Tetrahedron Vol 34, pp 791 to 798 Pergamon Press 1978 Printed in Great Britain

SPECTROSCOPIC BEHAVIOUR OF METHYL CHLOROOCTANOATES

J. FONT,* A. MORAL and F. SÁNCHEZ-FERRANDO
Departamento de Química Orgánica, Universidad Autónoma de Barcelona, Bellaterra, Spain

and

J. ELGUERO
Laboratoire de Chimie Moléculaire, Université d'Aix-Marseille III, 13397 Marseille, France

(*Received in UK 2 August 1977; Accepted for publication 3 October 1977*)

Abstract—The synthesis of the seven isomeric methyl chlorooctanoates is reported, in most cases for the first time, and their spectral characteristics are described and studied. Hypotheses are advanced to explain the abnormal spectral behaviour of some of them. The mass spectra show scrambling of hydrogen/chlorine and/or the chain carbons, as well as low ability to undergo the McLafferty rearrangement, in some cases. A complete set of ^{13}C NMR parameters is presented, including substituent effects for all positions, which are found to be exceptionally coherent within the series, except for three values.

The use of spectroscopic tools for identification and quantitation analyses has become routine amongst organic chemists, because of the availability of data on series of structurally related compounds, usually for a given type of spectroscopy. Thus, a wealth of tables for "substituent effects" have been published in the fields of UV, IR, ^{1}H NMR and ^{13}C NMR, while mass-spectrometric correlations are also usual. On the other hand, difunctional compounds are generally difficult to fit in these substituent effect tables, the additivity of recorded effects not being the common case.

In the present paper we wish to report our results on the IR, MS, ^{1}H NMR and ^{13}C NMR spectra of a whole series of difunctional compounds for which individual substituent effects have been compiled, namely the seven isomeric methyl chlorooctanoates (**2**, **3**, **4**, **5**, **6**, **7** and **8**, respectively), as well as the parent unsubstituted methyl octanoate, **1**.

MATERIALS AND METHODS

Methyl octanoate **1** was obtained by esterification from commercial acid. Methyl 2-chlorooctanoate **2** was obtained by malonic ester synthesis from 1-bromohexane, followed by saponification to the diacid, chlorination by sulfuryl chloride, decarboxylation and esterification by diazomethane.

Methyl 3-chlorooctanoate **3** was prepared by Wittig reaction between hexanal and methoxycarbonylmethylenetriphenylphosphorane, followed by addition of dry HCl across the double bond of the α,β-unsaturated ester.

Methyl 4-chlorooctanoate **4** was obtained through a sequence starting with 3-methoxycarbonylpropanoyl chloride (from succinic anhydride) and *n*-butylcadmium, saponification of the resulting ketoester and reduction of the ketoacid by sodium tetrahydridoborate, the lactone rather than the hydroxyacid being obtained upon acidic work up. Ring opening of the lactone by HCl in ether-MeOH afforded **4**.

Methyl 5-chlorooctanoate **5** was similarly prepared from 4-methoxycarbonylbutanoyl chloride (from glutaric anhydride) and *n*-propylcadmium in the initial step of the sequence.

Methyl 6-chlorooctanoate **6** was prepared from 1-ethylcyclohexene (from cyclohexanone and EtMgBr) by a sequence involving permanganate oxidation to the ketoacid, esterification, sodium tetrahydridroborate reduction to the hydroxyester and replacement of the OH group by means of thionyl chloride to give **6**.

Methyl 7-chlorooctanoate **7** was best prepared by BF_3 catalyzed acetylation of cyclohexanone to 2-acetylcyclohexanone, followed by alkaline ring opening (retroaldol) to the ketoacid, esterification, reduction to the hydroxyester and replacement of the OH group by means of thionyl chloride as above.

Methyl 8-chlorooctanoate **8** was prepared from cyclooctanone by a sequence involving Baeyer–Villiger oxidation, ring opening of the resulting lactone to the hydroxyester and replacement of the primary OH group by means of PCl_5, giving **8**.

Products **1**–**8** were purified by preparative glc on a 1 m, 3/8 in. 20% DEGS on Chromosorb W column, at 130°, over a Perkin–Elmer F-21 instrument.

IR spectra were recorded in CCl_4 soln (0.1 mm path length) on a Perkin–Elmer Infracord 720 instrument.

Proton NMR spectra were obtained in CCl_4 soln on a Perkin–Elmer R-12 instrument, at 60 MHz and with an internal reference of TMS.

Mass spectra were recorded in a Hewlett-Packard 5930 A spectrometer, at 70 eV.

Proton noise decoupled FT ^{13}C NMR spectra were recorded at Marseilles, in deuteriochloroform solution and with an internal reference of TMS, on a Varian CFT 20 instrument, at 20 MHz.

RESULTS AND DISCUSSION

IR spectra. Table 1 shows the IR spectra of compounds **1**–**8**, together with the spectrum of octanoyl chloride, included for comparison.

No conclusions can be drawn from the small intensity and frequency variations observed in the C–H stretching region.

In the CO stretching region, the only noticeable feature is the absence of a doublet of bands in the spectrum of **2**. This doublet is to be expected in the solution spectra of α-haloesters, since the two possible rotational "isomers" of these compounds (the synperiplanar and the synclinal rotamers) give rise to separate absorptions,[1] eclipsing between the halogen atom and the CO oxygen in the synperiplanar conformer resulting in a shift of the band to upper frequencies, while the synclinal rotamenrs show unmodified CO absorption bands. This effect is not observed, however, in compound **2**, and we must conclude that the more polar synperiplanar rotamer **2a** is much less populated than the synclinal rotamers **2b** and **2c** in the non-polar solvent used, carbon tetrachloride.

Table 1. The IR spectra of several octanoyl derivatives.

Compound	Bands (cm^{-1}), intensity[a]									
$CH_3(CH_2)_6COCl$	2975sh	2950b	2870sp	1800s	1460sh 1465sp	—	1405sp	1380sp	1345m	—
1	2980sh	2950b	2875sp	1740s	1460b	1440sp	1415sh	1380sh	1360b	1160sp
2	2980sh	2950b	2875sp	1740s	1460b	1440sp	--	1380sh	1360b	1160sp
3	2975sh	2950b	2880sp	1740s	1460b	1440sp	1415sh	1380sh	1360b	1160sp
4	2975b	2950sh	2885sp	1740s	1460sh	1440sp	1415sh	1380sh	1365b	1160sp
5	2980b	2955sh	2890sp	1740s	1460sh	1440sp	1415sh	1380sh	1365b	1160sp
6	2985sh	2960b	2885sp	1740s	1460sp	1440sp	1415sh	1380sh	1365sp	1160b
7	2980sh	2955b	2880sp	1740s	1460sh	1440sp	1415sh	1380sp	1360b	1160b
8	2980sh	2955b	2875sp	1740s	1460w	1440sp	1415sh	—	1360b	1160sp
Assignment	Note b	Note b	Note b	Note c	Note d	Note e	Note f	Note g	—	Note h

[a] *s*, strong; *m*; medium; *w*, weak; *sp*, sharp; *b*, broad; *sh*, shoulder.

[b] C–H stretching, unspecified.

[c] Carbonyl stretching.

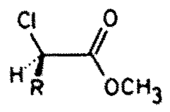
[d] C–Methyl asymmetric bending and scissoring of methylenes.

[e] O–Methyl symmetric bending (Ref. 2).

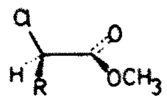
[f] $-CH_2CO-$ scissoring (Ref. 3).

[g] C–Methyl symmetric bending.

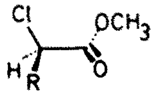
[h] C–O stretching.



2a



2b

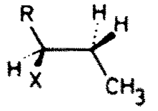


(R = n-C_6H_{13})

2c

Fig 1

In the 1400 cm^{-1} region three main bands are observed and can be easily assigned. At 1460 cm^{-1} the C-Me asymmetric bending and the methylene scissoring are shown in all cases. This band appears as a broad, weak or poorly defined absorption in all the isomers except **6**, in which it appears as a sharp band with the same intensity than the 1440 cm^{-1} absorption. Interestingly, the same effect is found in the case of other 6-substituted methyl octanoates,† such as the 6-bromo- and the 6-toluene-*p*-sulfonyloxy- derivatives. Assuming the preferred conformation for these compounds to be **6a** (Fig. 2), we tentatively assign this effect to an increase in the extinction coefficient of the terminal methyl asymmetric bending mode due to the bulkness and/or polarity of the 6-substituent.



(R = -$(CH_2)_4$-CO_2CH_3)

(X = Cl, Br, OTs)

Fig 2

The band at 1440 cm^{-1}, not present in octanoyl chloride, is due to the O–CH_3 symmetric bending mode in all methyl esters.[2]

The band at 1415 cm^{-1}, shown as a shoulder in all cases except compound **2**, is due to the scissoring of the methylene protons α to the CO group.[3]

The terminal C-Me symmetrical bending absorption is shown as a shoulder at 1380 cm^{-1} in compounds **1**–**6**, and is absent, of course, in **8**. In **7**, however, this absorption appears as a sharp, cleanly defined band, because the presence of the halogen on the C atom bearing the Me group promotes electrical and/or steric changes on the polarizability of the latter.‡

As expected, the strongest of the C–O stretching absorption bands due to the ester grouping appears in all cases at 1160 cm^{-1}, irrespective of the presence or position of the halogen.[4]

The C–Cl stretching and the CH_2 rocking absorptions could not be observed under the recording conditions used.

Proton NMR. The 60 MHz ^{1}H NMR spectra of compounds **1**–**8** are given in Table 2. We shall briefly comment on the more prominent features.

The singlet of the MeO group appears in all cases near 3.6 δ, except in the case of **2**, when a small

Table 2. The 60 MHz ^{1}H NMR spectra of methyl chlorooctanoates.

Compound	Chemical shift (δ), multiplicity[a], J (Hz)							
	Protons attached to							
	C_8	C_7	C_6	C_5	C_4	C_3	C_2	CO_2CH_3
1	0.85, bt	1.0-1.8, c	1.0-1.8, c	1.0-1.8, c	1.0-1.8, c	1.0-1.8, c	2.25, bt, 7	3.6, s
2	0.9, bt	1.1-1.6, c	1.1-1.6, c	1.1-1.6, c	1.1-1.6, c	1.7-2.1, c	4.1, t, 7	3.7, s
3	0.9, bt	1.1-1.95, c	1.1-1.95, c	1.1-1.95, c	1.1-1.95, c	3.95-4.45, m	2.7, d, 7	3.65, s
4	0.9, bt	1.1-2.1, c	1.1-2.1, c	1.1-2.1, c	3.7-4.1, m	1.1-2.1, c	2.4-2.6, m	3.6, s
5	0.9, bt	1.3-1.9, c	1.3-1.9, c	3.7-4.1, m	1.3-1.9, c	1.3-1.9, c	2.1-2.4, m	3.6, s
6	1.0, t, 7	1.3-1.9, c	3.5-3.9, m	1.3-1.9, c	1.3-1.9, c	1.3-1.9, c	2.25, bt, 7	3.55, s
7	1.5, d, 7	3.7-4.1, m	1.2-1.9, c	1.2-1.9, c	1.2-1.9, c	1.2-1.9, c	2.25, bt, 7	3.55, s
8	3.5, bt, 7	1.2-1.9, c	1.2-1.9, c	1.2-1.9, c	1.2-1.9, c	1.2-1.9, c	2.25, bt, 7	3.6, s

[a] *s*, singlet; *d*, doublet; *t*, triplet; *m*, multiplet; *c*, complex absorption; *b*, broad.

---

†Unpublished results from our laboratory (Bellaterra).

‡We have found the same effect in the IR spectrum of methyl 7-bromooctanoate,† which also shows a cleanly defined sharp band at 1380 cm^{-1}

downfield shift due to the electron-withdrawing halogen atom is apparent, the signal appearing at 3.7 δ.

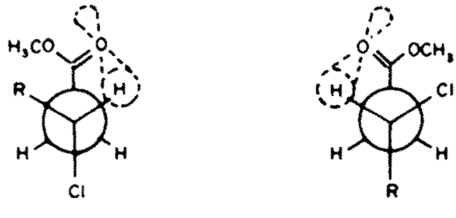
The agreement between observed and calculated chemical shifts for the methine protons in all isomers is poor, as shown in Table 3, except in the case of 2. More striking, however, is the position of this proton in compound 3. The modified Shoolery rules predict this proton in 3 to appear *upfield* from the corresponding proton in 2, while its observed position lies *downfield*. This fact can be explained by assuming that the more populated conformers of 3, namely 3a and 3b (Fig. 3), force the methine proton into the deshielding zone of the anisotropy cone of the ester CO group.

Table 3. The chemical shift of protons attached to chlorine-bearing carbons in methyl chlorooctanoates

Compound	$\delta_{\mathrm{Cl-C-H}}$[a]	
	observed	calculated[b]
2	4.1	4.2
3	4.25	3.7
4-7	3.9	3.5
8	3.5	3.25

[a] Highest point in complex bands.

[b] Modified Shoolery rules, assuming a value of −0.2 ppm for the β effect of the methoxycarbonyl group.



3a 3b

Fig. 3.

Mass spectra. The 70 eV mass spectra of compounds 1–8 are given in Table 4. As expected, the spectra of the chloroesters are quite different from that of the parent compound, although the McLafferty rearrangement furnishes the base peak in most cases.

The spectrum of 1 illustrates the fragmentation patterns to be expected in a medium–long chain carboxylic acid ester, i.e. two α-fission processes giving rise to peaks at *m/e* 129 and 59, the β-fission or McLafferty rearrangement (*m/e* 74, base peak), and the γ-fission producing a peak at *m/e* 87 very characteristic of aliphatic methyl esters. We can also point out the presence of a very intense peak at *m/e* 88, undoubtedly corresponding to the ionized form of methyl propanoate, although this peak is not present in the spectra of other methyl *n*-alkanoates. Other peaks are found at M-C_nH_{2n+1}, corresponding to the loss of alkyl groups which are known to contain the C atoms occupying the positions α, β, γ, . . ., etc. with respect to the CO group[3] (together with a H atom from elsewhere in the molecule[4]) rather than the terminal C atoms of the aliphatic chain.

The spectra of our chloroesters are quite distinct from the spectrum of the parent compound, although some characteristic fragmentations are retained. Thus, one α-fission process gives rise in 2–8 to the peak at *m/e* 59, $[CO_2CH_3]^+$, very intense in 3 and 5, while the other α-fission process, loss of OMe, gives rise to the Cl-containing acyl cations at *m/e* 161–163 shown by 3–8. In the case of 2 this peaks are not present because the electron withdrawing halogen atom in the α-carbon would destabilize the acyl cation.

The McLafferty rearrangement gives a very intense peak in all cases, compound 2 giving *m/e* 108–110 rather than 74 due to the presence of chlorine in the resulting ion-radical. The peak due to this process is the base peak except in the cases of 3 and 5.

The γ-fission process which gives rise to the peak at *m/e* 87, $[CH_2CH_2CO_2CH_3]^{+\cdot}$, in most methyl esters, is also present in all our isomers, and is very intense in 3 and 5, although scrambling of H and Cl atoms, similar to what happens between protium and deuterium[6] (or, alternatively, scrambling of the chain carbons[5]) must be operative in the formation of this fragment, since this 87 peak is shown even by 2 and 3. Simple γ-cleavage would give in these two compounds a fragment, $[C_2H_3ClCO_2CH_3]^+$, *m/e* 121–123, not shown by 3; peaks at 121–123 are found in the spectrum of 2, and after allowing for the contribution of peak 122–123, the intensity ratio 121–123 clearly demonstrates that they are originated by this simple γ-cleavage process.

A peak at *m/e* 88, $[CH_3CH_2CO_2CH_3]^{+\cdot}$, is present only in the spectrum of 5, and the corresponding chlorine-containing fragment, $[C_2H_4Cl{-}CO_2CH_3]^{+\cdot}$, *m/e* 122–124, is shown by 2. In this case, however, part of the peak at *m/e* 124 must come from a different origin (see below), since it accounts for more than one third of the intensity of the 122 peak.

Peaks at M-C_nH_{2n+1} are shown only by 2, which gives medium-intensity peaks at *m/e* 163–165 and 121–123, corresponding to the losses of $C_2H_5^{\cdot}$ and $C_5H_{11}^{\cdot}$, respectively. The relatively important loss of Et radical is also shown by methyl 2-bromooctanoate,† and this seems to indicate a great stability of the resulting cation. Indeed, the mass spectrum of methyl 2-bromohexanoate clearly contains the same peak,† corresponding to the relatively unusual loss of a H atom from the molecular ion. Since this feature is not particularly important in the spectrum of 1, and is absent in 3–8, the presence and position of the halogen must be decisive in the formation of this fragment.

Loss of HCl and subsequent (or simultaneous) loss of OMe from the molecular ion of 2–8 would give the unsaturated acyl cations, $[C_7H_{13}CO]^+$, *m/e* 125, shown by most of our chloroesters. More important, however, is the loss of MeOH from the unsaturated esters (or HCl and MeOH from the chloroesters), which gives the 124 peak, very intense in 3 and 5.

Loss of a Cl atom from the molecular ion is appreciable only in 2 and 3, giving a peak at *m/e* 157 which, in the case of the latter, is even more intense than the peak from the McLafferty rearrangement, as previously found for other methyl 3-chlorooctanoates.[7]

Finally, the molecular ion is not shown by any of the chloroesters, as opposed to the parent unsubstituted compound 1. This clearly shows that the presence of the

---

† Unpublished results from our laboratory (Bellaterra).

Table 4. The 70 eV mass spectra of methyl chlorooctanoates

Compound	m/e (% relative intensity)
1	27(16), 28(6), 29(20), 39(14), 41(31), 42(13), 43(23), 45(6), 55(27), 56(6), 57(25), 59(13), 60(16), 61(11), 69(11), 70(18), 73(17), 74(100), 75(11), 83(5), 84(5), 87(25), 88(44), 89(4), 101(14), 115(9), 127(14), 129(6.3), 158(0.9).
2	15(9), 27(32), 28(9), 39(28), 40(6), 41(57), 42(23), 43(48), 45(5), 53(12), 55(86), 56(10), 57(16), 59(28), 62(7), 67(10), 68(5), 69(14), 70(8), 71(7), 73(8), 74(6), 76(6), 81(6), 87(17), 94(16), 95(5), 96(7), 97(12), 108(100), 109(5), 110(32), 115(12), 121(9), 122(39), 123(5), 124(14), 129(9), 157(8), 163(11), 164(1.1), 165(3.7).
3	28(62), 29(58), 31(31), 32(12), 39(37), 40(7), 41(77), 42(21), 43(48), 45(18), 53(13), 54(17), 55(100), 56(20), 57(9), 59(83), 67(24), 68(6), 69(14), 70(5), 71(13), 74(72), 75(7), 81(17), 82(54), 83(29), 85(17), 87(28), 93(6), 95(9), 96(87), 97(28), 101(11), 113(10), 114(13), 124(50), 125(21), 127(6), 157(75), 158(8.7), 161(6.4), 162(0.3), 163(2.7).
4	27(20), 28(65), 29(21), 32(29), 39(30), 40(8), 41(51), 42(15), 43(38), 44(12), 53(11), 54(11), 55(67), 56(10), 57(14), 59(20), 67(18), 69(11), 71(8), 74(100), 75(10), 81(11), 82(18), 83(15), 85(22), 87(10), 96(25), 97(9), 124(18), 125(10), 161(2.8), 162(0.9), 163(0.9).
5	15(8), 27(25), 28(15), 29(22), 38(31), 39(6), 41(54), 42(18), 43(33), 45(6), 53(17), 54(16), 55(100), 56(10), 57(13), 59(45), 62(5), 67(29), 68(9), 69(14), 70(6), 71(9), 74(61), 75(8), 81(15), 82(37), 83(23), 85(8), 87(23), 88(10), 96(48), 97(15), 101(10), 124(46), 125(18), 161(5), 162(0.7), 163(1.9).
6	27(7), 29(6), 39(9), 41(18), 42(5), 43(16), 55(27), 59(16), 67(7), 74(100), 75(6), 82(9), 83(5), 87(7), 96(6), 101(3.4), 124(8), 125(5), 161(1.5), 163(0.5).
7	41(7), 43(7), 55(17), 59(10), 67(5), 69(5), 74(100), 75(10), 82(6), 83(5), 87(8), 96(8), 97(5), 101(2.4), 125(6), 126(4.3), 161(1.4), 163(0.6).
8	27(9), 28(12), 29(8), 32(8), 39(11), 41(24), 42(7), 43(18), 55(31), 57(5), 59(15), 69(7), 74(100), 75(7), 87(14), 96(5), 97(4), 124(5.6), 161(6.2), 163(2.5).

halogen atom opens a range of possible fragmentations in 2–8.

As seen, the compounds in which the McLafferty rearrangement does not give the base peak, namely 3 and 5, give rise to many other fragments, and particularly have their base peak at *m/e* 55 ($C_4H_7^+$, unsaturated). Why the McLafferty rearrangement is so scarce in these two compounds is not apparent. In the case of some other 3-chloroesters[7] the low feasibility of the McLafferty rearrangement has been explained in terms of a two-step mechanism[8] (γ-hydrogen transfer first, followed by C_2–C_3 bond breaking) by acepting that, after the hydrogen transfer, the presence of a Cl atom at the neighbour 3-position prevents C_2–C_3 bond breaking by allowing other easier fragmentation patterns, particularly loss of the halogen. This, of course, is observed in the case of 3, where M–Cl (*m/e* 157) is very intense. A similar argument can be invoked in the case of 5, where the Cl atom also flanks the γ-position from which hydrogen is transferred. However, in this case loss of Cl must not be the main fragmentation, since there is no peak at *m/e* 157.

^{13}C NMR. The assigned proton-noise decoupled FT ^{13}C NMR spectra, at 20 MHz of compounds 1–8 are given in Table 5. Assignments have been made according to the values given by Stothers for substituted alkanes.[9] Experimental substituent effects for Cl on the sp^3 carbons of compounds 2–8 are given in Table 6, in which doubly underlined values correspond to abnormal effects (more than 10% deviation relative to the mean value). Mean substituent effects for Cl on sp^3 carbons are given in Table 7, together with corresponding values reported by Stothers.

Table 5. The proton-noise decoupled FT ^{13}C NMR spectra of methyl chlorooctanoates

Compound	Chemical shift (δ)								
	C_8	C_7	C_6	C_5	C_4	C_3	C_2	C_1	OCH_3
1	14.2	22.9	32.1	29.3	29.5	25.3	34.2	173.7	51.2
2	14.0	22.6	31.6	28.6	26.0	35.0	57.2	170.4	52.8
3	13.9	22.5	31.2	26.0	38.1	57.9	43.5	170.6	51.9
4	13.9	22.2	28.6	38.3	63.0	33.4	31.0	173.5	51.6
5	13.6	19.8	40.7	62.9	37.9	22.1	33.5	173.6	51.4
6	10.9	31.5	65.4	37.7	26.1	24.5	33.9	174.0	51.5
7	25.4	58.4	40.2	26.4	28.7	24.8	33.9	173.8	51.3
8	45.0	32.6	26.7	28.6	29.0	24.8	34.1	174.1	51.4

From Table 5 a negative β effect can be deduced over C_1 for compound 2 (−3.3 ppm), similar to the known effect (−3.4 ppm) on the CO carbon of acetone upon Cl monosubstitution.[10] This effect undoubtedly arises from the enhanced contribution of the π canonical form in the description of the CO group when an α Cl atom is present, the inductive effect of the halogen atom destabilizing the singly-bonded, dipolar form. A negative γ effect (−3.1 ppm) is also found on the CO carbon for compound 3, part of which can be attributed to the same cause.

As seen in Table 6, substituent effects are exceptionally coherent within the series, except in three cases (doubly underlined values), so the normal effects will not be discussed further.

When compound 2 is considered as a Cl-substituted carboxylic acid ester, an abnormally low value is obtained for the α effect of Cl on C_2, namely 23.0 ppm (Table 6), some 10 ppm lower than the other α effects recorded within the series. Thus, the deshielding ability of Cl appears to be much smaller when adjacent to the CO carbon of the ester group. Compound 2, however, can also be considered as a methoxycarbonyl-substituted chloroalkane. Substracting from the observed chemical shift of C_2 in 2 (57.2 ppm) the chemical shift of C_1 in 1-chloroheptane (recorded in the literature,[11] 45.3 ppm) yields the substituent effect for the methoxycarbonyl group, 11.9 ppm, which must be compared with the mean effect computed by Stothers[9] for this group, 20.2 ppm.[†] As seen, the deshielding ability of the methoxycarbonyl group is now abnormally low when attached to a Cl-bearing carbon, and this can be linked with the low contribution of the singly-bonded, dipolar form of the CO group in 2-haloesters referred to above. Possibly neither approach (low effect for only one of the substituents) is correct, the real situation arising from diminished α effects of both substituents, in other words, non-additivity of the effects when the substituents are too near.[‡]

The abnormal value of the γ effect in the case of 8 is indicative of a more negative γ effect for "primary" than for "secondary" chlorine. A similar case has been pointed out for other substituents.[12]

The high value of the β effect (on C_8) in 7 is difficult to account for, and it might be related to the *increase* in the extinction coefficient of the symmetric bending mode of the Me group in the IR spectrum (1380 cm^{-1} band) referred to above. Both, ^{13}C chemical shifts and extinction coefficients in IR are dependent on electric charge and steric factors. However, we cannot furnish a precise relationship between both facts.

[†] Obtained as the difference between the chemical shifts of C_2 in methyl hexanoate and that of C_1 in pentane.

[‡] Non-additivity of substituent effects is also the rule, even at longer distances, in the case of diesters.[12]

Table 6. Individual substituent effects of chlorine on the sp^3 carbons of methyl chlorooctanoates[a,b]

Compound	Effect (ppm)												
	λ	φ	ε	δ	γ	β	α	β	γ	δ	ε	φ	λ
2	-0.2	-0.3	-0.5	-0.7	-3.5	9.7	23.0						
3		-0.3	-0.4	-0.9	-3.3	8.6	32.6	9.3					
4			-0.3	-0.7	-3.5	9.0	33.5	8.1	-2.7				
5				-0.6	-3.1	8.6	33.6	8.4	-3.2	-0.7			
6					-3.3	8.6	33.3	8.4	-3.4	-0.8	-0.3		
7						11.2	35.5	8.1	-2.9	-0.8	-0.5	-0.3	
8							30.8	9.5	-5.4	-0.7	-0.5	-0.5	-0.1

[a] Obtained by substracting the chemical shift of individual carbon atoms in 1 from the values observed for the corresponding carbons in compounds 2–8 (Table 5).

[b] Doubly underlined values deviate more than 10% from the mean value observed for the effect.

Table 7. Mean substituent effects of chlorine on the sp^3 carbons of methyl chlorooctanoates

Effect	α	β	γ	δ	ε	φ	λ
Reported[a]	31.2	10.5	-4.6	0.1	0.5	—	—
Exptl.[b]	33±3	9.0±0.7	-3.2±0.3	-0.7±0.2	-0.4±0.1	-0.4±0.1	-0.2±0.1

[a] From Ref. 9.

[b] Mean values from individual figures given in Table 6 (except doubly underlined figures in Table 6).

REFERENCES

[1] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 3rd. Edn, pp. 208 and Refs therein. Chapman & Hall, London (1975).

[2] J. Deschamps, M. T. Forel, N. Fuson and M. L. Josien, *Bull. Soc. Chim. Fr.* 88 (1959).

[3] S. A. Francis, *J. Chem. Phys.* 19, 942 (1951).

[4a] O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Analyt. Chem.* 22, 1498 (1950); [b] R. G. Sinclair, A. F. McKay and R. N. Jones, *J. Am. Chem. Soc.* 74, 2570 (1952).

[5] W. Sonneveld, D. van der Steen and H. J. J. Pabon, *Rec. Trav. Chim. Pays-Bas* 87, 1110 (1968).

[6] N. Dinh-Nguyen, A. Raal and E. Stenhagen, *Chem. Scripta* 1, 117 (1971).

[7] S. Meyerson, *Int. J. Mass Spectrom. Ion Phys.* 1, 309 (1968).

[8] N. Dinh-Nguyen, R. Ryhage, S. Stallberg-Stenhagen and E. Stenhagen, *Ark. Kemi.* 18, 393 (1961).

[9] J. B. Stohers, *Carbon*-13 *NMR Spectroscopy*, p. 128. Academic Press, New York (1972).

[10] J. B. Stohers and P. C. Lauterbur, *Can. J. Chem.* 42, 1563 (1964).

[11] E. Lipmaa and T. Pehk, *Eesti N. S. V. Tead. Akad. Toim. Keem. Geol.* 17, 210 (1968) quoted in Ref. 9, p. 133.

[12] D. E. James and J. K. Stille, *J. Org. Chem.* 41, 1504 (1976).