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 carbalkoxy 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 carbalkoxy 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 benzoylformicate (IV) spectra described in [1] was obtained in CD$_2$Cl$_2$, 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 acetics, which are similar to benzoylformates (IV), as an example [4], it was shown that all $\delta^C$ 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 benzoylformicate spectra obtained in CD$_2$Cl$_2$ with $\delta^C$ 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$_2$Cl$_2$ are not discussed in this paper.

In order to minimize inaccuracies connected with different $\delta^C$ basic parameters for the same compounds, it would be desirable that all $\delta^C$ 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 С 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: δ₁, δ₂, δ₃, δ₄ and δ₅) are defined by
symbols δᵢ and δⱼ (i and j are numbers of carbon atoms in
formula V). Differential spectral parameters Δδᵢⱼ = δᵢ − δⱼ
are design values and equal to the difference between two
basic parameters δᵢ. They are chosen depending on the
aim; in addition both basic parameters δᵢ and δⱼ are taken
from the same spectrum. In such a case values of differential
parameters Δδᵢⱼ 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) ¹³C NMR spectra [2] we chose four most informative
parameters Δδᵢⱼ, characterizing a phenyl part of the benzoyl
fragment: Δδ₂₅, Δδ₂₃, Δδ₃₄, Δδ₅₄.

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).

![Diagram](image)

Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Atom Z</th>
<th>Basic parameter values δᵢ, ppm</th>
<th>Differential parameter values Δδᵢⱼ, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIIa</td>
<td>Bz-H</td>
<td>H</td>
<td>192.28 136.47 129.68 128.98 134.43</td>
<td>+2.04  +6.79  +0.70  +5.45</td>
</tr>
<tr>
<td>VIIb</td>
<td>Bz-CH₃</td>
<td>C</td>
<td>197.85 137.23 128.56 128.29 133.04</td>
<td>+4.19  +8.67  +0.27  +4.75</td>
</tr>
<tr>
<td>VIIc</td>
<td>Bz-C₆H₅</td>
<td>C</td>
<td>196.50 137.58 128.96 128.21 132.33</td>
<td>+5.25  +7.62  +1.75  +4.12</td>
</tr>
<tr>
<td>VIId</td>
<td>Bz-NH(CH₃)</td>
<td>N</td>
<td>168.46 134.62 126.94 128.42 131.23</td>
<td>+3.39  +7.68  -1.48  +2.81</td>
</tr>
<tr>
<td>VIIe</td>
<td>Bz-N(CH₃)₂</td>
<td>N</td>
<td>171.56 136.40 127.01 128.30 129.46</td>
<td>+6.94  +9.39  -1.29  +1.16</td>
</tr>
<tr>
<td>VIII</td>
<td>Bz-OH</td>
<td>O</td>
<td>172.77 129.44 130.28 128.49 133.83</td>
<td>-4.39  -0.84  +1.79  +5.34</td>
</tr>
<tr>
<td>IIIa</td>
<td>Bz-O-CH₃</td>
<td>O</td>
<td>167.04 130.25 129.60 128.37 132.90</td>
<td>-2.65  +0.65  +1.23  +4.53</td>
</tr>
<tr>
<td>IIIc</td>
<td>Bz-O-C₆H₅</td>
<td>O</td>
<td>165.07 129.63 130.11 129.50 133.49</td>
<td>-3.86  -0.48  +0.61  +3.99</td>
</tr>
<tr>
<td>VIIf</td>
<td>Bz-S-C₆H₅</td>
<td>S</td>
<td>190.03 136.80 129.23 128.74 133.61</td>
<td>+3.19  +7.57  +0.49  +4.87</td>
</tr>
<tr>
<td>VIIg</td>
<td>Bz-Cl</td>
<td>Cl</td>
<td>168.27 133.21 131.39 129.01 135.39</td>
<td>-2.18  +1.82  +2.38  +6.38</td>
</tr>
<tr>
<td>VIIh</td>
<td>Bz-Br</td>
<td>Br</td>
<td>165.59 134.76 131.95 128.95 135.57</td>
<td>-0.81  +2.81  +3.00  +6.62</td>
</tr>
</tbody>
</table>
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, 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, −OC_H_3 and −OC_H_2.

Spectral parameters \( \delta^c \) and \( \Delta \delta^c \) 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 \( 1 \)-methyl derivatives (VIIId and VIIe) should be chosen. However in Table 1 data for benzamide are absent because of their reliability and self-descriptiveness. In [2, 3] 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 \( \delta_1 \) representing the absorption of ipso-carbon atoms for three oxygen derivatives I, IIIa and IIIc (\( \delta_1 = 129–130 \) ppm) essentially differ from other six types of compounds (VII). In the latest eight compounds the \( \delta_1 \) parameter is distributed inside the interval \( \delta^c_1 = 133–138 \) ppm without any regularity. On the contrary, for orto-carbon atoms only \( \delta^c_2 \) values for benzmides VIIId and VIle (\( \delta_2 \sim 127 \) ppm) are less than \( \delta_1 = 128.5–132 \) ppm for other 6 types of compounds. The same situation takes place with the \( \delta_3 \) parameter representing the absorption of para-carbon atoms. And there are no great differences between \( \delta_5 \) values for all 11 compounds in the case of meta-carbon atoms.

Taking into consideration \( \Delta \delta_{1,2} \) 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 \( \Delta \delta_{1,2} \) and \( \Delta \delta_{3,4} \) containing the most outlying from the X fragment “internal” atoms of a phenyl ring are low-informative\(^1\). Differential parameters \( \Delta \delta_{1,2} \) and especially \( \Delta \delta_{3,4} \) 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 \( \delta_1 \) and \( \delta_5 \) signals from the one hand, and \( \delta_3 \) signal from the other hand may be easily identified by their intensities (see also Figs. 1 and 2).
<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Subgroup number</th>
<th>Oxidation level</th>
<th>L, M, N</th>
<th>Basic parameter values $\delta_i$, ppm</th>
<th>Differential parameter values $\Delta \delta_{i,j}$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\delta_1$</td>
<td>$\delta_2$</td>
</tr>
<tr>
<td>VIIIb</td>
<td>Bz-CH$_3$</td>
<td>1</td>
<td>0</td>
<td>3H</td>
<td>197.85</td>
<td>137.23</td>
</tr>
<tr>
<td>VIIIa</td>
<td>Bz-C(CH$_3$)</td>
<td>1</td>
<td>0</td>
<td>3CH$_3$</td>
<td>209.11</td>
<td>138.52</td>
</tr>
<tr>
<td>VIIId</td>
<td>Bz-CH=CHCH$_3$</td>
<td>1</td>
<td>0</td>
<td>H$_2$=CH(CH$_3$)</td>
<td>190.66</td>
<td>137.96</td>
</tr>
<tr>
<td>VIIIc</td>
<td>Bz-CH$_2$-NH$_3$Cl</td>
<td>2</td>
<td>1</td>
<td>H,H, NH$_3$Cl</td>
<td>192.21</td>
<td>134.01</td>
</tr>
<tr>
<td>VIIIg</td>
<td>Bz-C(CH$_3$)=N=OH</td>
<td>3</td>
<td>2</td>
<td>CH$_3$,=NOH</td>
<td>191.98</td>
<td>136.39</td>
</tr>
<tr>
<td>VIIIe</td>
<td>Bz-CH$_2$-O-CH$_3$</td>
<td>2</td>
<td>1</td>
<td>H,H, OCH$_3$</td>
<td>194.06</td>
<td>134.80</td>
</tr>
<tr>
<td>VIIIa</td>
<td>Bz-CH$_2$-Cl</td>
<td>2</td>
<td>1</td>
<td>H,H,Cl</td>
<td>191.06</td>
<td>134.24</td>
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<tr>
<td>VIIIm</td>
<td>Bz-CN</td>
<td>4</td>
<td>3</td>
<td>CN</td>
<td>167.91</td>
<td>133.37</td>
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<tr>
<td>IVa</td>
<td>Bz-C(O)OH</td>
<td>4</td>
<td>3</td>
<td>=O,OH</td>
<td>185.66</td>
<td>131.82</td>
</tr>
<tr>
<td>IVb</td>
<td>Bz-C(O)OC$_2$H$_5$</td>
<td>4</td>
<td>3</td>
<td>=O,OC$_2$H$_5$</td>
<td>186.53</td>
<td>132.60</td>
</tr>
<tr>
<td>VIIIb</td>
<td>Bz-CF$_3$</td>
<td>4</td>
<td>3</td>
<td>3F</td>
<td>180.58</td>
<td>130.13</td>
</tr>
</tbody>
</table>
groups determined by the basic parameter $\delta_j$. The difference is that benzamide derivatives (VIIId and VIIe, $Z = N$) by values $\Delta\delta_{2,3}$ and $\Delta\delta_{2,5}$ are closer to the compounds containing benzaldehyde (VIIa), phenones (VIIb and VIIc) and phenyltiobenzoate (VIIIf) than to the benzoic acid derivative, including its haloiodanhydrides (VIIg and VIIh). Thus, the parameter $\Delta\delta_{2,5}$ 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 $\Delta\delta_{2,5}$ parameter for 9 compounds has the positive value and the small negative value for benzoic acid and phenylbenzoate. It should be noted that the $\Delta\delta_{2,3}$ value (−7–9 ppm) is several times greater for the first group than for the second group ($\Delta\delta_{2,3}$ 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 (VIIId and VIIe) may be the compounds with an intermediate character, to our mind.

Since benzoxyformic acid and its esters are benzoyl-containing compounds which have $Z=O$, it is advisable to examine this group in details, as the compounds of general formula (VIII). They may be represented by acetophenone derivatives $\text{Bz} – \text{CH}_2$ (VIIb), where one, two or 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 $\alpha$-benzoylcarbonyl compounds and their derivatives with oxidation level +2 (L and M are electron-acceptor groups). The forth sub-group includes $\alpha$-benzoylcarboxyl compounds and their derivatives with oxidation level +3. All three groups L, M and N are electron-acceptor ones. Examined benzoxyformic acid (II) and its esters (IV) are also in the forth group.

There is a general tendency of $\delta$ value decrease during the transfer from the first to the forth sub-group for 18 compounds (VIII) from Table 2. The $\delta$ values of the first sub-group (VIIb, VIIc, VIIId and VIIIf) are located in the downfield, within the interval of 190–210 ppm (the interval centre is ~ 200 ppm). The interval of $\delta$ values of the second sub-group (compounds VIIc–VIIIf) partially overlaps the interval of values of the first sub-group but its centre is shifted to the high-field ($\delta \sim 186–196$ ppm, the interval centre is ~ 191 ppm). The interval centers of the third (compounds VIIg–VIIIf) and the forth (IV, VIIIf 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 $\delta_j$, 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 $\delta$ 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 metoxy group in either VIIIe (L = OCH$_3$, bond C–O) essentially shifts $\delta$ 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 VIIIf and VIIIn) are connected with Z atom, the $\delta$ value is shifted to the high field as was expected. However the greatest upfield shift of the $\delta$ value (~ 168 ppm) is observed for nitrite VIIIm, in spite of the less electronegativity of the nitrogen atom (substituents 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 substituent atom connected with Z atom in the variable fragment X is not the single (and may be non-principal) reason of the $\delta_j$ signal shift.

The same tendencies may be observed investigating basic parameters $\delta$ and $\delta_j$ of phenyl ring atoms. The interval centers of the $\delta$ value of the first, second, third and forth sub-groups shift to the high field and equal to 138.1, 134.1, 133.9 and 131.8 ppm, correspondingly. For the $\delta_j$ 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 $\delta_j$ parameter.
parameters: 129.0, 129.2, 130.0, 130.4 ppm and for $\delta_i$ parameters: 128.2, 128.6, 129.1 ppm.

The $\delta_i$ 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 $\delta_2$ and the shift to the downfield – for $\delta_5$ and $\delta_3$. 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 $\delta_2$ and $\delta_5$ 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$_3^+$ 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 subgroup compounds. The difference between interval centers of $\delta_2$ and $\delta_3$ 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$_2$Cl$_2$ и CDCl$_3$).

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 $\Delta \delta_{5,4}$ are regularly changed with the increase of alcohol fragment unsaturation. Thus, corresponding parameters $\Delta \delta_{2,3}$ increase compared with characteristic parameter $\Delta \delta_{2,3}^\text{IVchar} = 2.25$ of saturated esters: 2.5 ppm for allyl ester and 3.0 ppm for propargyl ester. The $\Delta \delta_{2,3}$ 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).
Peculiarities of $^{13}$C NMR Spectra of Benzoylformic Acid and its Esters. 1. Benzoyl Fragment

So, saturated unsubstituted primary alkylbenzoylformates (IV) have basic and differential spectral parameters $\delta_i^{\text{IVchar}}$ 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: $\delta_1^{\text{IVchar}} = 186.5$ ppm, $\delta_2^{\text{IVchar}} = 132.5$ ppm, $\delta_4^{\text{IVchar}} = 130.0$ ppm, $\delta_5^{\text{IVchar}} = 129.0$ ppm, $\delta_5^{\text{IVchar}} = 135.0$ ppm. Differential parameters were calculated with the accuracy of 0.25 ppm: $\Delta \delta_2-5^{\text{IVchar}} = -2.25$ ppm, $\Delta \delta_2-3^{\text{IVchar}} = + 2.75$ ppm, $\Delta \delta_3-4^{\text{IVchar}} = + 1.0$ ppm, $\Delta \delta_5-4^{\text{IVchar}} = + 6.0$ ppm.

The $\delta_2-\delta_5$ 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 $\delta_i^{\text{IVchar}}$ and described in [2] $\delta_i^{\text{IIIchar}}$ 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 $\delta^C$ 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 $\delta^C$ 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.

References

ОСОБЛИВОСТІ СПЕКТРІВ ЯМР \( ^{13}C \) БЕНЗОЇЛМУРАШИНОЇ КИСЛОТИ ТА ЇЇ ЕСТЕРІВ. 1. БЕНЗОЇЛЬНИЙ ФРАГМЕНТ

Анотація. Досліджені особливості спектрів ЯМР \( ^{13}C \) 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 форми \( \text{Bz–X (X = H, NR}_2, \text{ OR, SR, Cl, Br)} \), а також з сполуками \( \text{Bz–C (L)(M)(N)} \). Доведено, що спектральні особливості фенільного фрагмента бензоїлформіатів визначає карбонільна, а не карбальдегідна група.

Ключові слова: спектри ЯМР \( ^{13}C \), бензоїльний фрагмент, базові та диференційні спектральні параметри.