certain tendencies could be ascertained. A series like this provides a test for the possible generality of some "anomalous" effects observed for individual isomers.

The general availability of IR spectrometers makes them important tools in structure elucidations and the electronic and steric factors which influence IR absorption frequencies play also important role in 13C shieldings.

EXPERIMENTAL

Materials. Methyl propanoate (1), methyl butanoate (4), methyl pentanoate (8) and methyl hexanoate (13) were obtained by the usual H_2SO_4-catalyzed esterification of commercial acids. Methyl 2-chloropropanoate (2), methyl 2-chlorobutanoate (5), methyl 2-chloropentanoate (9) and methyl 2-chlorohexanoate (14) were prepared from corresponding 2-chloroacids[1] by esterification as above. Methyl 3-chloroesters[2] 3-chloropropanoate (3), 3-chloro-butanoate (6), 3-chloropentanoate (10) and 3-chlorohexanoate (15), were synthesized from 2,3-unsaturated acids[3] according to the direction of 3-chloroisovaleric acid (methyl acrylate and methyl crotonate were commercial products of Fluka AG). Methyl 4-chlorobutanoate (7) and methyl 5-chloropentanoate (12) were prepared from commercial 4-chlorobutyryl chloride (Merck) and 5-chloropentanoic acid (Merck) respectively by appropriate esterification methods. Methyl 4-chloropentanoate (11), methyl 4-chlorohexanoate (16) and methyl 5-chlorohexanoate (17) were isolated by preparative GLC from the reaction mix-

tures of monochloroesters obtained by chlorinating the parent esters with molecular chlorine in the vapour phase. Methyl 6-chlorohexanoate (18) was synthesized by the method given by Kochi and Rust.[4]

Before spectral analysis the compounds were further purified by preparative GLC on a Perkin–Elmer F 21 instrument fitted with a 5 m × 3/8 in. 10% Carbowax 20 M column.

13C *NMR-spectra.* The noise decoupled and proton coupled FT carbon spectra were taken at 15 MHz on a JEOL FX 60 using a 4 KHz spectral width and 4 K data points. The concentrations were often unknown because most of the samples were purified by preparative gas chromatography and the droplets were directly eluted from the traps with CCl_4 and used after purity control by GLC for NMR experiment. The samples were examined in 5-mm sample tubes held concentrically inside the standard 10-mm sample tube and surrounded by D_2O which served as a heteronuclear lock. The samples were concentrated by this arrangement and a greater portion of computer memory was secured to sample instead of CCl_4. Carbon shifts are given as δ values downfield from TMS which was used as an internal standard.

To discover possible solvent shift effects one compound was submitted to several spectral analyses both neat and in various solvent concentrations. Solvent shift effects could not be detected.

1H *NMR-spectra* were obtained on a Perkin–Elmer Model R 12 B 60 MHz spectrometer in carbon tetrachloride solutions using TMS as an internal standard.

IR-spectra were recorded on a Perkin–Elmer 283 IR Spectrometer. 5 µl samples of pure esters were used in a standard Perkin–Elmer liquid cell.

DISCUSSION

13C *NMR spectra.* 13C Chemical shifts from proton noise decoupled FT spectra for compounds 1–18 are compiled in Table 1. Proton coupled carbon spectra were also run to assist in assigning signals and for J_{C-H} determinations. The latter will be published later.

Individual effects of chlorine substituents on each sp^3 carbon are given in Table 2. When these are compared with those of methyl monochlorooctanoates[5] some trends can be found which confirm the "abnormal" high effects obtained for chlorooctanoates.

Font *et al.*[5] have excluded from the mean values of effects three observed effects which differed from the mean values more than 10%. An exceptionally low α effect, 23 ppm, was obtained for 2-chlorooctanoate. They pointed out two explanations for this. Our results seem to strengthen one of these, namely, if 2-chloroesters are

Table 1. ^{13}C shift data for compounds 1–18

Compound	Chemical shift, ppm						
	C_1	C_2	C_3	C_4	C_5	C_6	OCO$\underline{C}H_3$
1	173.7	27.4	9.2				51.0
2	170.0	52.3	21.4				52.7
3	170.5	37.7	39.4				51.7
4	173.1	36.1	18.9	13.8			51.0
5	169.6	58.7	28.7	10.5			52.5
6	170.1	45.1	53.0	25.1			51.6
7	172.6	30.9	28.2	44.0			51.3
8	172.7	33.6	27.3	22.6	13.9		50.9
9	169.7	56.9	37.3	19.6	13.4		52.4
10	169.3	42.9	59.0	31.0	10.6		51.3
11	172.0	30.7	35.1	57.2	25.2		51.0
12	173.0	33.1	22.6	32.4	44.6		51.3
13	172.8	34.0	25.2	31.9	22.8	14.2	50.9
14	169.1	56.6	34.5	28.2	22.1	13.8	52.2
15	170.0	43.7	57.8	40.5	19.9	13.6	51.4
16	171.7	30.2	32.7	63.8	31.3	10.5	50.8
17	172.1	33.0	21.9	39.5	57.4	25.3	50.9
18	172.3	33.4	24.0	26.4	32.2	44.3	50.9

Table 2. Substituent effects of chlorine on the sp^3 carbon atoms of methyl monochloroesters of aliphatic (C_3, C_4, C_5 and C_6) carboxylic acids.

Compound	Effect (ppm)								
	ε	δ	γ	β	α	β	γ	δ	ε
2				12.2	24.9				
3					30.2	10.3			
5			-3.3	9.8	22.6				
6				11.3	34.1	9.0			
7					30.2	9.3	-5.2		
9		-0.5	-3.0	10.0	23.3				
10			-3.3	8.4	31.7	9.3			
11				11.3	34.6	7.8	-2.9		
12					30.7	9.8	-4.7	-0.5	
14	-0.4	-0.7	-3.7	9.3	22.6				
15		-0.6	-2.9	8.6	32.6	9.7			
16			-3.7	8.5	31.9	7.5	-3.8		
17				11.1	34.6	7.6	-3.3	-1.0	
18					30.1	9.4	-5.5	-1.2	-0.6

considered as chloroalkanes substituted by methoxy-carbonyl group, COOCH$_3$, and α substituent effects for COOCH$_3$ are calculated by subtracting from the shift of C_2 of 2-chloroester the shift of the chlorinated carbon in parent 1-chloroalkane,[6] following substituent effects are obtained for methoxycarbonyl: 12.4 ppm (2-chloro-propanoate), 12.0 ppm (2-chlorobutanoate), 12.3 ppm (2-chloropentanoate), 11.3 ppm (2-chlorohexanoate), and 11.9 ppm (2-chlorooctanoate). Font *et al.*[5] compared their experimental value with the computed[7] mean value 20.2 ppm for methoxycarbonyl and concluded that the lowered deshielding effect of COOCH$_3$ when attached to a chlorine bearing carbon associated with the low contribution from the singly-bonded, dipolar form of carbonyl group. This is supported by a slightly higher CO stretching frequency in IR for our 2-chloroesters.

Font *et al.* also found within 7-chlorooctanoate the β effect upon the terminal methyl group to be noticeably greater (11.2 ppm) than the mean value (9.0 ± 0.7 ppm). From Table 2 it is evident that chlorine substituent on the carbon atom bearing a terminal methyl enhances the β effect upon the methyl group. The observed effects are of the same size; 12.2 ppm (2-chloropropanoate), 11.3 ppm (3-chlorobutanoate), 11.3 ppm (4-chloro-pentanoate), 11.1 ppm (5-chlorohexanoate). The intimate proximity of the carbomethoxy group is undoubtedly responsible for the about 1 ppm greater β effect in 2-chloropropanoate.

Table 3. Mean substituent effects of chlorine on the sp^3 carbon atoms of methyl monochloroesters of aliphatic (C_3, C_4, C_5 and C_6) carboxylic acids.

	Effect				
	α	β	γ	δ	ε
Literature[a]	31.2	10.5	-4.6	+0.1	+0.5
Literature[b]	33±3	9.0±0.7	-3.2±0.3	-0.7±0.2	-0.4±0.1
Experimental	32.1±1.7	9.0±0.8	-3.3±0.3	-0.7±0.3	
	(23.3±0.9)[c]	(11.5±0.4)[d]	(-5.1±0.3)[e]		

[a]From Ref. 6.
[b]From Ref. 5.
[c]The mean value in parenthesis is of 2-chloroesters 2, 5, 9 and 14.
[d]The value in parenthesis is the mean β effect of compounds 2, 6, 11 and 17 upon the terminal methyl group.
[e]The mean value in parenthesis is of compounds 7, 12 and 18 containing a terminal CH_2Cl group.

Font *et al.* further observed a more negative γ effect within 8-chlorooctanoate and considered it to be associated with the "primary" chlorine. Analogous behavior was displayed by compounds 7, 12 and 18 containing a terminal chloromethyl group.

The methoxyl carbons of ester functions absorb at an average value of 51.5±0.3 ppm (the deshielding effect with respect to methanol is ~ +2.2 ppm). It is a commonly observed shift position for aliphatic methyl esters.[7-9] The frequent occurence of carbomethoxyl group in natural products emphasizes the importance of knowing the sensitivity of its carbon resonance towards substituent effects. Of the methoxyl carbons studied those of 2-chloroesters absorb slightly downfield from the others (52.4±0.2 ppm). The difference (about 1 ppm) being so small however, that further investigations are

needed before conclusions can be drawn. Di- and polychloroesters studied at the moment by the authors are expected to give supplementary information.

¹H NMR spectra. Proton spectra for compounds 1-18 are given in Table 4. The methoxy group gives rise to a singlet absorption near 3.60δ. Substituent position seems to have insignificant effect upon this absorption resonance except in the case of 2-chloro isomers.[5,10] Chlorine substituent next to a carboxyl carbon causes a downfield shift of about 0.1 ppm. The terminal CH_2Cl absorption seems to suffer a slight diamagnetic shift with increasing carbon chain. Font *et al.*[5] explained the low methine proton resonance in 3-chloro-octanoate compared with that of 2-chloro isomer by the deshielding effect of the anisotropic ester CO group. In the favoured conformers these methine protons are forced into the

Table 4. ¹H NMR shifts of compounds 1-18

Compound	Chemical shift (δ) , multiplicity [a]					
	Protons attached to					
	COOCH₃	C_2	C_3	C_4	C_5	C_6
1	3.66, s	2.30, q	1.11, t			
2	3.75, s	4.32, q	1.65, d			
3	3.68, s	2.73, t	3.70, t			
4	3.65, s	2.24, t	1.63, m	0.94, t		
5	3.70, s	4.21, t	1.72-2.23, m	1.01, t		
6	3.66, s	2.70, d	4.08-4.64, m	1.55, d		
7	3.64, s	2.46, t	1.90-2.25, m	3.60, t		
8	3.62, s	2.26, t	1.25-1.90, c	1.25-1.90, c	0.92, t	
9	3.72, s	4.25, t	1.92, q	1.18-1.71, m	0.95, d	
10	3.67, s	2.71, d	4.00-4.43, m	1.57-2.07, m	1.06, t	
11	3.65, s	2.49, t	1.75-2.14, m	3.81-4.36, m	1.52, d	
12	3.61, s	2.32, t	1.53-1.95, c	1.53-1.95, c	3.56, t	
13	3.63, s	2.26, t	1.09-1.89, c	1.09-1.89, c	1.09-1.89, c	0.91, t
14	3.75, s	4.16, t	1.63-2.12, q	1.19-1.63, c	1.19-1.63, c	0.95, t
15	3.66, s	2.72, d	4.07-4.50, m	1.19-1.91, c	1.19-1.91, c	0.94, t
16	3.57, s	2.46, t	1.42-2.14, c	3.60-4.00, m	1.42-2.14, c	1.03, t
17	3.58, s	2.28, t	1.59-1.99, c	1.59-1.99, c	3.69-4.14, m	1.50, d
18	3.58, s	2.27, t	1.32-2.00, c	1.32-2.00, c	1.32-2.00, c	3.50, t

[a]s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; c, complex absorption.

deshielding zone of carbonyl group. Also in **6, 10, 11, 15, (16)** and **17** the CHCl group protons appear at relatively low resonances compared with those of the corresponding 2-chloro isomers.

IR spectra. The characteristic IR absorptions of compounds **1–18** are given in Table 5. The most intense band in the spectra is due to the C=O stretching absorption. This absorption is quite constant in intensity and

Table 5. Characteristic IR absorptions of compounds 1–18

Compound	Bands (cm^{-1}), intensity[a]					
1	2990 m sh	-	2955 m b	2860 m b	1750 s sp	1460 m sp
2	2990 m sp	-	2955 m sp	2870 w sp	1750 s b	1460 m sh
3	2995 m b	2970 m sh	2955 s sp	2885 w sh	1735 s b	1460 m sh
4	2995 m sh	-	2955 s sp	2880 m sp	1740 s b	1460 m sp
5	2995 m sh	2975 s sp	2955 s sp	2880 m sp	1750 s b	1460 s b
6	2995 m sh	2980 m b	2955 m sp	2870 w sh	1740 s b	1460 m sh
7	2995 m b	-	2955 s sp	2870 w b	1735 s b	1460 m sh
8	2990 m sh	-	2955 s sp	2870 m sp	1740 s sp	1460 m b
9	2995 m sh	-	2960 s b	2875 m sp	1750 s b	1460 s b
10	2995 m sh	2975 s sp	2955 s b	2880 m sp	1740 s b	1460 m b
11	2995 m sh	2975 s b	2955 s sp	2870 m b	1740 s b	1460 m sh
12	2995 m b	-	2955 s sp	2875 m sp	1735 s b	1460 m sh
13	2995 m sh	-	2960 s sp	2870 m sp	1740 s sp	1460 m b
14	2995 m sh	-	2960 s sp	2870 s sp	1750 s b	1460 s b
15	2995 m sh	-	2960 s sp	2875 m sp	1745 s b	1460 m b
16	2995 m sh	2970 s b	2950 s b	2875 m sp	1740 s b	1460 m sh
17	2995 m sh	2970 s b	2950 s sp	2870 m b	1735 s b	1460 m sh
18	2995 m b	-	2950 s sp	2870 m sp	1735 s b	1460 m sh
Assigment	Note b	Note b	Note b	Note b	Note c	Note d

Compound	Bands (cm^{-1}), intensity[a]					
1	1440 m sh	1415 w sh	1380 m sp	1355 m sp	1200 m sp	-
2	1440 s b	-	1380 m sp	1345 s b	1195 s b	685 m sp
3	1440 s sp	1415 m b	1380 m sh	1365 s b	1210 s b	665 m sp
4	1435 s sp	1415 m sh	1380 m sh	1355 m sp	1195 s b	-
5	1440 s sp	-	1380 m sp	1355 m sp	1170 s b	700 m sp
6	1440 s sp	1415 m b	1380 m b	1360 m b	1165 s b	635 m sp
7	1440 s sp	1415 m sh	1380 m sh	1365 m sp	1210 s b	640 m sp
8	1435 m sp	1415 m sh	1380 m sp	1360 m sp	1170 s sp	-
9	1435 s sp	-	1380 m sp	1355 m b	1165 s b	700 m sp
10	1435 s sp	1415 m b	1380 m b	1365 m b	1160 s b	635 m sp
11	1435 s sp	1415 m sh	1380 s sp	1365 m b	1165 s b	600 m sp
12	1435 s sp	1415 m sh	1380 m sh	1365 m b	1200 s b	640 m sp
13	1435 s sp	1415 m sh	1380 m sh	1360 m sp	1165 s sp	-
14	1435 s sp	-	1380 m sp	1355 m b	1170 s b	700 m sp
15	1435 s sp	1415 m b	1380 m b	1360 m sp	1165 s b	635 m sp
16	1435 s sp	1415 m sh	1380 m b	1365 m sp	1165 s b	600 m sp
17	1435 s sp	1415 m sh	1380 m sp	1365 m b	1165 s b	600 m sp
18	1435 s sp	1415 m sh	1380 m sh	1365 m sp	1200 s b	640 m sp
Assigment	Note e	Note f	Note g	-	Note h	Note i

[a] s, strong; m, medium; w, weak; sp, sharp; b, broad; sh, shoulder.
[b] C–H stretching, unspecified.
[c] Carbonyl stretching.
[d] C-Methyl asymmetric bending and scissoring of CH_2 groups.
[e] O-Methyl symmetric bending.
[f] –CH_2CO-scissoring.
[g] C-Methyl symmetric bending.
[h] The strongest band in the C–O stretching region.
[i] C–Cl stretching.

frequency occuring near $1740\,cm^{-1}$ except within 2-chloroisomers. A chlorine substituent next to carbonyl carbon shifts the C=O stretching frequency slightly to $1750\,cm^{-1}$. The tendency of carbonyl oxygen to attract electrons ($\overset{+}{C}-\overset{-}{O}$) results in a weakening of the C=O force constant and a lowering of the C=O frequency. Electron attracting groups attached to the carbon compete with the oxygen for electrons, resulting in less contribution from the polar form ($\overset{+}{C}-\overset{-}{O}$) and a higher frequency. A change in the carbonyl force constant due to a change in substituent electronegativity is known[11a] to have the largest effect on the carbonyl stretching frequency. In α-chlorocarbonyl compounds, a difference is observed between rotational isomers due to a field effect.[11b] When the chlorine is near the carbonyl oxygen in space, a higher frequency results relative to the isomer in which the chlorine is rotated away from the oxygen.

Methyl esters show O–CH$_3$ symmetric bending absorption at $1435\,cm^{-1}$ and this is quite strong in all spectra. This intense absorption is accompanied by two poorly resolved bands, namely, a shoulder visible at $1460\,cm^{-1}$ arising from C-Me asymmetric bending and the other at $1415\,cm^{-1}$. The latter is due to the CH$_2$ next to the carbonyl in saturated esters[12] and it is scarcely discernible in the spectra of 2-chloroisomers. Font et al.[5] found the symmetrical bending absorption of C-Me at $1380\,cm^{-1}$ as a shoulder within methyl monochloroocta-noates and only 7-chloroisomer showed a sharp defined band. According to them this results from a change in the polarizability of the therminal methyl due to a neigh-bouring halogen atom. This absorption appeared in our spectra as a medium sized sharp or broad band with the exception of those bearing a terminal chloromethyl group and exhibiting only a shoulder at $1380\,cm^{-1}$. The last column in Table 5 gives the strongest absorption bands in the C–Cl stretching region.[13]

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