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PECULIARITIES OF NMR ^{1}H AND ^{13}C SPECTRA OF BENZOATES AND BENZOYLFORMATES CARBALKOXYL FRAGMENTS

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Abstract. Peculiarities of NMR ^{1}H and ^{13}C spectra of benzoates and benzoylformates carbalkoxyl fragments have been studied. Characteristic values of chemical shifts of three types: carboxyl, α- and β-carbon atoms of alkoxyl groups have been presented in NMR ^{13}C spectra. Characteristic values of protons attached to the mentioned atoms have been given in PMR spectra. Analogous parameters of some carbalkoxyl-containing compounds of general formula Y–COO–CH_2–R have been presented for comparison.

Keywords: NMR ^{1}H and ^{13}C spectra, alkylbenzoates, alkylbenzoylformates, basic and differential (spectral) parameters.

1. Introduction

Peculiarities of NMR ^{1}H spectra of alkylbenzoates (I) and alkylbenzoylformates (II) phenyl fragment [1], as well as NMR ^{13}C spectra of benzoyl fragments of these compounds and acids (III and IV) from which they were synthesized [2-4] have been described in our previous works [1-4]. It is of interest to determine peculiarities of spectral fragments of benzoylformic acid (IV) and alkylbenzoylformates (II) carbalkoxyl fragment. Out of different types of esters (II) benzoylformates, derivatives of primary linear saturated alcohols, have been studied in this work. They have been compared with spectra of analogous alkylbenzoates (I) and some model aliphatic carbonic acids (V, VII, IX) and their alkyl esters (VI, VIII, X).

Let us designate all compounds (I–X) by one of two general formulas: formula (XI) – for Y–COO–H acids and formula (XII) – for their alkyl esters Y–COO–R. In both cases COO– carboxyl group and hydrogen atom in acids (XI) are invariable fragments. Fragments Y in the acid part of a molecule and alkyl group R in alkoxyl fragment of esters (XII) are variable fragments. If fragment Y is benzoyl group, then benzoylformic acid (IV) is an investigated acid (XI) and alkylbenzoylformates (II) are esters (XII). The structure of variable fragments Y (Y = CH_3, C_2H_5, CH_3CO, C_6H_5) in the acid part of auxiliary compounds (I, III, V–X) is selected especially for the effective comparison between chemical shifts of carbon carboxyl atom and the first two carbon atoms of alkoxyl groups presented in COOR fragment and for the determination of its specific peculiarities in benzoylformates (II) and acid (IV).

Y–C(O)–O–H	Y–C(O)–O–R
I, III, V, VII, IX, XI	II, IV, VI, VIII, X, XII

where: Y = C_6H_5– (I, II), C_6H_5–C(O)– (III, IV), CH_3– (V, VI), CH_3–CH_2– (VII, VIII), CH_3–C(O)– (IX, X);

R = CH_3– (a), C_2H_5– (b), *n*-C_3H_7– (c), *n*-C_4H_9– (d), *n*-C_5H_{11}– (e), *n*-C_6H_{13}– (f), *n*-C_7H_{15}– (g), n-C_8H_{17}– (h).

It seems to us that investigated ratio between benzoates (I) and benzoylformates (II) in aromatic row may be modulated in aliphatic row taking acetates (VI) and propionates (VIII) from the one side and pyruvates (X) from the other side. Moreover, benzoates (I) modulate phenyl part of benzoyl fragment Y in (II) and aliphatic acetyl fragment Y in pyruvates (X) modulates its carbonyl group.

The choice of linear alkyl fragments R structure in esters (XII) is defined by the presence of their spectral data in literature [1, 5, 6]. We investigated regularities of basic (δ^H and δ^C) and differential ($\Delta\delta^H$ and $\Delta\delta^C$) spectral parameters only for the first two carbon atoms (α- and β-) of alkyl chain because they are the most sensitive to the structure changes in variable fragment Y.

2. Experimental

In order to discuss spectral peculiarities of benzoylformic acid (IV) and its esters (II) we use only their ^{1}H and ^{13}C NMR spectra obtained in deuterochloroform and described in literature, as well as spectra of model compounds (I, III, V–X) which were also recorded in $CDCl_3$. Detailed recording conditions of NMR spectra which are mentioned in [1, 5, 6] and requirements to them are described in [4].

For all spectra in [6] authors give their own signals assignment. We do not agree with them in some cases.

For the spectra mentioned in [2, 5] we carried out own signals assignment. Values of chemical shift δ^H and δ^C represented in Tables 1 and 2 are given in origins with the accuracy of 0.001 ppm for PMR spectra and 0.01 ppm for NMR ^{13}C spectra. Inaccuracy of measurements we estimate as value ≤0.02 ppm for PMR spectra and ≤0.1 ppm for NMR ^{13}C spectra. Differential parameters $\Delta\delta^C$ were calculated with the accuracy of 0.01 ppm but we used values with the accuracy of 0.1 ppm.

3. Results and Discussion

Three types of esters (acetates (VI), propionates (VIII) and pyruvates (X)) were chosen as compounds able to modulate comparable pair of aromatic esters in aliphatic row: benzoates (I) – benzoylformates (II). Acetates and propionates are aliphatic models of benzoates and pyruvates are models of benzoylformates.

Linear alkyl radicals as a part of alcohol fragments of ester differ by chain length. The comparison of spectral data of esters with similar alkyl groups is completely well-reasoned. On the other hand, it should be corrected to compare some differential parameters in esters which are derivatives of long-chain alcohols with different length of chain [2] starting from butyl alcohol (in the case of NMR ^1H spectra) and pentyl alcohol (in the case of NMR ^{13}C spectra). Values δ^H and δ^C are such parameters in both NMR spectra (^1H and ^{13}C) only for the first two methylene groups.

In [6] there are data only for three first members of linear aliphatic pyruvates row (Xa–Xc). Therefore, we have to limit the composition of acetates (VI) and propionates (VIII) by derivatives of methyl (a), ethyl (b) and *n*-propyl (c) alcohols. Basic (δ^H and δ^C) and differential ($\Delta\delta^H$ and $\Delta\delta^C$) spectral parameters of model compounds (V–X) are represented in Table 1.

Table 2 represents δ and $\Delta\delta$ spectral data (sometimes incomplete) of aromatic acids (III and IV) and their esters (I an II), derivatives of linear alcohols C_1–C_8 taken from [1, 6] in $CDCl_3$ (and in some cases in CD_2Cl_2). In those cases when spectral data are present in both sources [2, 6] we chose data from [6] as more accurate ones.

Let us consider peculiarities of basic and differential parameters of carbonic acids (XI) and their esters (XII).

Table 1

Some basic (δ_i) and differential ($\Delta\delta_{i-j}$) spectral parameters of acids (V, VII, IX) and short chain esters (VI, VIII, X) alkyl fragments in NMR ^1H and ^{13}C spectra

No. of subst.	Quant. of C atoms in OR	Structural formulae	NMR ^1H			NMR ^{13}C				
			$O–C^{\alpha}H_m$	$O–C^{\alpha}–C^{\beta}H_n$	$\Delta\delta_{m-n}$	$\underline{C}OO$	C^{α}	C^{β}	$\Delta\delta_{COO-\alpha}$	$\Delta\delta_{C\alpha-C\beta}$
V	0	$CH_3–COOH$	-	-	-	78.12	-	-	-	-
VII	0	$CH_3–CH_2–COOH$	-	-	-	81.46	-	-	-	-
IX	0	$CH_3–C(O)–COOH$	-	-	-	61.37	-	-	-	-
VIa	1	$CH_3–COO–CH_3$	3.662	-	-	71.52	51.59	-	119.93	-
VIIIa	1	$CH_3–CH_2–COO–CH_3$	3.674	-	-	74.86	51.49	-	123.37	-
Xa	1	$CH_3–C(O)–COO–CH_3$	3.881	-	-	61.42	52.99	-	108.43	-
VIb	2	$CH_3–COO–CH_2–CH_3$	4.119	1.260	2.859	71.08	60.44	14.28	110.64	46.16
VIIIb	2	$CH_3–CH_2–COO–CH_2–CH_3$	4.132	1.259	2.873	74.40	60.26	14.32	114.14	45.94
Xb	2	$CH_3–C(O)–COO–CH_2–CH_3$	4.332	1.376	2.946	61.01	62.46	14.04	98.55	48.42
VIc	3	$CH_3–COO–CH_2–CH_2–CH_3$	4.023	1.650	2.373	71.09	66.10	22.14	104.99	43.96
VIIIc	3	$CH_3–CH_2–COO–CH_2–CH_2–CH_3$	4.032	1.647	2.385	74.51	65.94	22.18	108.57	43.76
Xc	3	$CH_3–C(O)–COO–CH_2–CH_2–CH_3$	-	-	-	61.01	67.99	21.79	93.02	46.20

Table 2

Some basic (δ_i) and differential ($\Delta\delta_{i-j}$) spectral parameters of acids (III, IV) and esters (I, II) alkyl fragments in NMR ^1H and ^{13}C spectra

No. of sub st.	Quant. of C atoms in OR	Structural formulae	NMR ^1H			NMR ^{13}C				
			$O–C^{\alpha}H_m$	$O–C^{\alpha}–C^{\beta}H_n$	$\Delta\delta_{m-n}$	$\underline{C}OO$	C^{α}	C^{β}	$\Delta\delta_{COO-\alpha}$	$\Delta\delta_{C\alpha-C\beta}$
III	0	$C_6H_5–COOH$	-	-	-	172.77	-	-	-	-
IV	0	$C_6H_5–C(O)–COOH$	-	-	-	164.67	-	-	-	-
Ia	1	$C_6H_5–COO–CH_3$	3.886	-	-	167.04	52.01	-	115.03	-
IIa	1	$C_6H_5–C(O)–COO–CH_3$	3.94[1]	-	-	164.14	52.74	-	111.40	-
Ib	2	$C_6H_5–COO–CH_2–CH_3$	4.355	1.380	2.975	166.54	60.90	14.33	105.64	46.57
IIb	2	$C_6H_5–C(O)–COO–CH_2–CH_3$	4.449	1.465	2.984	163.97	62.38	14.11	101.59	48.27
Ic	3	$C_6H_5–COO–CH_2–CH_2–CH_3$	4.28	1.78	2.50	166.60	66.54	22.20	100.06	44.34
IIc	3	$C_6H_5–C(O)–COO–CH_2–CH_2–CH_3$	4.35	1.80	2.55	-	-	-	-	-
Id	4	$C_6H_5–COO–(CH_2)_3–CH_3$	4.32	1.75	2.57	166.61	64.80	30.88	101.81	33.92
IId	4	$C_6H_5–C(O)–COO–(CH_2)_3–CH_3$	4.39	1.77	2.62	-	65.95	29.59	-	36.36
Ie	5	$C_6H_5–COO–(CH_2)_4–CH_3$	4.31	1.76	2.55	166.64	65.12	28.58	101.51	36.54
IIe	5	$C_6H_5–C(O)–COO–(CH_2)_4–CH_3$	4.35	1.76	2.59	163.80	66.13	27.90	97.67	38.23
If	6	$C_6H_5–COO–(CH_2)_5–CH_3$	4.31	1.75	2.56	166.50	65.04	28.75	101.46	36.29
IIf	6	$C_6H_5–C(O)–COO–(CH_2)_5–CH_3$	4.36[2]	1.73[2]	2.63[2]	-	66.16[2]	28.56[2]	-	37.60[2]
Ig	7	$C_6H_5–COO–(CH_2)_6–CH_3$	4.308	1.754	2.554	166.61	65.13	28.82	101.48	36.31
IIg	7	$C_6H_5–C(O)–COO–(CH_2)_6–CH_3$	4.33[2]	1.74[2]	2.59[2]	-	-	-	-	-
Ih	8	$C_6H_5–COO–(CH_2)_7–CH_3$	4.31	1.75	2.56	166.59	65.11	28.82	101.48	36.29
IIh	8	$C_6H_5–C(O)–COO–(CH_2)_7–CH_3$	4.33	1.73	2.60	163.93	66.20	28.43	97.73	37.77

Notes: [1] Data obtained in CD_2Cl_2 solution.

[2] This signal is taken from spectrum of two (or more) component mixture containing ketoacetal $PhCOCH(OR)_2$ [7] as a main product (a) and ester PhCOCOOR (II) as a by-product (b) [2].

3.1. NMR ^1H Spectra. Basic and Differential Parameters

The position of acid proton signals in compounds (XI) is not discussed due to their heightened sensibility to the recording conditions.

The absorption of methyl group protons in all methyl esters (Ia, IIa, VIa, VIIIa and Xa) takes place within the range of 3.65–3.95 ppm. The absorption of α-methene group protons in other esters is observed in lower field from ~4.0 to 4.5 ppm.

It should be noted that for all α-protons (both methyl and methene) benzoylformate (II) protons are the most downfield. They are shifted towards the downfield by approximate value of 0.1–0.2 ppm compared with similar signals of model compounds: benzoates (I) on the one hand and pyruvates (X) – on the other hand (*vide* Fig. 1). Corresponding signals of alkyl protons of aliphatic acetates and propionates are practically the same and are located in the most upper-field.

On the other hand, values of chemical shifts of α-protons (both methyl and methylene) in α-ketoesters (II and X) are shifted towards the downfield compared with esters without carbonyl groups (I, VI and VIII). This difference (~0.2 ppm) is greater for the model aliphatic compounds (VI, VIII and X) than for aromatic esters (I

and II). In the pair of aromatic esters the value $\Delta\delta_{\alpha}^{II-I} = \delta_{\alpha}^{II} - \delta_{\alpha}^{I}$ for short-chain methyl esters (IIa and Ia) is ~0.1 ppm and it is even smaller (0.05–0.07 ppm) for the compounds with longer alkyl chains starting from the ethyl one.

In ethyl esters Ib, IIb, VIb, VIIIb and Xb signals of methyl group protons representing β-carbon atom of alkyl chain are observed in the region of 1.25–1.5 ppm. The ratio between δ^H values for these compounds is the same as for the α-protons mentioned above, *i.e.* protons of aromatic and ketoesters are absorbed in downfield (Fig.1). Protons of β-methene groups in long-chain (butyl and higher) benzoates (I) and benzoylformates (II) differ slightly between each other by their chemical shift (δ^H_{β} ~ 1.75 ppm). Signals of β-protons of intermediate propyl esters of aliphatic acids (for VIc and VIIIc δ^H = 1.65 ppm) are shifted towards upper-field by ~0.1–0.15 pm compared with aromatic esters (Ic and IIc). It is impossible to compare compounds VIc, VIIIc and Xc on the one hand and IIc and Xc on the other hand because of the lack of PMR spectra data for propylpyruvate (Xc) in [5, 6].

For alkoxyl fragments of PMR spectra of all esters (XII) except methyl ones it is advisable to calculate only one differential parameter $\Delta\delta^H_{\beta-\alpha}$ because of low sensibility of protons outlying from oxygen atom in alkoxyl chain to the changes in variable fragment Y. For short-chain aliphatic esters – ethylacetate and ethylpropionate – $\Delta\delta^H_{\beta-\alpha}$ parameters are practically the same (2.86 and 2.87 ppm, respectively). Their values, however, are less by ~0.1 ppm compared with ethylpyruvate ($\Delta\delta_{\beta-\alpha}^{Xb}$ = 2.95 ppm).

For the analogous pair of short-chain aromatic esters (ethylbenzoylformate – ethylbenzoate) the difference between $\Delta\delta^H_{\beta-\alpha}$ parameters is practically zero ($2.98_4 - 2.97_5 =$ = 0.01 ppm, *vide* Fig. 1). For the rest medium- and long-chain benzoates (I) and benzoylformates (II) values $\Delta\delta^H_{\beta-\alpha}$ are within the range of 2.5 – 2.6 ppm. These values are the smallest ($\Delta\delta_{\beta-\alpha}^{IIc}$ = 2.55 ppm for IIc and $\Delta\delta_{\beta-\alpha}^{Ic}$ = =2.50 ppm for Ic) in the case of medium-chain propyl esters. For long-chain esters the average value of $\Delta\delta^H_{\beta-\alpha}$ parameter is approximately 2.6 ppm for benzoylformates (II) and 2.55 ppm for benzoates (I).

Thus we may conclude that electron-acceptor effect of additionally introduced carbonyl group in the variable fragment Y in ketoesters (II and X) shifts proton signals to the downfield. These protons are connected with α-, as well as β -carbon atoms of alkyl chain. The value of such shift decreases from α- to β-atom due to the dying of electron-acceptor effect of carbonyl group. As the result $\Delta\delta^H_{\beta-\alpha}$ parameters typical for such effect are higher for benzoylformates (II) and pyruvates (X) compared with benzoates and acetates (propionates).

In the single ketoesters pair – aliphatic ethylpyruvate (Xb) and aromatic ethylbenzoylformate (IIb) – both basic parameters δ^H in (IIb) are shifted towards the downfield (Fig.1). We explain this by stronger electron-acceptor properties of phenyl group compared with those of methyl group.

It is interesting that $\Delta\delta^H_{\beta-\alpha}$ parameters are sensitive to the structure of alkoxyl group. Let us designate the difference between $\Delta\delta^H_{\beta-}$ parameters as $\Delta\Delta\delta^H_{\beta-\alpha}$ (*e.g.* for butyl ethers $\Delta\Delta\delta_{\beta-\alpha}^{Hd} = \Delta\delta_{\beta-\alpha}^{IId} - \Delta\delta_{\beta-\alpha}^{Id}$ ~0.05 ppm). For long-chain benzoylformates (IId–IIg) and benzoates (Id–Ig), where methene group is in β-position, $\Delta\Delta\delta^H_{\beta-\alpha}$ parameter is half of that for the compounds where β-carbon atom belongs to methyl group, *i.e.* $\Delta\Delta\delta_{\beta-\alpha}^{Hb} = \Delta\delta_{\beta-\alpha}^{IIb} - -\Delta\delta_{\beta-\alpha}^{Ib}$ ~0.09 ppm. At the same time for ethyl esters of aliphatic acids this difference practically equals to zero ($\Delta\Delta\delta_{\beta-\alpha}^{Hb} = = \Delta\delta_{\beta-\alpha}^{Xb} - \Delta\delta_{\beta-\alpha}^{VIIIb}$ ~0.001 ppm).

The average δ^H values for the first two methene groups in long-chain benzoates and benzoylformates have been calculated with the accuracy of 0.05 ppm. For benzoates (I): $\delta_{\alpha}^{Hav.}$ = 4.30 ppm; $\delta_{\beta}^{Hav.}$ = 1.75 ppm. For benzoylformates (II): $\delta_{\alpha}^{Hav.}$ = 4.35 ppm; $\delta_{\beta}^{Hav.}$ = 1.75 ppm.

3.2. NMR ^{13}C Spectra. Carboxyl Group

In all esters (XII) carboxyl carbon is absorbed in higher field compared with the corresponding acids (XI). But whereas in the compounds without additional carbonyl group (I and III, V and VI, VII and VIII) the downfield shift of δ^C_{COO} signals in acids is ~7 ppm, in ketocarbonic acids (IV and IX) it decreases to ~0.5–1.0 ppm compared with their esters (II and X, *vide* Tables 1 and 2). In methylpyruvate the carboxyl carbon is absorbed in lower field (δ^C_{COO} = 161.42 ppm) compared with that in pyruvic acid (δ^C_{COO} = 161.37 ppm).

Acetic (V, δ^C_{COO} = 178.12 ppm) and propionic (VII, δ^C_{COO} = 181.46 ppm) aliphatic acids without keto-group and their esters (VI and VIII) absorb in lower field (171–175 ppm) compared with aromatic benzoic acid (III, δ^C_{COO} = 172.77 ppm) and benzoates (I, δ^C_{COO} = 166–167 ppm). At the same time ketoacids (IV and IX) and their esters (II and X) absorb in still higher field (δ^C_{COO} = 161–165 ppm). It is interesting that for aliphatic ketoacids and their esters taking pyruvic acid (IX) and pyruvates (X) as an example δ^C_{COO} signals are discovered in higher field (~161 ppm) compared with those for aromatic benzoylformates (IX, X, δ^C_{COO} ~164 ppm). It is the principal difference between them and acids and esters without α-carbonyl group.

Analyzing δ^C_{COO} signals of all esters (XII) we may conclude that only short-chain methyl esters absorb in lower filed (~ by 0.5 ppm) compared with medium- and long-chain esters. For the latter ones the minimum scattering of δ^C_{COO} values inside all classes of compounds does not exceed 0.5 ppm.

The average δ^C values of carboxyl group carbon atom in long-chain benzoates and benzoylformates have been calculated with the accuracy of 0.1 ppm. For benzoates (I) $\delta^{Cav.}_{COO}$ = 166.6 ppm [2]; for benzoylformates (II) $\delta^{Cav.}_{COO}$ = 163.9 ppm.

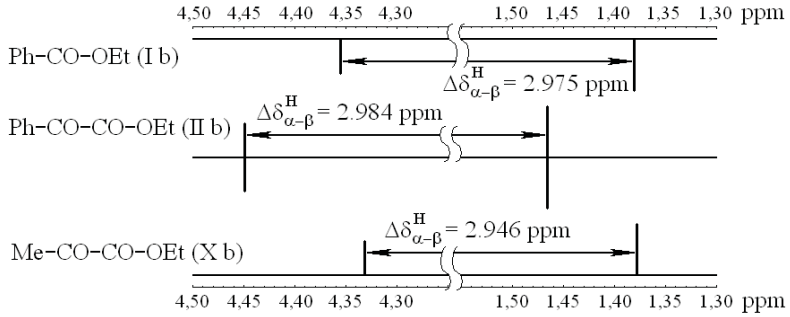

Fig. 1. Schematically pictured parts of ^{1}H NMR spectra for Ib, IIb, Xb compounds

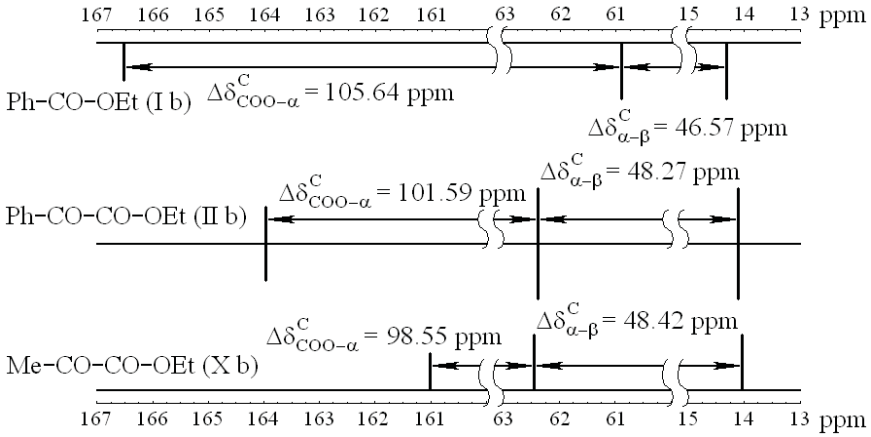

Fig. 2. Schematically presented parts of ^{13}C NMR spectra for Ib, IIb, Xb compounds

3.3. NMR ^{13}C Spectra. α-, β-Carbon Atoms of Alkoxyl Chain. Basic Parameters

Downfield signals shift of α-carbon atoms of alkoxyl group compared with esters without carbonyl group in α-position towards carbalkloxyl one (I, VI and VIII) are discovered in NMR ^{13}C spectra of ketoesters (II and X). For short- and medium-chain esters (XIIa–XIIc) this shift (~1.5–2.0 ppm) is greater than that for long-chain esters (~1 ppm). On the contrary, for β-carbon atoms of alkoxyl chain signals in ketoesters (II and X) are slightly (by 0.2–0.4 ppm) but clearly shifted towards the upper-field[1].

So-called end effect of short chains influences the values of δ^{C}_{α} and δ^{C}_{β} basic parameters due to the different length of alkyl chains in the investigated esters (XII). Therefore it is advisable to compare δ^{C}_{α} and δ^{C}_{β} values only in the case when alkyl chain length exceeds 4 carbon atoms. In other cases it is correctly to compare basic spectral parameters of esters with similar alkyl groups.

Owing to the absence of spectral data concerning medium- and long-chain pyruvates (Xd–Xg) and medium-chain propylbenzoylformate (IIc) it is possible to compare basic parameters of aliphatic and aromatic ketoesters only for short-chain esters. For methyl ketoesters (Xa and IIa) δ^{C}_{α} parameters are very similar and equal to 52.99 and 52.74 ppm, respectively. Corresponding parameters δ^{C}_{α} and δ^{C}_{β} for ethyl esters (Xb) and (IIb) practically coincide as well (Fig. 2). One can see from the tables that the difference between these values does not exceed 0.1 ppm. In spite of small difference δ^{C}_{α} signals of aliphatic methyl- and ethylpyruvates (Xa) and (Xb) are observed in lower field than the same δ^{C}_{α} signals of aromatic esters – benzoylformates (IIa) and (IIb). The ratio between δ^{C}_{β} signals of β-carbon atom absorption in ethyl group of esters (Xb) and (IIb) has the opposite character.

The average δ^{C} values of the first two methene groups in long-chain benzoates and benzoylformates have

[1] The part of benzoylformates (II) spectra described in [2] was obtained in CD_2Cl_2. It is close by its structure to deuterochloroform. For the estimated comparison these spectral data may be "overlapped" with spectral data obtained in $CDCl_3$. From experimental results, taking as an example similar to benzoylformates (IV) phenylglyoxal acetals [7], one can see that all δ^{C}_{mcl} values are shifted toward the downfield depending upon carbon atom type by ~0.2–0.4 ppm in deuteromethenechloride compared with those (δ^{C}_{clf}) in $CDCl_3$. Therefore for the overlapping of benzoylformate spectral data obtained in CD_2Cl_2 (δ^{C}_{mcl}) and δ^{C} values obtained in $CDCl_3$ (δ^{C}_{clf}) [2] it is necessary to subtract average systematic correction equal to 0.3 ppm from the first ones. Nevertheless, due to indefinite amendment values for every carbon type in benzoyl fragment of the compounds (IV), spectral parameters obtained in CD_2Cl_2 and presented in [2] were not discussed.

been calculated with the accuracy of 0.1 ppm. For benzoates (I): $\delta_{\alpha}^{Cav.}$ = 65.1 ppm; $\delta_{\beta}^{Cav.}$ = 28.7 ppm. For benzoylformates (II): $\delta_{\alpha}^{Cav.}$ = 66.2 ppm; $\delta_{\beta}^{Cav.}$ = 28.5 ppm .

3.4. NMR ^{13}C Spectra. α-, β-Carbon Atoms of Alkoxyl Chain. Differential Parameters

Owing to the different end effects of alkyl chains with various lengths it is advisable to compare both $\Delta\delta^C$ differential spectral parameters for short- and medium-chain esters by pairs. For the long-chain benzoates (Ie–Ig) and benzoylformates (IIe–IIg) one can see from Table 2 that both types of differential parameters are practically the same inside every class of compounds. For benzoates $\Delta\delta^C_{COO\text{-}\alpha}$ parameter (~101.5 ppm) is higher than that for benzoylformates (~97.7 ppm). On the opposite, $\Delta\delta^C_{\alpha\text{-}\beta}$ parameter for benzoates (~36.4 ppm) is lower than that for benzoylformates (~37.7 ppm).

The same ratio between $\Delta\delta^C_{\alpha\text{-}\beta}$ differential parameters is for ethyl esters (XIIb) (Fig. 2). These compounds are the single case when all spectral data for esters (XII) with the same alkyl group are present (except methyl group, for which $\Delta\delta^C_{\alpha\text{-}\beta}$ parameter is impossible by definition). For both ketoesters (Xb) and (IIb) $\Delta\delta^C_{\alpha\text{-}\beta}$ values are almost equal (48.27 and 48.42 ppm, respectively). For esters without carbonyl groups (Ib, VIb and VIIIb) such values are less (~46.0–46.5 ppm). It should be noted that for aliphatic ethylacetate (VIb, $\Delta\delta^C_{\alpha\text{-}\beta}$ = 45.9 ppm) and ethylpropionate (VIIIb, $\Delta\delta^C_{\alpha\text{-}\beta}$ = 46.2 ppm) these values are less compared with aromatic ethylbenzoate (Ib, $\Delta\delta^C_{\alpha\text{-}\beta}$ = 46.6 ppm).

The increase of $\Delta\delta^C_{\alpha\text{-}\beta}$ differential parameter in ketoesters (X, II) compared with esters without ketogroup (I, VI and VIII) is determined by the opposite change of δ^C_{α} and δ^C_{β} parameters, which are minuend and subtrahend in the formula, respectively.

The average $\Delta\delta^C$ values for the first two methene groups in long-chain benzoates and benzoylformates have been calculated with the accuracy of 0.05 ppm. For benzoates (I): $\Delta\delta^C_{\alpha\text{-}\beta}$ = 36.4 ppm; for benzoylformates (II): $\Delta\delta^C_{\alpha\beta}$ = 37.7 ppm. The difference between them: $\Delta\Delta\delta^{C\ II\text{-}I}_{\alpha\text{-}}$ = = 37.7 – 36.4 = 1.3 ppm. This difference is greatly contributed by the summand determined by the difference of the minuends: $\Delta\Delta\delta^{C\ II\text{-}I}_{\alpha}$ = 66.2 – 65.1 = 1.1 ppm. The summand determined by the difference of the subtrahends is 5 times less: $\Delta\Delta\delta^{C\ II\text{-}I}_{\beta}$ = 28.7 – 28.5 = 0.2 ppm.

4. Conclusions

Based on the above mentioned discussion of the peculiarities of NMR ^{1}H and ^{13}C spectra of benzoates (I) and benzoylformates (II) carboxyl fragment the following conclusions can be made:

1. Averaged values of δ^H_{α}, δ^H_{β}, δ^C_{α} and δ^C_{β} basic parameters, as well as $\Delta\delta^{C\ I}_{\alpha\text{-}\beta}$ and $\Delta\delta^{C\ II}_{\alpha\text{-}\beta}$ differential parameters for long-chain benzoates (I) and benzoylformates (II) have been calculated. The ratio between these values is schematically shown in Figs. 1 and 2 for ethyl esters.

2. In both protonic and carbon spectra the greater similarity of ketoesters (II) is observed in the case with aliphatic ketoesters – pyruvates (X), not with aromatic benzoates (I). This fact indicates domination of ketogroup contribution compared with contribution of phenyl group in benzoylformates (II) benzoyl fragment, *i.e.* variable fragment Y in formula (XII). The similar conclusion has been done previously [4] with regard to peculiarities of NMR ^{13}C spectra of benzoylformic acid and its esters benzoyl fragment.

3. Owing to the greatest electron withdrawing effect of benzoyl group in benzoylformates (II) compared with other groups Y in esters (I, VI, VIII and X) the following values are shifted to the downfield: (i) protons absorption in α- and β-methylene, as well as β-methyl groups in PMR spectra and (ii) α-carbon atom of alkoxyl groups in NMR ^{13}C spectra.

4. The absorption of β-carbon atom of alkoxyl groups in NMR ^{13}C spectra of benzoylformates (II) is shifted to the upper field compared with analogous absorption of benzoates (I). Due to the non-uniform movement of δ^C_{α} and δ^C_{β} basic parameters in benzoates and benzoylformates, the values which are characteristic for benzoylformates (II) – $\Delta\delta^{C\ II}_{\alpha\text{-}\beta}$ differential parameters – increase compared with corresponding $\Delta\delta^{C\ I}_{\alpha\text{-}\beta}$ parameters for benzoates (I).

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ОСОБЛИВОСТІ ЯМР ^{1}H і ^{13}C СПЕКТРІВ КАРБАЛКОКСИЛЬНИХ ФРАГМЕНТІВ БЕНЗОАТІВ ТА БЕНЗОІЛФОРМІАТІВ

Анотація. *Досліджено особливості ЯМР ^{1}H и ^{13}C спектрів карбалкоксильного фрагменту алкілбензоатів і алкілбензоілформіатів. В спектрах ЯМР ^{13}C приведені характеристичні величини хімічних зсувів трьох типів його атомів: карбоксильного, α- і β-вуглецевих атомів алкоксильних груп, а також протонів при цих атомах в спектрах ПМР. Проведено порівняння з аналогічними параметрами деяких карбалкоксилвмісних сполук загальної формули Y–COO–CH$_2$–R.*

Ключові слова: *ЯМР ^{1}H и ^{13}C спектри, алкілбензоати, алкілбензоілформіати, основні та диференційні спектроальні параметри.*