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# PECULIARITIES OF NMR $^{13}C$ SPECTRA OF BENZOIC ACID AND SATURATED ALKYLBENZOATES. I. CHEMICAL SHIFT OF BENZOYL FRAGMENT CARBON ATOMS

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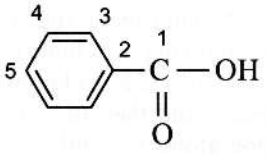
**Abstract**. It has been shown that chemical shift of 5 types of carbon nuclei of benzoyl fragment in saturated alkylbenzoates depends upon alkyl radical degree of branching near α-carbon atom of alkoxyl group. Typical values of chemical shifts of five nuclei for primary, secondary and tertiary alkylbenzoates have been admitted.

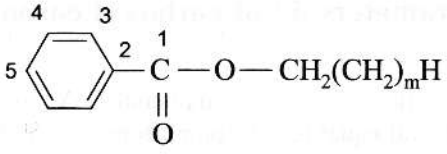
**Key words:** NMR $^{13}C$ spectra, chemical shift, saturated alkylbenzoates, benzoyl fragment, alkoxyl group.

## 1. Introduction

Earlier [1] we examined peculiarities of NMR $^{1}H$ spectra of benzoic acid (I) and several alkelbenzoates (II-V), as well as benzoylformic acid and its esters:

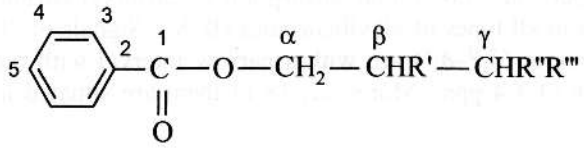


I



II

$m = 0–7$ ($a = m = 0$; $b = m = 1$; $c = m = 2$)



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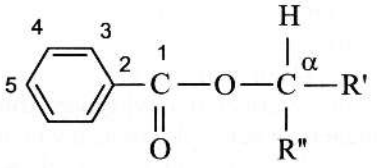
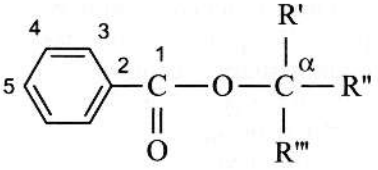


IV



V

here R = H or primary alkyl group; R′, R″, R‴ = primary alkyl group.

This work deals with some peculiarities of NMR $^{13}C$ spectra of I–V compounds. Some spectra of the mentioned compounds were obtained while determining by-products structure of photoinitiators synthesis such as 2,2-dialkoxy-1-arylethanols [2], some spectral data were taken from the special accuracy investigations of spectral characteristics (including spectra NMR $^{13}C$ and $^{1}H$) of a great amount of organic compounds [3]. Because of the doubts [1] concerning accuracy and reliability of obtained results from other sources where benzoates spectra are described, we preferred to confine ourselves to two literature sources [2, 3], in spite of data insufficiency for secondary (IV) and particularly tertiary (V) alkylbenzoates. To our mind, the reliability of spectral investigations is more important than their number.

The accuracy of $\delta_i^C$ values in NMR $^{13}C$ spectra presented in [2], was specially limited by the first sign after comma, since these spectra were recorded as one of analytic characteristics of synthesized compounds and

sometimes temperature and concentration conditions did not stand the parameters necessary for accuracy investigations. At the same time spectral data were the main objects of investigations in [3] and these parameters were definitely controlled. Therefore, $\delta_i^C$ values are presented with the accuracy of 0.01 ppm.

The mentioned spectra were recorded on the instruments with different frequencies using two chlorinated solvent similar by their structures – $CDCl_3$ and $CD_2Cl_2$. Their chemical shifts substantially differ from those in spectra obtained in DMSO-$d_6$, therefore here we do not consider NMR $^{13}C$ spectra recorded in DMSO-$d_6$. The working frequency of an instrument actually does not affect the $\delta_i^C$ values of chemical shift ($i = 1–5$) of each 5 types of benzoyl fragment carbon nucleus. Concerning the effect of solvent type ($CDCl_3$ or $CD_2Cl_2$) on the $\delta_i^C$ value it should be noted that this effect is minor but systematic one [4]. Carbon nuclei of the same type absorb in lower field in deuteromethylenchloride (MCh) in comparison with deuterochloroform (ChF) ($\Delta\delta_i^{C\,solv} = \Delta\delta_i^{C\,MCh} - \Delta\delta_i^{C\,ChF} \geq 0$). It means that parameter describing the solvent influence ($\Delta\delta_i^{C\,solv}$) is usually of little positive value (tenth part of ppm).

Similar to [1] our analysis is based on the systematic investigations of the effect of alkyl group structure on the spectral parameters of benzoyl fragment which is common for all compounds (I–V). In this work we consider spectral data only for benzoates which are derivatives of unsubstituted saturated alcohols: primary – compounds II and III (further called primary benzoates), secondary – compounds IV and tertiary – compound V.

So, the aim of the present work was to establish the presence of characteristic spectral parameters of benzoyl fragment common for alkylbenzoates (II–V) in NMR $^{13}C$ spectra as it was in PMR [1]. This would permit to distinguish $^{13}C$ spectra of benzoates from spectra of other benzoylcontaining compounds, for instance benzoylformates.

## 2. Experimental

The values of chemical shifts of benzoyl fragment carbon nuclei for I–V compounds in NMR $^{13}C$ spectra are represented in Table 1. The first spectral data being recorded in $CDCl_3$ and other ones – in $CD_2Cl_2$. They are considered separately.

## 3. Results and Discussion

### 3.1. General principles

Let us introduce the following symbols for differential parameters for $^{13}C$ spectra as well as for NMR $^1H$ spectra [1]. For instance, $\delta_i^N$ value interval will be defined by extreme values $\delta_i^{Nx}$ and $\delta_i^{Ny}$: $\Delta\delta_i^N = \Delta\delta_i^{Nx} - \delta_j^{Ny}$, where numbers of corresponding carbon nuclei in benzoyl fragment are indicated by subscript "i" and Arabic numbers and compound numbers are indicated by superscript (Roman numbers and letters).

In order to study the effect of alkyl fragment structure on $\delta_j^C$ and $\Delta\delta_i^N$ parameters let us divide all 12 primary alkylbenzoates (II, III), the spectra of which are recorded in $CDCl_3$, into two groups on the basis of alkyl chain structure. The first group will consist of eight esters (IIa–IIh) with linear unbranched alkyl chains from C-1 to C-8 and the second group will contain four compounds (IIIa–IIId) branched near carbon atom, which is farther than $\alpha$-atom connected with oxygen atom, *i.e.* near either $\beta$-atom (IIIa, IIIb, IIIc compounds) or $\gamma$-atom (IIId compound). NMR $^{13}C$ spectrum for one more compound of such a type (IIIe) is recorded only in $CD_2Cl_2$.

For the secondary benzoates (IV) one branching in alkyl chain is obligatory, namely near $\alpha$-carbon atom. For the tertiary benzoates (V) two branchings near $\alpha$-carbon atom are maximum possible.

So we have spectra only for three secondary benzoates (IVa–IVc) in $CDCl_3$, IVc compound being a derivative of alicyclic secondary saturated alcohol (cyclohexanol), and only one tertiary benzoate – *tert*-butylbenzoate (Va). NMR $^{13}C$ spectra for IVd–IVf compounds are recorded only in $CD_2Cl_2$. Such minor amount of spectral data recorded in ChF for compounds (IV) and especially for compounds (V) complicates the establishment of reliable regularities for the whole class of secondary and tertiary benzoates and makes pointless the division of secondary alkylbenzoates into groups (as it has been done for their primary analogues II and III). We also decided not to divide into two mentioned groups spectra of three primary benzoates (IId, IIe and IIh) recorded in $CD_2Cl_2$ because of information lack.

Let us examine peculiarities of chemical shifts of all five types of benzoyl fragment carbon nuclei in I–V compounds. Since the carbon atom of carboxyl group absorbs in the lowest field (about 165–173 ppm) and six carbon atoms of phenyl ring – in higher field (moreover, the interval is very narrow 128–134 ppm), let us consider at first $\delta_1^C$ parameters, and then ($\delta_2^C$–$\delta_5^C$) parameters of phenyl group carbon atoms cojointly.

### 3.2. Parameters $\delta_1^C$ of carboxyl carbon atom

Signals $\delta_1^C$ of all 21 compounds (I–V) are situated in the interval equal to 7.12 ppm, from $\delta_1^V = 165.65$ ppm till $\delta_1^I = 172.77$ ppm. There is a significant shift of $\delta_1^I$ signal (for 6-7 ppm) in benzoic acid to the downfield in comparison with similar absorption of carboxyl carbon atom in all types of alkylbenzoates (II–V). Signals of 20 benzoates ($\delta_1^{II}$–$\delta_1^V$) are within narrow interval with the width of 1.4 ppm. Moreover, 18 of them are situated in

*Table 1*

**Chemical shifts ($\delta_i^C$) of benzoyl fragment carbon nuclei for I–V compounds**

| No | Radical R | Solvent | Literature source | $\delta_i^C$ for | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | C-1 | C-2 | C-3 | C-4 | C-5 |
| I | H | $CDCl_3$ | 3 | 172.77 | 129.44 | 130.28 | 128.49 | 133.83 |
| IIa | $CH_3$ | $CDCl_3$ | 3 | 167.04 | 130.25 | 129.60 | 128.37 | 132.90 |
| IIb | $CH_2CH_3$ | $CDCl_3$ | 3 | 166.54 | 130.62 | 129.57 | 128.34 | 132.80 |
| IIb | $CH_2CH_3$ | $CDCl_3$ | 2 | 166.0 | 130.9 | 129.7 | 128.4 | 132.8 |
| IIc | $(CH_2)_2CH_3$ | $CDCl_3$ | 3 | 166.60 | 130.67 | 129.59 | 128.34 | 132.79 |
| IId | $(CH_2)_3CH_3$ | $CDCl_3$ | 3 | 166.61 | 130.66 | 129.58 | 128.34 | 132.79 |
| IIe | $(CH_2)_4CH_3$ | $CDCl_3$ | 3 | 166.64 | 130.83* | 129.61 | 128.34 | 132.72 |
| IIf | $(CH_2)_5CH_3$ | $CDCl_3$ | 3 | 166.50 | 130.62 | 129.53 | 128.27 | 132.70 |
| IIg | $(CH_2)_6CH_3$ | $CDCl_3$ | 3 | 166.61 | 130.65 | 129.57 | 128.30 | 132.75 |
| IIh | $(CH_2)_7CH_3$ | $CDCl_3$ | 3 | 166.59 | 130.65 | 129.56 | 128.30 | 132.74 |
| IIh | $(CH_2)_7CH_3$ | $CDCl_3$ | 2 | 166.6 | 130.7 | 129.5 | 128.2 | 132.6 |
| IIIa | $CH_2CH(CH_3)_2$ | $CDCl_3$ | 3 | 166.48 | 130.67 | 129.58 | 129.35 | 132.79 |
| IIIa | $CH_2CH(CH_3)_2$ | $CDCl_3$ | 2 | 166.6 | 130.7 | 129.6 | 128.35 | 132.75 |
| IIIb | $CH_2CH(CH_3)C_3H_7$ | $CDCl_3$ | 3 | 166.63 | 130.65 | 129.57 | 128.35 | 132.80 |
| IIIc | $CH_2CH(C_2H_5)C_4H_9$ | $CDCl_3$ | 3 | 166.65 | 130.68 | 129.54 | 128.33 | 132.75 |
| IIId | $(CH_2)_2CH(CH_3)_2$ | $CDCl_3$ | 3 | 166.56 | 130.63 | 129.56 | 128.32 | 132.76 |
| IVa | $CH(CH_3)_2$ | $CDCl_3$ | 3 | 165.98 | 131.05 | 129.54 | 128.26 | 132.65 |
| IVa | $CH(CH_3)_2$ | $CDCl_3$ | 2 | 165.8 | 131.3 | 129.8 | 128.6 | 132.9 |
| IVb | $CH(CH_3)CH_2CH_3$ | $CDCl_3$ | 3 | 166.14 | 130.99 | 129.51 | 128.26 | 132.64 |
| IVc | $CH(CH_2)_5$ | $CDCl_3$ | 3 | 165.92 | 131.28 | 129.57 | 128.26 | 132.60 |
| Va | $C(CH_3)_3$ | $CDCl_3$ | 3 | 165.65 | 132.11 | 129.41 | 128.13 | 132.36 |
| IId | $(CH_2)_3CH_3$ | $CD_2Cl_2$ | 2 | – | 131.0 | 129.8 | 128.7 | 133.1 |
| IIh | $(CH_2)_7CH_3$ | $CD_2Cl_2$ | 2 | 166.6 | 131.2 | 129.8 | 128.6 | 132.9 |
| IIIc | $CH_2C(CH_3)_3$ | $CD_2Cl_2$ | 2 | 166.6 | 131.0 | 129.8 | 128.7 | 133.1 |
| IVd | $CH(C_2H_5)CH(CH_3)_2$ | $CD_2Cl_2$ | 2 | – | – | 129.8 | 128.6 | 133.0 |
| IVe | $CH(CH_3)CH_2CH_2(CH_3)_2$ | $CD_2Cl_2$ | 2 | – | – | 129.8 | 128.6 | 133.0 |
| Vf | $CH[CH_2CH(CH_3)_2]_2$ | $CD_2Cl_2$ | 2 | – | – | 129.8 | 128.6 | 133.0 |

* the value seems to be incorrect.

the narrower interval from 165.9 to 166.6 ppm except $\delta_1^{IIa}$ and $\delta_1^{Va}$.

Let us compare $\delta_1^{II}$, $\delta_1^{III}$, $\delta_1^{IV}$ and $\delta_1^{V}$ values for the 4 types of esters (II–V). It is interesting to observe the effect of placement and character of branching in alkyl chain on the chemical shift of carboxyl carbon atom in these compounds. Since we marked out two groups – linear (II) and branched (III) groups between primary alkylbenzoates, it is necessary to examine them separately.

We use the known [4, 5] and fruitful approach, when the chain length in linear alkyl groups essentially affects the chemical shift of carbon and/or hydrogen distant atoms.

All linear alkyl groups are divided into three types depending upon chain length, *i.e.* $m$ value in general formula – $(CH_2)_mH$. The only group with a short chain is a methyl group ($m = 1$). Its properties differ from other linear alkyl groups; therefore it can be considered as non-

typical alkyl group. Starting from butyl group ($m$ = 4) alkyl groups are considered long-chain groups and their properties are typical for the whole class of compounds with linear alkyl groups. Usually ethyl and propyl groups are intermediate ($m$ = 2 and 3, correspondingly) and their properties are intermediate between the properties of compounds with methyl group and long-chain alkyl groups. However, sometimes properties of compounds with long-chain alkyl groups are typical for ethyl group and particularly for propyl group.

From this point of view we consider $\delta_i^{II}$ values of linear primary benzoates (IIa–IIh) presented in [3], not taking into account less accurate analogous parameters presented in [2]. Value $\delta_i^{IIa}$ = 167.04 ppm. of short-chain methylbenzoate (IIa) is sufficiently greater (for about 0.4–0.5 ppm) than ($\delta_i^{IId}$–$\delta_i^{IIh}$) parameters of long-chain benzoates (IId–IIh), which are within the range from 166.50 ppm to 166.64 ppm Parameters $\delta_i^{IIb}$ = 166.54 ppm and $\delta_i^{IIc}$ = 166.60 ppm of ethyl and propyl groups are in the mentioned interval and in such a case they are not intermediate groups. Thus, seven from eight $\delta_i^{II}$ parameters are in the very narrow (0.14 ppm) interval of $\delta^C$ values, which has symbol $\Delta\delta_i^{IIb\text{-}h}$. We admit averaging $\delta_i^{IIav}$ value calculated for those 7 compounds (IIa–IIh) as characteristic parameter for all typical primary linear alkylbenzoates (II) and indicate it as $\delta_i^{IIchar.}$ (here and further average ($\delta_i^{Nav.}$) and characteristic ($\delta_i^{IIchar.}$) parameters are calculated with the accuracy of 0.05 ppm): $\delta_i^{IIav.} = \delta_i^{IIchar.}$ = = 166.6 ppm. The same value $\delta_i^{IIh}$ = 166.6 ppm is calculated by us for oktylbenzoate (IIh) in [2]. However, for the ethylbenzoate (IIb) we received lower value ($\delta_i^{IIb}$ = =166.0 ppm) which falls out from the row. Taking into account that our investigations had less accuracy we assume that the last number may be erroneous and needs additional examination.

The value of $\delta_i^{IIIchar.}$ parameter for the four branched primary alkylbenzoates is also equal to 166.6 ppm and $\Delta\delta_i^{IIIa\text{-}d}$ = 0.17 ppm. This interval fully exceeds above mentioned $\Delta\delta_i^{IIb\text{-}h}$ interval for linear alkylbenzoates (II).

Equality of characteristic parameters ($\delta_i^{IIchar.}$ = = $\delta_i^{IIIchar.}$) of carboxyl group carbon atom in the typical primary alkylbenzoates (II and III) allows to admit that $\Delta\delta_i^{Nchar.}$ parameter (N = II, III) practically does not depend upon presence or absence of branching in alkyl chain. The width of interval, where 11 $\delta_i^N$ values of 12 primary alkylbenzoates (II and III) are kept within, *i.e.* $\Delta\delta_i^{IIb\text{-}III}$ parameter, is defined by the value of wider interval $\Delta\delta_i^{IIIa\text{-}d}$, which is equal to 0.17 ppm.

Parameters $\Delta\delta_i^{IV}$ for the three secondary alkylbenzoates have noticeably lower values: from $\delta_i^{IVc}$ = = 165.92 ppm to $\Delta\delta_i^{IVb}$ = 166.14 ppm, and their interval $\Delta\delta_i^{IVa\text{-}c}$ = 0.22 ppm is wider than $\Delta\delta_i^{IIb\text{-}III}$ interval (0.17 ppm) for the primary alkylbenzoates. We admit that $\delta_i^{IVchar.}$ = 166.05 ppm is characteristic parameter for the secondary alkylbenzoates (IV). The value $\delta_i^{IVa}$ = 165.8 ppm calculated by us in [2] is correlated with above mentioned value. Taking into consideration the possible correction for scale shift[1], the correlation should be better.

Still lesser value was determined for the single representative of tertiary alkylbenzoate ($\delta_i^{Va}$ = 165.65 ppm).

Thus, the regular monotonic reduction of $\delta_i^C$ parameter is observed in the transition from benzoic acid (I) through primary (II and III) and secondary (IV) to tertiary (V) alkylbenzoates. Fig. 1 presents the change of $\delta_i^C$ parameter in a row of I–V compounds. We mentioned above about a great jump of $\Delta\delta_i^{I\text{-}II}$ values between benzoic acid (I) and its esters (II–V). This jump is obvious in Fig. 1. After the abrupt reduction one can observe the monotonic, practically the linear decrease of $\delta_i^C$ parameter in esters row (II–V) and the slope angle between the curve and abscissa axis is lesser. Values $\delta_i^{IIa}$ and $\delta_i^{Va}$ are the greatest and the least values of $\delta_i^C$ parameters in spectra of 16 alkylbenzoates (II–V) obtained in $CDCl_3$, which determine the width of $\Delta\delta_i^{II\text{-}IV}$ interval (~ 1.4 ppm).

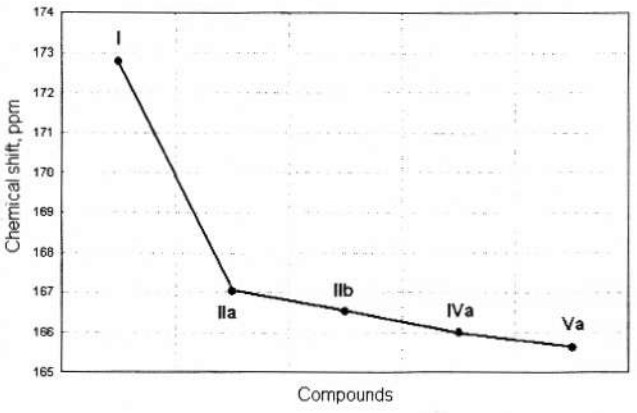



**Fig. 1.** The change of $\delta_i^C$ in the row:

I → IIa → IIb → IVa → Va

Parameters $\delta_i^C$ = 166.6 ppm are presented only in two spectra of alkylbenzoates obtained in $CD_2Cl_2$ for IIh and IIIe compounds [2]. This value is equal to the above-mentioned characteristic value of parameters in deuterochloroform: $\delta_i^{IIchar.} = \delta_i^{IIIchar.}$ = 166.6 ppm. In spite of lack of data we may assume that just for carboxyl carbon atom one can see the particular case when $\Delta\delta_i^{II\,solv.}$ = $=\Delta\delta_i^{III\,solv.} = 0$.

## 3.3. Signals of phenyl group carbon atoms ($\delta_2^C$–$\delta_5^C$)

All regularities mentioned above for $\delta_i^N$ and $\Delta\delta_i^N$ parameters may be referred to those of phenyl group (here $i$ = 2–5, and $N$ = 1–5). The results are presented in Tables 2–4.

[1] It may be assumed that in the isopropylbenzoate spectrum (IVa) the scale starting shifts to the upfield by 0.1-0.2 ppm. In such a case an introduction of systematic correction of 0.15 ppm is advisably.

*Table 2*

**Values $\delta_i^{II}$ ($i$ = 2–5) for IIa–IIh compounds in $CDCl_3$ [3]**

| Carbon atom | | $\delta_i^{I}$ for benzoic acid, ppm | $\delta_i^{IIa}$ for methyl-benzoate, ppm | Max & min values of $\delta_i^{II}$ stipulated the low- and highfield limits of range | | | | Width of the $\delta_i^{II}$ interval, ppm | $\delta_i^{IIchar.}$, ppm |
|---|---|---|---|---|---|---|---|---|---|
| | | | | downfield | | upfield | | | |
| No. of atom in the formula | Position relative to carboxy group | | | No. of compound | $\delta_i^{II}$, ppm | No. of compound | $\delta_i^{II}$, ppm | | |
| 2 | *ipso-* | 129.44 | 130.25 | IIc* | 130.67 | IIb,f | 130.62 | 0.05 | 130.65 |
| 3 | *orto-* | 130.28 | 129.60 | IIc | 129.59 | IIf | 129.53 | 0.06 | 129.55 |
| 4 | *meta-* | 128.49 | 128.37 | IIb,c,d | 128.34 | IIf | 128.27 | 0.07 | 128.30 |
| 5 | *para-* | 133.83 | 132.90 | IIb | 132.80 | IIf | 132.70 | 0.10 | 132.75 |

* – $\delta_2^{IIe}$ value seems to be incorrect, so we don't consider it.

*Table 3*

**Values $\delta_i^{III}$ ($i$ = 2–5) for IIIa–IIId compounds in $CDCl_3$ [3]**

| Carbon atom | | Max & min values of $\delta_i^{III}$ stipulated the low- and highfield limits of range | | | | Width of the $\delta_i^{III}$ interval, ppm | $\delta_i^{IIIchar.}$, ppm |
|---|---|---|---|---|---|---|---|
| | | downfield | | upfield | | | |
| No. of atom in the formula | Position relative to carboxy group | No. of compound | $\delta_i^{III}$, ppm | No. of compound | $\delta_i^{III}$, ppm | | |
| 2 | *ipso-* | IIIc | 130.68 | IIId | 130.63 | 0.05 | 130.65 |
| 3 | *orto-* | IIIa | 129.58 | IIIc | 129.54 | 0.04 | 129.56 |
| 4 | *meta-* | IIIa,b | 128.35 | IIId | 128.32 | 0.03 | 128.34 |
| 5 | *para-* | IIIb | 132.80 | IIIa,b | 132.75 | 0.05 | 132.77 |

*Table 4*

**Values $\delta_i^{IV}$ ($i$ = 2–5) for IVa–IVc compounds and $\delta_i^{Va}$ in $CDCl_3$ [3]**

| Carbon atom | | Max & min values of $\delta_i^{IV}$ stipulated the low- and highfield limits of range | | | | Width of the $\delta_i^{IV}$ interval, ppm | $\delta_i^{IVchar.}$, ppm | $\delta_i^{V}$ for *tert*-butylbenzoate |
|---|---|---|---|---|---|---|---|---|
| | | downfield | | upfield | | | | |
| No. of atom in the formula | Position relative to carboxy group | No. of compound | $\delta_i^{IV}$, ppm | No. of compound | $\delta_i^{IV}$, ppm | | | |
| 2 | *ipso-* | IVc | 131.28 | IVb | 130.99 | 0.29 | 131.10 | 132.11 |
| 3 | *orto-* | IVc | 129.57 | IVb | 129.51 | 0.06 | 129.55 | 129.41 |
| 4 | *meta-* | IVa,b,c | 129.26 | IVa,b,c | 128.26 | 0.00 | 129.26 | 128.13 |
| 5 | *para-* | IVa | 132.65 | IVc | 132.60 | 0.05 | 132.65 | 132.36 |

Values $\delta_2^{I}$ = 133.0 ppm and $\delta_5^{I}$ = 135.0 ppm presented in [2], seem to be erroneous and further will not be discussed.

In Fig. 2 there is a change diagram of $\delta_i^{N}$ ($i$ = 2–5) which is similar to that for carboxyl carbon atom (Fig. 1).

Nuclei absorption of all 4 types of phenyl group carbon atoms $\delta_i^{N}$ ($i$ = 2–5) takes place in higher field (~ 130 ppm) in comparison with carboxyl carbon. The signals of carbon atoms in *para*-position (C-5) are observed in the lowest field and those in *meta*-position (C-4) – in the highest field.

It should be noted the atypical direction of $\delta_2^{I} \rightarrow \delta_2^{V}$ change. In contrast to other four parameters $\delta_i^{I} \rightarrow \delta_i^{V}$ (including above mentioned $\delta_1^{I} \rightarrow \delta_1^{V}$ parameter, the benzoic acid signal (I) has the least value ($\delta_2^{I}$ = 129.44 ppm) and the *tert*-butylbenzoate one has the greatest value ($\delta_2^{V}$ = 132.11 ppm). The absence of abrupt jumps is characteristic for mentioned curve but two extreme zones are steeper than the middle one. It is interesting that upfield zone described by $\delta_1^{IVa} \rightarrow \delta_1^{V}$ is steeper than we expected studying $\delta_1^{I} \rightarrow \delta_1^{IIa}$ zone.

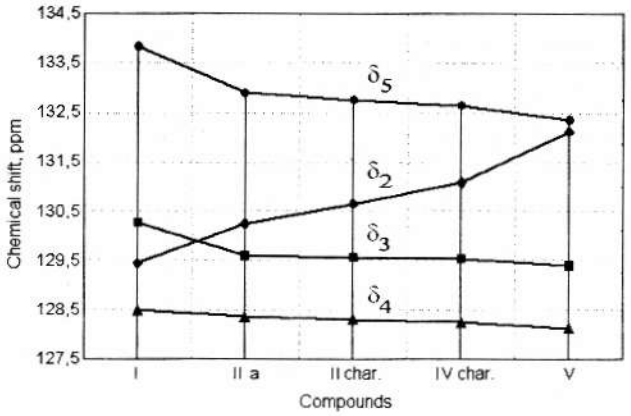



**Fig. 2.** The change of $\delta_i^C$ in the row:

$I \rightarrow IIa \rightarrow II^{char.} \rightarrow IV^{char.} \rightarrow V$ ($i = 2–5$)

Zones $\delta_3^I \rightarrow \delta_3^V$ and $\delta_5^I \rightarrow \delta_5^V$ at the transfer from benzoic acid to its esters are similar to $\delta_1^I \rightarrow \delta_1^V$ of carboxyl atom of C-1 carbon presented in Fig. 1, except those fact that $\delta_i^I \rightarrow \delta_i^{IIa}$ ($i$ = 3, 5) zones are less steeper than $\delta_1^I \rightarrow \delta_1^{IIa}$. The curve $\delta_4^I \rightarrow \delta_4^V$, which is almost parallel to abscise axis, is similar to $\delta_2^I \rightarrow \delta_2^V$ curve (if we don't take into consideration the opposite sign of $\Delta\delta_4^N$), because its highest and lowest field zones are steeper than the middle zone.

Intervals $\Delta\delta^N$ ($i$ = 2–5) in which signals of 21 compounds (I–V) for all four types of carbon atom are situated are more narrow than $\delta_i^{I\text{-}V}$ (~7 ppm) interval for carboxyl carbon atom. The narrowest of $\delta_1^{I\text{-}V}$ intervals is an interval of highest field signals for C-4 *meta*-carbon atoms ($\delta_4^{I\text{-}V}$ = 0.36 ppm) and the widest one is an interval of C-2 *ipso*-carbon atoms ($\delta_2^{I\text{-}V}$ = 2.67 ppm).

All four parameters $\delta_i^{II}$ (i = 2–5) are also advisably divided into two groups. The first group consists of the single $\delta_i^{IIa}$ parameter for short-chain methylbenzoate and the second group contains other seven parameters $\delta_i^{IIb\text{-}h}$ for long-chain esters (IIb–IIh), starting from ethylbenzoate. There is practically full coincidence between corresponding $\delta_i^{IIchar.}$ and $\delta_i^{IIIchar.}$ parameters for all $i$ values ($i$ = 2–5) for typical long-chain, linear and branched primary benzoates (IIb–III). The intervals width ($\Delta\delta^N$) varies from 0.03 ppm ($\Delta\delta_4^{III}$) to 0.10 ppm ($\Delta\delta_5^{II}$), if the value $\delta_2^{IIe}$ = 130.83 ppm is not included into calculation $\Delta\delta_2^{II}$. These values are comparable with experiment error, which is ~0.02 ppm according to our estimation. Moreover, for carboxyl carbon atom these values are noticeably less than $\Delta\delta_1^{II}$ and $\Delta\delta_1^{III}$ (0.14 та 0.17 ppm, correspondingly). Coincidence of $\delta_i^{IIchar.}$ and $\delta_i^{IIIchar.}$ parameters, as well as narrowness[2] of mentioned intervals ($\Delta\delta^N$) testifies to the accuracy of measurements in [3] as well as to the absence of effect of alkyl group structure in primary benzoates (II, III) on the absorption of phenyl ring carbon atoms.

If $\delta_3^{IIchar.}$ and $\delta_3^{IIIchar.}$ values are given with 0.05 ppm accuracy, they are similar and equal to 129.55 ppm but if the accuracy is only 0.01 ppm, the mentioned values are slightly different: $\delta_3^{IIchar.}$ = 129.57 ppm, and $\delta_3^{IIIchar.}$ = = 129.54 ppm.

Another situation is observed in the case of $\delta_i^{IV}$ and $\Delta\delta_i^{IV}$ ($i$ = 2–5) parameters for secondary alkylbenzoates. There is a considerable spread in $\delta_2^{IV}$ values for $\delta_2^{IVa\text{-}c}$ parameters, similar to $\delta_1^{IVa\text{-}c}$, which results in the formation of the widest $\Delta\delta_i^N$ interval: $\Delta\delta_2^{IVa\text{-}c}$ = 0.29 ppm. It is interesting that for other three parameters $\Delta\delta_i^{IVa\text{-}c}$ ($i$ = 3–5) the intervals are again very narrow, less than 0.06 ppm. We may assume that unlike to the primary alkyl group the secondary one essentially affects the chemical shift of the nearest to this group C-1 and C-2 atoms. The width of $\Delta\delta_1^{IVa\text{-}c}$ та $\Delta\delta_2^{IVa\text{-}c}$ intervals confirms this fact. At the same time the chemical shifts of distant *ortho*-, *meta*- and *para*-carbon atoms actually are insensitive to such an effect.

Spectral data of the 4 alkylbenzoates (IIb, IIh, IIIa and IVa) recorded in $CDCL_3$ are presented in Table 1 and described in [2, 3]. The comparison of 16 analogous parameters $\delta_i^N$ ($i$ = 2–5) of phenyl ring carbon atoms shows the sufficient coincidence of the results with those presented in [2]. In 9 from 16 experiments the discrepancy in values of $\delta_i^N$ parameter does not exceed 0.10 ppm and 0.30 ppm – in other experiments. We may assume that shift of scale beginning (by ~0.25 ppm)[1] towards downfield in the isopropylbenzoate (IVa) spectra [2] is the reason for such discrepancy.

In spectra of 6 alkylbenzoates (IId, IIh, IIIe, IVd–IVf) recorded in $CD_2Cl_2$ [2] the corresponding $\delta_i^N$ ($i$ = 2–5) parameters for primary (II and III) and secondary (IV) alkylbenzoates are practically similar (see Table 1) and situated in quite narrow interval (0.2–0.3 ppm). Taking into account the insufficient measurement accuracy of $\delta_i^N$ values in [2], we would not compare them as we have done with parameters from [3]. It should be noted that $\delta_i^N$ ($i$ = 2–5) parameters obtained in $CD_2Cl_2$ [2] are shifted towards downfield in expected value [4] of 0.3–0.6 ppm in comparison with those obtained in $CDCl_3$. This shift is determined by the above-mentioned solvent effect ($\Delta\delta_i^{N\,solv.}$).

Adduced results allow us to assume that the following parameters of benzoyl fragment carbon atoms are characteristic for typical primary alkylbenzoates: $\delta_1^{IIchar.}$ = 166.6 ppm, $\delta_2^{IIchar.}$ = 130.65 ppm; $\delta_3^{IIchar.}$ = 129.55 ppm; $\delta_4^{IIchar.}$ = 128.3 ppm and $\delta_5^{IIchar.}$ = 132.75 ppm. The following values for the secondary alkylbenzoates (IV) are obtained in $CDCl_3$: $\delta_1^{IVchar.}$ = 166.05 ppm; $\delta_2^{IVchar.}$ =

[2] All $\delta_i^{IIf}$ ($i$ = 2–5) parameters are extreme. It means they determine the width of every $\Delta\delta^{II}$ interval from the side of upfield. Therefore, it is possible that during recording of NMR $^{13}C$ spectrum of IIf compound there was a shift of scale zero line to the upfield by 0.05 ppm [3]. If it is true, the introduction of systematic correlation +0.05 ppm for every $\delta_i^{IIf}$ value will result in the essential narrowing of all $\Delta\delta^{II}$ intervals.

$= 131.1$ ppm; $\delta_3^{IVchar.} = 129.55$ ppm; $\delta_4^{IVchar.} = 128.25$ ppm; $\delta_5^{IVchar.} = 132.65$ ppm. The comparison of these values is represented in Fig. 3 using the same method as for NMR $^1H$ spectra [1]. Characteristic parameters $\delta_i^{Nchar.}$ for methylbenzoate (IIa) and *tert*-butylbenzoate (Va) are presented in Fig. 4. Mentioned compounds differ alkylbenzoates (II–V).

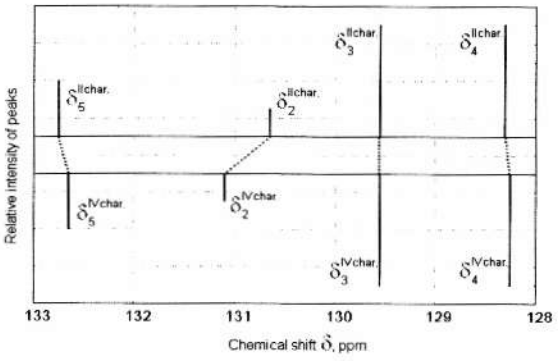



**Fig. 3.** Characteristic values $\delta_i^C$ for II and IV compounds

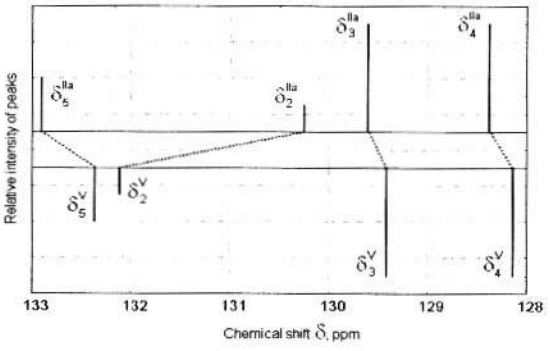



**Fig. 4.** Values $\delta_i^C$ for IIa and V compounds

## 4. Conclusions

Thus, joint spectral parameters of benzoyl fragment for the saturated unsubstituted alkylbenzoates (II–V) characterizing this class, do exist. Most of them have values similar to the parameters of initial benzoic acid and there are definite differences between them due to the structure of alkyl group.

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### ОСОБЛИВОСТІ СПЕКТРІВ ЯМР $^{13}C$ БЕНЗОЙНОЇ КИСЛОТИ ТА НАСИЧЕНИХ АЛКІЛБЕНЗОАТІВ. І. ХІМІЧНИЙ ЗСУВ ЯДЕР ВУГЛЕЦЕВИХ АТОМІВ БЕНЗОЇЛЬНОГО ФРАҐМЕНТУ

***Анотація.*** *Показано, що хімічні зсуви 5 типів ядер вуглецю бензоїльного фрагменту в насичених алкілбензоатах закономірно залежать від ступеню розгалуження алкільного радикалу біля α-вуглецевого атому алкоксильної групи. Прийнято типові значення хімічних зсувів цих п'яти типів ядер для первинних, вторинних та третинних алкілбензоатів.*

***Ключові слова:*** *спектри ЯМР $^{13}C$, хімічний зсув, насичені алкілбензоати, бензоїльний фрагмент, алкоксильна група.*