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PECULIARITIES OF ^{13}C NMR SPECTRA OF BENZOYLFORMIC ACID AND ITS ESTERS. 1. BENZOYL FRAGMENT

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Abstract. Peculiarities of ^{13}C NMR spectra of benzoyl fragment of benzoylformic acid and its esters have been investigated and characteristic values of a chemical shift of all five types of fragment atom have been examined. Similar parameters of other benzoyl-containing compounds by general formula Bz–X (X = H, NR_2, OR, SR, Cl, Br), as well as those of compounds Bz–C (L)(M)(N) have been compared. It has been shown that spectral peculiarities of a benzoylformates phenyl fragment are defined by the carbonyl, not by the carbalkoxyl group.

Key words: NMR ^{13}C spectra, benzoyl fragment, basic and differential (spectral) parameters.

1.Introduction

During investigations of synthesized by-products of such effective photoinitiators as 2,2-dialkoxyacetophenones, benzoic (I) and benzoylformic (II) acids as well as their esters have been separated and identified using ^{1}H and ^{13}C NMR [1].

Previously [2, 3] we described peculiarities of ^{13}C NMR spectra of the acid (I) and alkylbenzoates benzoyl fragments (III) allowing to distinguish them from other benzoyl-containing compounds. Therefore, it would be interesting to define the similar peculiarities of ketoacid (II) and its esters – alkylbenzoylformates (IV) and compare them with those of alkylbenzoate.

It is advisable to divide benzoylformates tentatively into two parts: benzoyl and carboxyl fragments and investigate them separately. Each of these fragments is present in the molecules of different organic substances which allow to compare their spectral peculiarities in alkylbenzoylformates (IV).

Depending on the aim of investigations we designate all II and IV compounds by general formulas Bz-X (V) and Y-COOR (VI), correspondingly. Benzoyl fragment (Bz) is an invariable value for all compounds in formula (V) and functional groups are variable fragments designated by letter X. At X = COOH (R = H) the investigated compound is benzoylformic acid (II) and at R = alkyl – alkylbenzoylformates (IV). In formula (VI) the carbalkoxyl group COOR (carboxyl group R=H in particular case) is the invariable value and alkyl, aryl or other functional groups are variable fragments designated by letter Y. If Y is a benzoyl group, then the acid (II) is the investigated compound at R=H and acid esters (IV) are investigated compounds at R=alkyl.

This article deals with peculiarities of only benzoyl fragments of compounds (V), including the benzoylformic acid (II) and its esters (IV). In the accompanying article the spectral peculiarities of esters in compounds by the general formula (VI) are examined.

2. Experimental

To discuss the spectral peculiarities of benzoylformic acid (II) and its esters (IV) we used only their ^{13}C NMR spectra obtained in deuterochloroform and published in literature, as well as spectra of model compounds in $CDCl_3$. A part of benzoylformiate (IV) spectra described in [1] was obtained in CD_2Cl_2, which is similar to deuterochloroform by its structure. These spectral data may be "overlapped" with the spectra obtained in $CDCl_3$ in order to compare them. Taking phenylglyoxale acetals, which are similar to benzoylformates (IV), as an example [4], it was shown that all δ^C values in deuterochloroform are shifted to the downfield by $\Delta\delta \sim$ 0.2–0.4 ppm compared with similar parameters in $CDCl_3$. Hence, in order to overlap benzoylformiate spectra obtained in CD_2Cl_2 with δ^C values of analogous compounds obtained in $CDCl_3$ [1], it is necessary to subtract an average systematic correction equal to 0.3 ppm. Due to the uncertainty and inaccuracy of correction for every type of the carbon atom in benzoyl fragment of compounds (IV), spectral parameters obtained in CD_2Cl_2 are not discussed in this paper.

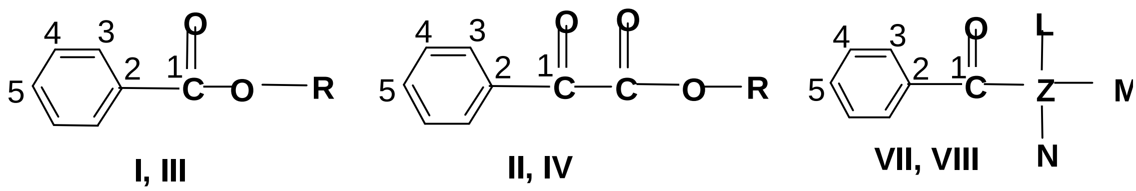
In order to minimize inaccuracies connected with different δ^C basic parameters for the same compounds, it would be desirable that all δ^C values should be taken from one informational source. However we had to use data from two sources, which are the most reliable ones, to our mind. The main source is the atlas of NMR spectra, Aldrich firm [5] and the additional source is the internet-site [6]. Each of them contains data absent in another one. We decided to “combine” data from both sources because δ^C values for the same compounds differed not more than by 0.2 ppm and only in rare cases the difference is greater.

For all spectra in [6] the authors gave their own signals attribution. We do not agree with them in some cases. For the spectra represented in [5] the author gave only values but not signals attribution. Chemical shift values in both sources have accuracy of 0.01 ppm; we estimate the accuracy as ≤0.1 ppm. In Tables 1 and 2 there are data from both sources with accuracy of 0.01 ppm but in discussion we round off values to 0.1 ppm. If the difference between data from [5] and [6] was more than 0.1 ppm, we used values from [5].

3. Results and Discussion

Let us examine dependencies of spectral parameters of two types in the invariable fragment (Bz) of compounds (V) upon structure of the variable fragment X. Basic spectral parameters (chemical shifts of carbon atoms of all five types in benzoyl fragment: δ_1, δ_2, δ_3, δ_4 and δ_5) are defined by symbols δ_i and δ_j (*i* and *j* are numbers of carbon atoms in formula V). Differential spectral parameters $\Delta\delta_{i\text{-}j} = \delta_i - \delta_j$ are design values and equal to the difference between two basic parameters δ^C. They are chosen depending on the aim; in addition both basic parameters δ_i and δ_j are taken from the same spectrum. In such a case values of differential parameters $\Delta\delta_{i\text{-}j}$ do not practically depend upon recording conditions (including the used solvent), which are very important for comparison of spectral peculiarities of different compounds. Analogously to the discussion of benzoates (III) ^{13}C NMR spectra [2] we chose four most informative parameters $\Delta\delta_{i\text{-}j}$, characterizing a phenyl part of the benzoyl fragment: $\Delta\delta_{2\text{-}5}$, $\Delta\delta_{2\text{-}3}$, $\Delta\delta_{3\text{-}4}$, $\Delta\delta_{5\text{-}4}$.

To compare invariable fragments of different benzoyl-containing compounds (V) we chose two rows of model compounds by general formulas Bz-Z(L)(M)(N) (VII) and Bz-C(L)(M)(N) (VIII).



I, III   II, IV   VII, VIII

R = H (I), R = Alkyl (III)   R = H (II), R = Alkyl (IV)   Z = C (VIII)

Table 1

No.	Formula	Atom Z	Basic parameter values δ^C_i, ppm					Differential parameter values $D\delta^C_{i\text{-}j}$, ppm			
			δ_1	δ_2	δ_3	δ_4	δ_5	$D\delta_{2\text{-}5}$	$D\delta_{2\text{-}3}$	$D\delta_{3\text{-}4}$	$D\delta_{5\text{-}4}$
VIIa	Bz-H	H	192.28	136.47	129.68	128.98	134.43	+2.04	+6.79	+0.70	+5.45
VIIb	Bz-CH_3	C	197.85	137.23	128.56	128.29	133.04	+4.19	+8.67	+0.27	+4.75
VIIc	Bz-C_6H_5	C	196.50	137.58	128.96	128.21	132.33	+5.25	+7.62	+1.75	+4.12
VIId	Bz-NH(CH_3)	N	168.46	134.62	126.94	128.42	131.23	+3.39	+7.68	-1.48	+2.81
VIIe	Bz-N$(CH_3)_2$	N	171.56	136.40	127.01	128.30	129.46	+6.94	+9.39	-1.29	+1.16
I	Bz-OH	O	172.77	129.44	130.28	128.49	133.83	-4.39	-0.84	+1.79	+5.34
IIIa	Bz-O-CH_3	O	167.04	130.25	129.60	128.37	132.90	-2.65	+0.65	+1.23	+4.53
IIIc	Bz-O-C_6H_5	O	165.07	129.63	130.11	129.50	133.49	-3.86	-0.48	+0.61	+3.99
VIIf	Bz-S-C_6H_5	S	190.03	136.80	129.23	128.74	133.61	+3.19	+7.57	+0.49	+4.87
VIIg	Bz-Cl	Cl	168.27	133.21	131.39	129.01	135.39	-2.18	+1.82	+2.38	+6.38
VIIh	Bz-Br	Br	165.59	134.76	131.95	128.95	135.57	-0.81	+2.81	+3.00	+6.62

The structure of variable fragment X in formula (V) is detailed in formula (VII) as following. We consider atom Z, directly bonded with the carbonyl atom of carbon in the benzoyl group (which is an invariable fragment), as a central atom of the whole variable fragment X. If valency of atom Z equals to 2 or more (for instance, C, N, O, S), then a variable fragment X must contain one more atom or the functional group. Such substituents are defined by symbols L, M and N.

As a rule the central atom Z belongs to the metalloids. The order in the row of model compounds (VII) in Table 1 is chosen by the following principle: the position of fragment Z central atom gradually shifts from the left to the right and top-down in Mendeleyev's Periodical system. In [5, 6] there are data only for the following central atoms: Z = H, C, N, O, S, Cl, Br. Data for Z = B, F, Si, P and other metalloids are absent.

The choice of the Z(L)(M)(N) variable fragment structure, i.e. the choice of substituents L, M and N depending upon the aim is determined by the presence or absence of spectral data in [5, 6] for the compounds in $CDCl_3$. Actually we chose the simplest substituents, such as a hydrogen atom, methyl, ethyl or phenyl group. For example, (–Z–L) oxygen-containing fragments were –OH, $–OCH_3$, $–OC_2H_5$ and $–OC_6H_5$.

Spectral parameters δ_i^C and $\Delta\delta_{i\text{-}j}$ of the compounds (VII) are represented in Table 1. There are 11 compounds with 7 different central atoms Z of Z(L)(M)(N) variable fragment. If Z is one-valent atom (***e.g.*** H, Cl and Br) then benzoyl derivatives are benzaldehyde (VIIa), benzoylchloride (VIIg) and benzoylbromide (VIIh), correspondingly. Compounds with such central atom as carbon are represented in Table 2. Only "phenone" derivatives – acetophenone (VIIb) and benzophenone (VIIc) are their examples here. If nitrogen is the central atom Z, then benzamide and both its ***N***-methyl derivatives (VIId and VIIe) should be chosen. However in Table 1 data for benzamide are absent because δ_i^C values taken from [5] were obtained in the mixture of $CDCl_3$ and DMSO-d_6. To our mind, they may be incompatible with δ_i^C data obtained in pure $CDCl_3$ due to the possible influence of different solvents. For Z as an oxygen atom, spectral data of benzoic acid (I) and methylbenzoate (IIIa) represented in Table 1, were examined previously [2, 3]. To compare spectral parameters of thiobenzoates represented by a phenyl ester (VIIf) with benzoates (III) we decided to introduce the additional compound with the same phenyl group – phenylbenzoate (IIIc).

The value of the basic parameter δ_1 means the absorption of the carbon carbonyl atom which is connected with Z atom of the variable fragment X determined mainly by electronegativity of Z atom [7] along with other factors. All 11 compounds in Table 1 may be divided into two groups by the value δ_1. Benzaldehyde (VIIa), both "phenones" (VIIb and VIIc) and thiophenylbenzoate (VIIf) belong to the first group. Their Z atoms are hydrogen, sulphur and carbon with the lowest electronegativity [7]. The value δ_1 of these compounds ranges from 190 to 210 ppm. The second group unites 7 compounds with N, O, Cl and Br atoms, whose electronegativity is more than that of the carbon atom. The value δ_1 for these compounds is less than 175 ppm.

Data from Table 1 for the benzoyl-containing compounds of the second group (I, III VIId–VIIg) confirm the known paradoxical and still unexplained inverse dependence of δ_1 values upon electronegativity of the central atom Z of variable parameter X.

The phenyl group of a benzoyl fragment does not bond directly with Z atom, therefore its polar influence is less. Owing to the great difference between natures of Z atoms the essential difference in spectral peculiarities of phenyl groups should be expected. Previously [2] it was shown that all 4 types of carbon atoms in phenyl group (C-2–C-5) are connected in a spectral relation; therefore it should be examined as one group. Hence, differential parameters would be more informative than the basic ones.

Actually, the values of basic parameters δ_2 representing the absorption of ***ipso***-carbon atoms for three oxygen derivatives I, IIIa and IIIc (δ_2 = 129–130 ppm) essentially differ from other six types of compounds (VII). In the latest eight compounds the δ_2 parameter is distributed inside the interval δ_2^C = 133–138 ppm without any regularity. On the contrary, for ***orto***-carbon atoms only δ^C values for benzamides VIId and VIIe (δ_3 ~127 ppm) are less than δ_3 = 128.5–132 ppm for other 6 types of compounds. The same situation takes place with the δ_5 parameter representing the absorption of ***para***-carbon atoms. And there are no great differences between δ_4 values for all 11 compounds in the case of ***meta***-carbon atoms.

Taking into consideration $\Delta\delta_{i\text{-}j}$ differential parameters one can see that differences between 7 types of compounds with different Z atoms have a more regular character. As it was shown previously [2, 3], the parameters $\Delta\delta_{3\text{-}4}$ and $\Delta\delta_{5\text{-}4}$ containing the most outlying from the X fragment "internal" atoms of a phenyl ring are low-informative[1]. Differential parameters $\Delta\delta_{2\text{-}3}$ and especially $\Delta\delta_{2\text{-}5}$ on the contrary are the most valuable ones because of their reliability and self-descriptiveness.

Above mentioned results show that all 7 types of compounds (VII) may again be divided into two groups. These new groups are similar by their compositions to the

[1] In many respects it depends upon reliability of designation of *orto*- and *meta*-carbon atoms similar by their signals value and intensity. The authors [6] usually do not prove attribution of these signals. At the same time δ_1 and δ_2 signals from the one hand, and δ_5 signal from the other hand may be easily identified by their intensities (see also Figs. 1 and 2).

Table 2

No.	Formula	Subroup number	Oxidation level	L, M, N	Basic parameter values δ^C_i, ppm					Differential parameter values $\Delta\delta^C_{i\text{-}j}$, ppm			
					δ_1	δ_2	δ_3	δ_4	δ_5	$\Delta\delta_{2\text{-}5}$	$\Delta\delta_{2\text{-}3}$	$\Delta\delta_{3\text{-}4}$	$\Delta\delta_{5\text{-}4}$
VIIb	Bz-CH_3	1	0	3H	197.85	137.23	128.56	128.29	133.04	+4.19	+8.67	+0.27	+4.75
VIIIa	Bz-C(CH_3)	1	0	3CH_3	209.11	138.52	127.98	127.77	130.74	+7.74	+10.54	+0.21	+2.97
VIIIb	Bz-CH=CHCH_3	1	0	H,=CH(CH_3)	190.66	137.96	128.50	128.50	132.56	+5.40	+9.46	+0.00	+4.06
VIIIc	Bz-CH_2-$NH_3^+Cl^-$	2	1	H,H, $NH_3^+Cl^-$	192.21	134.01	129.55	128.61	135.26	-1.25	+4.46	+0.94	+6.65
VIIId	Bz-CH_2-NO_2	2	1	H,H,NO_2	185.96	133.30	129.29	128.22	135.09	-1.79	+4.01	+1.07	+6.87
VIIIe	Bz-CH_2-O-CH_3	2	1	H,H,OCH_3	196.06	134.80	128.69	127.77	133.51	+1.29	+6.11	+0.92	+5.74
VIIIf	Bz-CH_2-Cl	2	1	H,H,Cl	191.06	134.24	128.89	128.48	133.98	+0.26	+5.36	+0.41	+5.50
VIIIg	Bz-C(CH_3)=N-OH	3	2	CH_3,=NOH	191.98	136.39	130.23	128.20	132.83	+3.56	+6.16	+2.03	+4.63
VIIIh	Bz-CH(OC_2H_5)$_2$	3	2	H,2OC_2H_5	193.95	133.75	129.71	128.30	133.41	+0.34	+4.04	+1.41	+5.11
VIIIi	Bz-C(CH_3)=O	3	2	CH_3,=O	191.32	131.71	130.26	128.79	134.53	-2.82	+1.45	+1.47	+5.74
VIIIk	Bz-C(C_6H_5)=O	3	2	C_6H_5,=O	194.50	132.91	129.82	128.98	134.85	-1.94	+3.09	+0.84	+5.87
VIIIl	Bz-CHCl_2	3	2	H,2Cl	185.89	131.37	129.70	128.92	134.54	-3.17	+1.67	+0.78	+5.62
VIIIm	Bz-CN	4	3	CN	167.91	133.37	130.46	129.58	136.94	-3.57	+2.91	+0.88	+7.36
II	Bz-C(O)OH	4	3	=O,OH	185.66	131.82	130.75	128.99	135.54	-3.72	+1.07	+1.76	+6.55
IVa	Bz-C(O)OCH_3	4	3	=O,OCH_3	186.14	132.47	130.06	128.94	135.01	-2.54	+2.41	+1.12	+6.07
IVb	Bz-C(O)OC_2H_5	4	3	=O,OC_2H_5	186.53	132.60	129.99	128.95	134.92	-2.32	+2.61	+1.04	+5.97
VIIIn	Bz-CF_3	4	3	3F	180.58	130.13	130.16	129.16	135.51	-5.38	-0.03	+1.00	+6.35

groups determined by the basic parameter δ_1. The difference is that benzamide derivatives (VIId and VIIe, Z = N) by values $\Delta\delta_{2\text{-}3}$ and $\Delta\delta_{2\text{-}5}$ are closer to the compounds containing benzaldehyde (VIIa), phenones (VIIb and VIIc) and phenyltiobenzoate (VIIf) then to the benzoic acid derivative, including its haloidanhydrides (VIIg and VIIh). Thus, the parameter $\Delta\delta_{2\text{-}5}$ has the positive value for the first group of compounds (VIIa, VIIb – VIIf) and the negative value – for the second group (I, IIIa, IIIc, VIIg, VIIh). The $\Delta\delta_{2\text{-}3}$ parameter for 9 compounds has the positive value and the small negative value for benzoic acid and phenylbenzoate. It should be noted that the $\Delta\delta_{2\text{-}3}$ value (~7–9 ppm) is several times greater for the first group than that for the second group ($\Delta\delta_{2\text{-}3}$ is from –1 to +3 ppm).

Presented in Table 1 data of spectral parameters of both types show that the benzoic acid (I) and its derivatives (III, VIIg and VIIh) essentially differ from benzaldehyde (VIIa), ketones (VIIb and VIIc) and phenylbenzoate (VIIf) by their spectral peculiarities. Benzamides (VIId and VIIe) may be the compounds with an intermediate character, to our mind.

Since benzoylformic acid and its esters are benzoyl-containing compounds which have Z=C, it is advisable to examine this group in details, as the compounds of general formula (VIII). They may be represented by acetophenone derivatives Bz–CH_3 (VIIb), where one, two or all three hydrogen atoms are substituted for different functional groups – substituents L, M and N.

The order of compounds represented in Table 2 was selected in such a way, that variable substituents L, M and N gradually increase the general polarity of C(LMN) fragment from the electron-donor to the electron-acceptor ones. Therefore all compounds in Table 2 are divided into 4 sub-groups, their compositions being determined by the structure of L, M and N substituents. The difference in their structure leads to the difference in oxidation level of the central carbon atom Z.

“Phenones” with a zero oxidation level are in the first sub-group. All their bonds C–L, C–M and C–N are non-polar without the dipole negative end located on the substituent L, M and N. Phenacyl derivatives with the oxidation level of atom Z = +1 are in the second sub-group. Here substituent L is the electron-acceptor group. Such group usually contains polar bond of the Z atom with the central atom of L substituent which is more electronegative than carbon. O, N and Hal may be such atoms. The third sub-group contains *a*-benzoylcarbonyl compounds and their derivatives with oxidation level +2 (L and M are electron-acceptor groups). The forth sub-group includes *a*-benzoylcarboxyl compounds and their derivatives with oxidation level +3. All three groups L, M and N are electron-acceptor ones. Examined benzoylformic acid (II) and its esters (IV) are also in the forth group.

There is a general tendency of δ_1 value decrease during the transfer from the first to the forth sub-group for 18 compounds (VIII) from Table 2. The δ_1 values of the first sub-group (VIIb, VIIc, VIIIa and VIIIb) are located in the downfield, within the interval of 190–210 ppm (the interval centre is ~ 200 ppm). The interval of δ_1 values of the second sub-group (compounds VIIIc–VIIf) partially overlaps the interval of values of the first sub-group but its centre is shifted to the high-field (δ_1 ~ 186–196 ppm, the interval centre is ~ 191 ppm). The interval centers of the third (compounds VIIIg–VIIIl) and the forth (II, IV, VIIIm and VIIIn) sub-groups are shifted still more to the high field (~ 190 and ~ 177 ppm, correspondingly).

As it was mentioned above, absorption of the carbonyl carbon atom, ***i.e.*** basic parameter δ_1 depends upon not only Z atom electronegativity (the carbon atom in compounds VIII) but also upon other factors. Electronegativity of L, M and N group atoms, connected with Z atom, is of great importance. Analogously to the compounds of the general formula (VII) the δ_1 signal shift to the high field with the increase of all atoms electronegativity may be expected. However in all 4 groups there are divergences of predicted tendency. For example, between the compounds of the second sub-group the metoxyl group in ether VIIIe (L = OCH_3, bond C–O) essentially shifts δ_1 value to the downfield. Nitro-group in VIIId (L = NO_2, bond C–N, where the nitrogen atom is less electronegative than the oxygen atom) on the contrary shifts the mentioned value to the high field

If two or three haloids (compounds VIIIe and VIIIn) are connected with Z atom, the δ_1 value is shifted to the high field as was expected. However the greatest upfield shift of the δ_1 value (~ 168 ppm) is observed for nitrile VIIIm, in spite of the less electronegativity of the nitrogen atom (substitutuents L,M,N = N) than two oxygen atoms in II and IV or three fluorine atoms in VIIIn. This example confirms once more that electronegativity of the substitutent atom connected with Z atom in the variable fragment X is not the single (and may be non-principal) reason of the δ_1 signal shift.

The same tendencies may be observed investigating basic parameters δ_2, δ_3 and δ_5 of phenyl ring atoms. The interval centers of the δ_2 value of the first, second, third and forth sub-groups shift to the high field and equal to 138.1, 134.1, 133.9 и 131.8 ppm, correspondingly. For the δ_5 parameters all interval centers shift to the downfield: 131.9, 134.4, 133.7 and 135.9 ppm[2]. The same tendency but with the narrower intervals is observed also for the δ_3

[2] The reason of abnormal behavior of the δ_5 parameter is explained by unsuccessful selection of the second sub-group components. Salt-like phenacylammonium chloride (VIIIc) and nitrophenacyl (VIIId) contain the most electron-withdrowing substituents L. These compounds are closer by both their values of spectral parameters (basic and differential) to the compounds of the third and even the forth sub-groups than to the compounds of the second sub-group, which they belong to. Therefore, to our mind, the interval center of the δ_5 parameter groundlessly is shifted to the downfield.

parameters: 129.0, 129.2, 130.0, 130.4 ppm and for δ_4 parameters: 128.2, 128.2, 128.6, 129.1 ppm.

The δ_4 basic parameter representing absorption of meta-phenyl carbons is non-informative parameter. It changes randomly in the narrow interval with the width of ~ 1.5 ppm. Differential parameters $\Delta\delta_{3-4}$ and $\Delta\delta_{5-4}$ are also non-informative [2, 3].

Two other differential parameters $\Delta\delta_{2-5}$ and $\Delta\delta_{2-3}$ are the most informative between all spectral parameters, both basic and differential. The reason is the difference between shift directions of basic parameter components: the shift to the high field – for δ_2, and the shift to the downfield – for δ_5 and δ_3. The change of these differential parameters in going from the first sub-group to the forth sub-group confirms the correctness of all compounds (VIII) division into 4 sub-groups.

The $\Delta\delta_{2-5}$ parameter for the first-group compounds has the greatest value (from ~4 to ~8 ppm). The difference between interval centers of the δ_2 and δ_5 parameters equals to 138.1 – 131.9 = 6.2 ppm. For the second and the third group their values are within the interval from ~ -3 to ~ +3 ppm. Taking into account all above-mentioned facts about peculiarities of the nitrogen atom in the substituents L, M and N (including NO_2 in VIIId and $NH_3^+Cl^-$ in VIIIc) we may assume that the $\Delta\delta_{2-5}$ parameter for the second sub-group compounds should be within the interval from 0 to +2 ppm and within the interval from –2 to 0 ppm – for the third sub-group compounds. All $\Delta\delta_{2-5}$ parameters of the forth sub-group compounds have negative values in the interval from ~ -5.5 to ~ –2 ppm. The difference between interval centers equals to 131.4 – 135.2 = -3.8 ppm.

The similar situation is for the $\Delta\delta_{2-3}$ parameter. Its greatest value (~ 8-10 ppm) is observed for the first sub-group compounds. The difference between interval centers of δ_2 and δ_3 parameters equals to 138.1 – 129.0 = 9.1 ppm. Taking into consideration all above-mentioned we estimated averaged values of ~ 5–6 and ~ 3–4 ppm for the second and third sub-groups, correspondingly. The minimum value of ~ 0– +3 ppm is for the $\Delta\delta_{2-3}$ parameter of the forth sub-group.

One can see from obtained data that benzoylformic acid (II), methyl- (IVa) and ethyl- (IVb) benzoylformates are typical compounds of the forth sub-group by the general formula (VIII). Described in [1] basic and calculated differential spectral parameters of the methyl- (IVa) and ethyl- (IVb) benzoylformates are in good agreement with parameters taken from [6]. The good coincidence of analogous parameters is also observed for the benzoylformates, alcohol esters with longer alkyl chains described in [1] taking into account the correction for different solvents (CD_2Cl_2 и $CDCL_3$)[3].

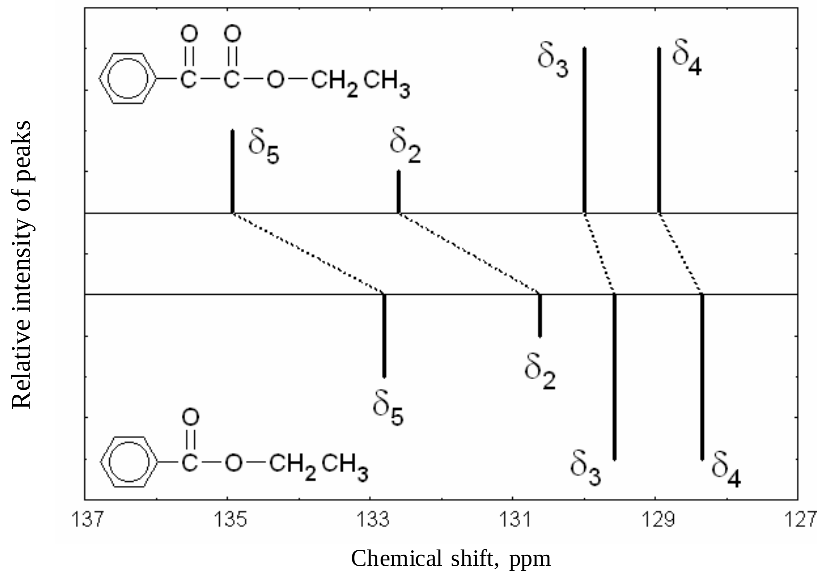


Fig. 1. Values δ_i^C for IVb and IIIb compounds

[3] In [1] there are ^{13}C NMR spectral parameters for two unsaturated benzoylformiates – allyl and propargyl esters. Calculated differential parameters $\Delta\delta_{2-3}$ and $\Delta\delta_{2-5}$ are regularly changed with the increase of alcohol fragment unsaturation. Thus, corresponding parameters $D\delta_{2-3}$ increase compared with characteristic parameter $\Delta\delta_{2-3}^{IVchar}$ = 2.25 of saturated esters: 2.5 ppm for allyl ester and 3.0 ppm for propargyl ester. The $\Delta\delta_{2-5}$ parameters decrease in the mentioned row: 2.75→2.4→ 2.2 ppm. However the lack of experimental results does not allow us to assert the regularity of these tendencies for unsaturated alkylbenzoylformiates (IV).

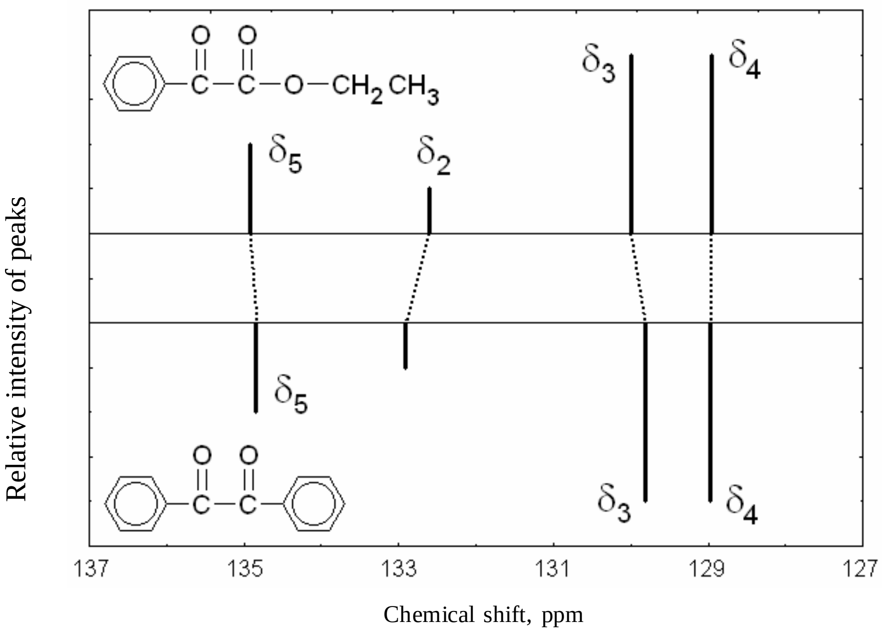


Fig. 2. Values δ_i^C for IVb and VIIIk compounds

So, saturated unsubstituted primary alkylbenzoylformates (IV) have basic and differential spectral parameters $\delta_i^{IVchar.}$ of the benzoyl fragment, which are typical for this class of carbonyl-containing substances. Similar to characteristic parameters for alkylbenzoates (III) [2] we calculated characteristic parameters for alkylbenzoylformates (IV) using data from [1, 6]. Basic parameters were calculated with the accuracy of 0.5 ppm: $\delta_1^{IVchar.}$ = 186.5 ppm, $\delta_2^{IVchar.}$ = 132.5 ppm, $\delta_3^{IVchar.}$ = =130.0 ppm, $\delta_4^{IVchar.}$ = 129.0 ppm, $\delta_5^{IVchar.}$ = 135.0 ppm. Differential parameters were calculated with the accuracy of 0.25 ppm: $\Delta\delta_{2-5}^{IVchar.}$ = -2.25 ppm, $\Delta\delta_{2-3}^{IVchar.}$ = =+ 2.75 ppm, $\Delta\delta_{3-4}^{IVchar.}$ = + 1.0 ppm, $\Delta\delta_{5-4}^{IVchar.}$ = + 6.0 ppm.

The δ_2–δ_5 values of basic spectral parameters of alkylbenzoylformates (IV) phenyl ring and alkylbenzoates (III) were taken from [6]. The ratio between them is represented in Fig. 1 as a schematic picture [2] of their ethyl esters spectra (IVb and IIIb, correspondingly). It should be noted that spectral values in ethyl esters (IVb) and (IIIb) slightly differ from the corresponding above-mentioned δ_i^{IVchar} and described in [2] $\delta_i^{IIIchar}$ characteristic parameters.

Fig.2 represents the similar ratio between ethylbenzoylformiate (IVb) and diketone-benzil (VIIIk) which is a typical specimen of the third sub-group (VIII).

Minimal deviation from a vertical direction of the dotted line connecting the similar parameters of both compounds we consider as an index of resemblance of δ^C basic spectral parameters. One can see from Figs. 1 and 2 that characteristic basic spectral parameters $\delta^C(\delta_2$–$\delta_5)$ of alkylbenzoylformates (IV) phenyl ring are more similar to the analogous parameters of diketone (VIIIk) (see Fig. 2) represented in the third sub-group than to the parameters δ^C of alkylbenzoates (III) with long chains, described in [2] and depicted in Fig. 1.

4. Conclusions

Thus, joint spectral parameters of benzoyl fragment for saturated unsubstituted alkylbenzoylformates (IV) characterizing this class, do exist. Benzoyl group in benzoylformates (IV) has all typical features of benzoyl fragments connected with electron-withdrawing substituents in phenylketones by general formula (VIII).

Spectral peculiarities of benzoyl fragments in benzoylformates are determined by belonging namely to ketones, not esters.

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ОСОБЛИВОСТІ СПЕКТРІВ ЯМР ^{13}С БЕНЗОЇЛМУРАШИНОЇ КИСЛОТИ ТА ЇЇ ЕСТЕРІВ. 1. БЕНЗОЇЛЬНИЙ ФРАГМЕНТ

Анотація. *Досліджені особливості спектрів ЯМР ^{13}С бензоїльного фрагмента бензоїлмурашиної кислоти та її естерів. Наведені характеристичні величини хімічних зсувів усіх п'яти типів його вуглецевих атомів. Проведено порівняння з аналогічними параметрами інших бензоїлвмісних сполук загальної формули Bz–X (X = H, NR_2, OR, SR, Cl, Br), а також з сполуками Bz–C (L)(M)(N). Доведено, що спектральні особливості фенільного фрагменту бензоїлформіатів визначає карбонільна, а не карбалкоксильна група.*

Ключові слова: *спектри ЯМР ^{13}С, бензоїльний фрагмент, базові та диференційні спектральні параметри.*