CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 2, No. 4, 2008 Chemistry

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PECULIARITIES OF NMR ^{13}C SPECTRA OF BENZOIC ACID AND ALKYLBENZOATES.
II. REGULAR SPECTRA DIFFERENCES BETWEEN BENZOIC FRAGMENTS OF ALKYLBENZOATES, DERIVATIVES OF PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

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Received: May 05, 2008

Abstract. Differential spectral parameters $D\delta^C$ of some primary, secondary, and tertiary alkylbenzoates have been calculated. Such parameters are the differences between the two basic spectral parameters – δ^C values in NMR ^{13}C spectra. The effective usage of differential spectral parameters has been shown using particular spectral task for primary alkylbenzoates as an example.

Key words: NMR ^{13}C spectra, primary, secondary and tertiary alkylbenzoates, basic and differential (spectral) parameters.

1. Introduction

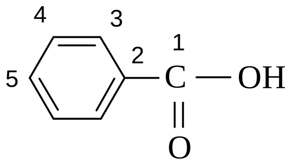
Making a comparison between NMR ^{1}H spectra of alkylbenzoates and alkylbenzoylformiates [1] we have establish the presence of minimum differences between differential parameters $D\delta^H$. It is impossible to reveal such differences using only basic parameters – chemical shift values δ^H. Very often differential parameters are relative to the group of atoms or even to the whole molecule, not to the particular atom. Virtual mathematic functions $D\delta^H$ usually have no physical meaning. We used them only for convenience and chose them *ad arbitrium* with the aim of visual illustration of subtle dependencies between substance composition and its spectral characteristics. The same approach is used in this work concerning the analysis of alkykbenzoates NMR ^{13}C spectra using differential parameters $D\delta^C$.

We have used two types of differential parameters $D\delta^C$. Parameters $\Delta\delta_{i-j}^{Nx} = \delta_i^{Nx} - \delta_j^{Nx}$ are used for different carbon atoms in one compound while parameters $\Delta\delta_i^{Nx-y} = \delta_i^{Nx} - \Delta\delta_i^{Ny}$ – for carbon atoms of one type in different compounds. The advantage of the parameters of the first type is high accuracy as they are calculated using basic parameters δ_i^{Nx} obtained from the same spectrum. Therefore, they are error-free. Measuring error is stipulated by condition non-identity of spectra record, constructive inaccuracy of different devices and inevitable human factor. However prevalence of differential parameters is limited by special investigations like this work. At the same time less accurate differential parameters of the second type $\Delta\delta_i^{Nx-y}$ are used widely for comparison of chemical shifts of carbon atoms of the same type in spectra of different substances.

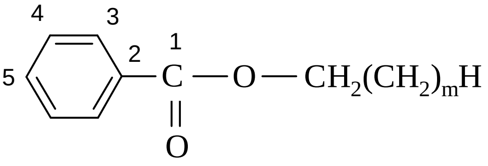
Interval parameters $\Delta\Delta\delta_{i-j}^{Nx-y} = \Delta\delta_{i-j}^{Nx} - \Delta\delta_{i-j}^{Ny}$ or $\Delta\delta_i^{Nx-y} - \Delta\delta_i^{Nx-y}$ are also used. They indicate interval width in which values $\Delta\delta_{i-j}^{Nx}$ or $\Delta\delta_i^{Nx-y}$ for all N compounds are laid, *i.e.* difference between maximum and minimum values of these parameters. In all equations numbers of corresponding carbon nuclei in benzoyl fragment are indicated by subscript Arabic numbers and letters (*i, j*= 1–5) and compound numbers are indicated by superscript Roman numbers and letters (I–V).

2. Experimental

Using values of basic parameters δ^C [2] we calculated values of differential parameters $D\delta^C$ of benzoyl fragment in NMR ^{13}C spectra of benzoic acid (I), its esters (II and III), derivatives of primary alcohols (so called primary benzoates), secondary (IV) and tertiary (V) alkylbenzoates.

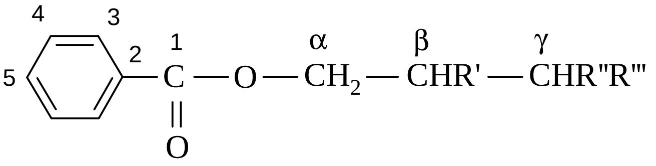


I

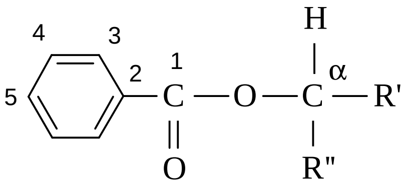


II

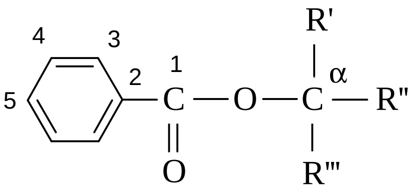
m=0–7 (a=m=0; b=m=1; c=m=2)



III



IV



V

The majority of δ_i^C values [2] have been taken from precision spectral investigations [3] with accuracy 0.01 ppm. We consider these values to be the most accurate though one of the values δ_2^{IIe} = 130.83 ppm is doubtful because it differs from other analogous parameters δ_2^{IIx} ($x = b - h$) in very narrow interval of δ values: from 130.62 to 130.67 ppm[1]. The accuracy of δ_i^C values from [4] and [2] is 0.1 ppm. Values of differential parameters (in brackets) have the same accuracy and are used only as auxiliary values for the comparison with analogous parameters calculated from data [3]. In all cases when the same basic parameters [3, 4] had different values (for instance, for benzoic acid) we preferred the data from [3].

3. Results and Discussion

Calculated values of 6 of 10 possible[2] differential parameters $\Delta\delta_{i\text{-}j}^{Nx}$ for compounds I–V are represented in the table. These 10 parameters may be conventionally divided into two groups: six parameters for phenyl fragment (i, j = 2–5) and 4 parameters – for all benzoyl group (i, j = = 1–5) when basic parameter δ_1^{Nx} is necessarily used. We examined 5 of 6 parameters $\Delta\delta_{i\text{-}j}^{Nx}$ of phenyl group (except parameter $\Delta\delta_{3\text{-}5}^{Nx}$) and 1 of 4 parameters $\Delta\delta_{1\text{-}2}^{Nx}$ of all benzoyl fragment because of the following reasons.

The first three parameters of phenyl group were chosen as distances between two adjoined peaks in phenyl region of the spectrum (125–135 ppm). Parameter $Dd_{5\text{-}2}$ is a difference between two most downfield signals of phenyl fragment. Then, as we moved toward upper-field parameters $Dd_{2\text{-}3}$ and $Dd_{3\text{-}4}$ were calculated. The forth parameter $Dd_{5\text{-}4}$ is an integral one and characterizes the distance between the most downfield and the most upper-field peaks of phenyl fragment in NMR ^{13}C spectrum. This nonindependent parameter[2] is equal to the sum of parameters $Dd_{5\text{-}2}$, $Dd_{2\text{-}3}$ and $Dd_{3\text{-}4}$.

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[1] We have no explanation of this deviation. Probably human factor (author's mistake or misprint) has taken place. Hence, δ_2^{IIe} = 130.83 ppm was excluded from our calculations.

[2] Theoretically maximum possible amount of $\Delta\delta_{i\text{-}j}^{Nx}$ parameters for all 5 types of carbon atoms (i, j = 1–5) is 10 pairs of conjugated parameters ($\Delta\delta_{i\text{-}j}^{Nx}$ and $\Delta\delta_{j\text{-}i}^{Nx}$), i.e. 20 items in all. Absolute values of both parameters in every pair (if they are not equal to zero) are the same, parameters differ only by sign. Since we are interested only in one parameter, for convenience we operated only with "plus" sign. Among 10 possible pairs of conjugative parameters (e.g. $\Delta\delta_{2\text{-}5}^{Nx}$ and $\Delta\delta_{5\text{-}2}^{Nx}$) we chose the parameter having positive value ($\Delta\delta_{5\text{-}2}^{Nx}$ in our case) for all or majority (in case of $\Delta\delta_{2\text{-}3}^{Nx}$ parameter) of compounds N_x = I–V.

Thus only 4 of 10 possible differential parameters are independent values. The other 6 parameters may be derived by combination of the mentioned 4 parameters.

Table

Values of differential parameters $Dd_{i\text{-}j}^{Nx}$ for compounds I–V

No	Radical R	Solvent	Literature	Parameter values, ppm					
				$\Delta\delta_{5\text{-}2}$	$\Delta\delta_{2\text{-}3}$	$\Delta\delta_{3\text{-}4}$	$\Delta\delta_{5\text{-}4}$	$\Delta\delta_{2\text{-}4}$	$\Delta\delta_{1\text{-}2}$
I	H	$CDCl_3$	3	4.39	-0.84	1.79	5.34	0.95	43.33
IIa	CH_3	$CDCl_3$	3	2.65	0.65	1.23	4.53	1.88	36.79
IIb	CH_2CH_3	$CDCl_3$	3	2.18	1.05	1.23	4.46	2.28	35.92
IIc	$(CH_2)_2CH_3$	$CDCl_3$	3	2.12	1.08	1.25	4.45	2.33	35.1
IId	$(CH_2)_3CH_3$	$CDCl_3$	3	2.13	1.08	1.24	4.45	2.32	36.93
IIb	CH_2CH_3	$CDCl_3$	4	(1.9)	(1.2)	(1.3)	(4.4)	(2.5)	35.95
IIe*	$(CH_2)_4CH_3$	$CDCl_3$	3	-	-	1.27	4.38	-	35.81
IIf	$(CH_2)_5CH_3$	$CDCl_3$	3	2.08	1.09	1.26	4.43	2.35	35.88
IIg	$(CH_2)_6CH_3$	$CDCl_3$	3	2.13	1.08	1.27	4.45	2.35	35.96
IIh	$(CH_2)_7CH_3$	$CDCl_3$	3	2.09	1.09	1.26	4.44	2.35	35.94
IIh	$(CH_2)_7CH_3$	$CDCl_3$	4	(1.9)	(1.2)	(1.3)	(4.4)	(2.5)	35.9
IIIa	$CH_2CH(CH_3)_2$	$CDCl_3$	3	2.12	1.08	1.23	4.44	2.32	35.81
IIIa	$CH_2CH(CH_3)_2$	$CDCl_3$	4	(2.1)	(1.1)	(1.3)	(4.4)	(2.4)	35.9
IIIb	$CH_2CH(CH_3)C_3H_7$	$CDCl_3$	3	2.15	1.08	1.22	4.45	2.30	35.98
IIIc	$CH_2CH(C_2H_5)C_4H_9$	$CDCl_3$	3	2.07	1.14	1.21	4.42	2.35	35.97
IIId	$(CH_2)_2CH(CH_3)_2$	$CDCl_3$	3	2.13	1.07	1.24	4.44	2.31	35.93
IVa	$CH(CH_3)_2$	$CDCl_3$	3	1.60	1.51	1.28	4.39	2.79	34.93
IVa	$CH(CH_3)_2$	$CDCl_3$	4	(1.6)	(1.5)	(1.3)	(4.4)	(2.8)	34.5
IVb	$CH(CH_3)CH_2CH_3$	$CDCl_3$	3	1.65	1.48	1.25	4.38	2.73	35.15
IVc	$CH(CH_2)_5$	$CDCl_3$	3	1.32	1.71	1.31	4.34	3.02	34.64
Va	$C(CH_3)_3$	$CDCl_3$	3	0.25	2.70	1.28	4.23	3.98	33.54
IId	$(CH_2)_3CH_3$	CD_2Cl_2	4	2.1	1.2	1.1	4.4	2.4	-
IIh	$(CH_2)_7CH_3$	CD_2Cl_2	4	1.7	1.4	1.2	4.3	2.6	35.4
IIIe	$CH_2C(CH_3)_3$	CD_2Cl_2	4	2.1	1.2	1.1	4.4	2.3	35.6
IVd	$CH(C_2H_5)CH(CH_3)_2$	CD_2Cl_2	4	-	-	1.2	4.4	-	-
IVe	$CH(CH_3)CH_2CH_2(CH_3)_2$	CD_2Cl_2	4	-	-	1.2	4.4	-	-
IVf	$CH[CH_2CH(CH_3)_2]_2$	CD_2Cl_2	4	-	-	1.2	4.4	-	-

*See note 1 to the text.

Application of other two differential parameters $Dd_{1\text{-}2}$ and $Dd_{2\text{-}4}$ is based on change of chemical shift d_i^{Nx} in the row I→IIa→IIb→IVa→Va [2]. The value of basic parameter d_2^{Nx} increases in the mentioned row and decreases for other four basic parameters d_1^{Nx} and d_3^{Nx} – d_5^{Nx}. These back changes of basic parameters d_i^{Nx} and d_j^{Nx} are useful for us and may be illustrated by calculation of differential parameter $Dd_{2\text{-}4}^{Nx}$. The increase of minuend $\delta_i^{Nx} = \delta_2^{Nx}$ and decrease of subtrahend $\delta_j^{Nx} = \delta_4^{Nx}$ essentially increase difference in equation $\Delta\delta_{i\text{-}j}^{Nx} = \delta_i^{Nx} - \delta_j^{Nx}$, *i.e.* specific differential parameter $\Delta\delta_{2\text{-}4}^{Nx}$. As a result, parameter's informability also increases allowing to fix even little but important differences between values of basic parameters δ_i^{Nx} and δ_i^{Ny} in those cases when they were unnoticeable due to their contiguity. The similar situation is characteristic for three other[2] parameters $\Delta\delta_{2\text{-}j}^{Nx}$. We consider them as informative parameters and examined them in details.

Parameter $\Delta\delta_{1\text{-}2}$ has unusually high value (~ 35–45 ppm) because the value of carboxyl group chemical shift (δ_1^{Nx} ~ 165–175 ppm), which is minuend, is much higher than chemical shift of *ipso*-carbon atom of phenyl ring, which is subtrahend. However this parameter is informative by the criterion of different directions of minuend and subtrahend.

Two other parameters of phenyl group $\Delta\delta_{3\text{-}4}^{Nx}$ and $\Delta\delta_{5\text{-}4}^{Nx}$ are low-informative because of the same directions of their minuend and subtrahend (in all cases parameters δ_3^{Nx}– δ_5^{Nx} decrease in the row I→IIa→IIb →IVa →Va). Thus they will not be discussed.

Values changes of all 6 differential parameters are represented in Fig. 1. In order to preserve figure scale we used ($\Delta\delta_{1\text{-}2}^{Nx}$ – 37.00) parameter, which is less by 37 ppm, instead of $\Delta\delta_{1\text{-}2}$. From Fig. 1 one can see that informative parameters $\Delta\delta_{2\text{-}j}^{Nx}$ are changed monotonically in the row I→IIa→IIb→II$_{\text{char.}}$→IVa→IVc→Va: parameters $\Delta\delta_{1\text{-}2}^{Nx}$ and $\Delta\delta_{5\text{-}2}^{Nx}$ decrease and parameters $\Delta\delta_{2\text{-}3}^{Nx}$ and $\Delta\delta_{2\text{-}4}^{Nx}$ increase. Such change, as mentioned, is larger than the change of basic parameters δ_i^{Nx} and δ_j^{Nx} reported in [2]. Low-informative parameters $\Delta\delta_{3\text{-}4}^{Nx}$ and $\Delta\delta_{5\text{-}4}^{Nx}$ in the above-mentioned row are insignificantly changed, especially in ester part of the row (IIa→IIb→IVa →Va).

The values contiguity of each of four informative parameters inside the same type of alkyl group should be noted. For primary alkylbenzoates (IId–IIh) and (IIIa–IIId) with long chain [2] intervals with high-accuracy values of each of three informative parameters of phenyl group ($\Delta\Delta\delta_{5\text{-}2}^{II,III}$ = 0.10 ppm, $\Delta\Delta\delta_{2\text{-}3}^{II,III}$ = 0.07 ppm, $\Delta\Delta\delta_{2\text{-}4}^{II,III}$ = = 0.05 ppm) do not exceed 0.1 ppm, as well as the values of initial basic parameters δ_i^{Nx} (i = 2–5) [2]. At the same time the value of “benzoyl” interval parameter $\Delta\Delta\delta_{1\text{-}2}^{II,III}$ as well as corresponding basic parameter $\Delta\delta_1^{II,III}$ is rather higher and equal to 0.17 ppm. All these data reveal that interval width of differential parameter $\Delta\Delta\delta_{i\text{-}j}^{Nx\text{-}y}$ is determined by maximum width of $\Delta\delta_i^{Nx\text{-}Ny}$ interval of initial basic parameter δ_i^{Nx}. Subtraction of the two basic parameters in all 4 cases does not result in the increase of interval between maximum and minimum values of differential parameters.

One can see from the Table that for primary alkylbenzoates less-accurate differential parameters calculated on the basis of data reported in [4], including the parameters obtained using deuteromethylenechloride as a solvent, are similar to corresponding accurate parameters obtained from the data reported in [3]. Lesser values of parameter $\Delta\delta_{5\text{-}2}^{II,III}$ in $CDCl_3$ and CD_2Cl_2, as well as parameter $\Delta\delta_{5\text{-}2}^{IIb}$ in $CDCl_3$ [4] are exclusions. We can not explain the reasons of such deviations; probably values of basic parameters δ_2^{IIb}, δ_2^{IIh}, δ_5^{IIb} and δ_5^{IIh} were measured inaccurately (see also [2]).

If we compare the values of informative differential parameters of three secondary benzoates, it should be advisable to single out cyclohexylbenzoate (IVc), which

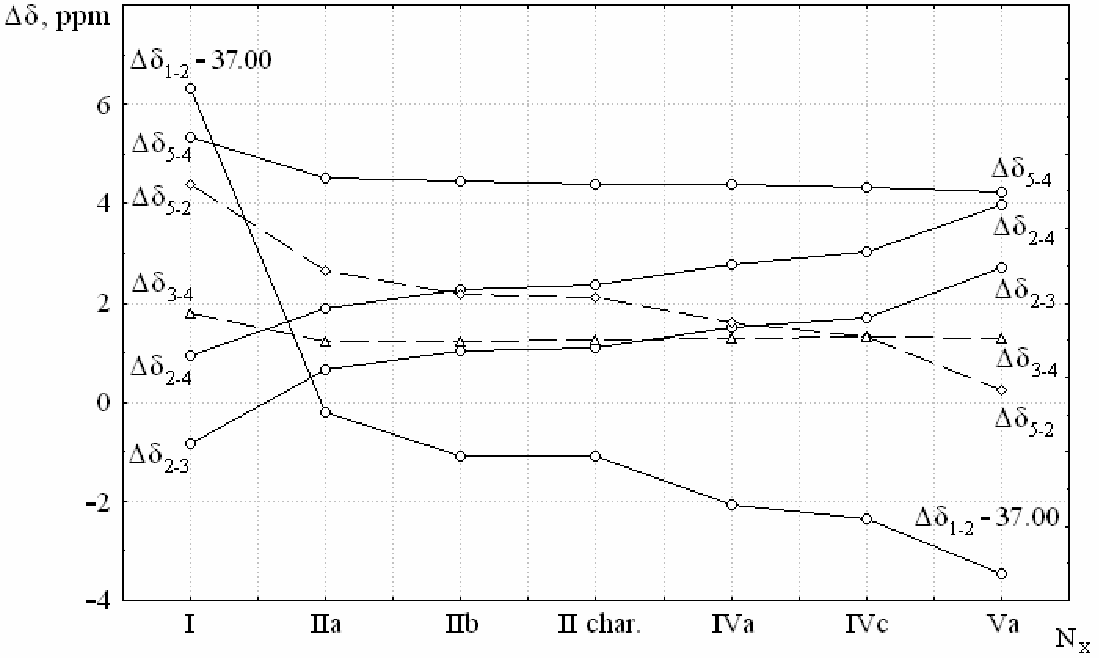

Fig. 1. The change of some differential parameters $\Delta\delta_{i\text{-}j}^{Nx}$ (i, j = 1–5) in the row I→IIa→IIb→II$_{\text{char}}$→IVa→IVc→Va

does not definitely relate to alkylbenzoates but to cycloalkylbenzoate. Parameters of isopropylbenzoate (IVa) and secondary butylbenzoate (IVb) are very similar but essentially differ from cyclohexylbenzoate (IVc). The latter shift towards values of *tert*-butylbenzoate (Va) though they are close to values of secondary benzoates (IVa and IVb).

Thus, informative differential parameters $\Delta\delta_{i-j}^{Nx}$, being similar to each other inside the class of primary alkylbenzoates, are essentially changed while transferred to other classes, *i.e.* to secondary and tertiary classes. Moreover there is a clear difference between differential parameters of acyclic alkylbenzoates and cyclohexylbenzoate containing secondary alicyclic alkyl group. It should be also noted that such a difference was insignificant for basic parameters δ_i^{Nx} of the mentioned compounds. Therefore, changes of all six differential parameters $\Delta\delta_{i-j}^{Nx}$ in the row I→IIa→IIb→IVa→IVc→Va, including cyclohexylbenzoate (IVc) and generalized characteristic augmented parameters $\mathrm{II}_{\mathrm{char.}}$, are present in Fig. 1.

The effect of solvent in which NMR ^{13}C spectra were obtained on the values of differential parameters is weaker compared with that on values of basic parameters δ_i^{Nx} [2].

In order to check the efficiency of differential parameters $\Delta\delta_{i-j}^{Nx}$ for interpretation of thin spectral differences we examined change character of spectral parameters δ_i^{Nx} in the intermediate ethyl- (IIb) and propyl- (IIc) benzoates, which was not done earlier while investigating the basic parameters δ_i^{Nx} only [2]. Based on the mentioned values propylbenzoate (IIc) should be added to typical long-chain linear alkylbenzoates starting from butylbenzate (IId). Ethylbenzoate (IIb) is a doubtful compound. It may be intermediate between short-chain methylbenzoate (IIa) and typical long-chain alkylbenzoates or it may be enlisted to the latter ones similar to propylbenzoate. Since we expected that comparable informative differential parameters $\Delta\delta_{i-j}^{IIx}$ differ by less than 0.1 ppm we did not consider the two parameters $\Delta\delta_{i-j}^{IIx}$ ($\Delta\delta_{i-j}^{IIb}$ and $\Delta\delta_{i-j}^{IIh}$), calculated from [4].

While investigating all 4 parameters $\Delta\delta_{i-j}^{IIx}$ and $\Delta\delta_{i-j}^{IIIx}$ of primary benzoates (II, III) essential difference between values of short-chain methylbenzoate (IIa) and typical long-chain esters (IId–IIh) has been observed.

Investigation results of 4 differential parameters $\Delta\delta_{i-j}^{Nx}$ are represented in Fig. 2.

The value of parameter $\Delta\delta_{5-2}^{IIx}$ (x = d–h) for five long-chain primary benzoates (except amylbenzoate IIe[1]) changes within the narrow range of 2.08–2.13 ppm, therefore the width of the change interval is narrow too (interval parameter $\Delta\Delta\delta_{5-2}^{IId-h} = 0.05$ ppm). We denominated arithmetic average between maximum ($\Delta\delta_{5-2}^{IId} = \Delta\delta_{5-2}^{IIg} = 2.13$) and minimum ($\Delta\delta_{5-2}^{IIf} = 2.08$ ppm) values as averaged parameter for unbranched primary alkylbenzoates with symbol $\Delta\delta_{5-2}^{IIav}$ (analogously to [2]). It is equal to 2.105 ppm and after its rounding with accuracy to 0.01 ppm $\Delta\delta_{5-2}^{IIav.} = 2.11$ ppm.

The value of parameter $\Delta\delta_{5-2}^{IIIx}$ (x = a–d) for four long-chain branched primary benzoates (IIIa–IIId) varies within the wider range of 2.07–2.15 ppm. Hence, interval parameter $\Delta\Delta\delta_{5-2}^{IIIa-d}$ is wider as well and equal to 0.08 ppm. The value of averaged parameter $\Delta\delta_{5-2}^{IIIav.}$ is equal to: (2.07 + 2.15)/ 2 = 2.11 ppm.

Whereas $\Delta\delta_{5-2}^{IIav} = \Delta\delta_{5-2}^{IIIav} = 2.11$ ppm, we assumed this value as characteristic value of both parameters $\Delta\delta_{5-2}^{IIx}$ and $\Delta\delta_{5-2}^{IIIx}$ for typical long-chain primary alkylbenzoates II and III and denominated it analogously to [2] as $\Delta\delta_{5-2}^{IIchar} = 2.11$ ppm. The characteristic interval parameter $\Delta\Delta\delta_{i-j}^{Nxchar}$ in such case (when wider[3] interval merges the narrower one) is equal to the wider interval: $\Delta\Delta\delta_{5-2}^{IIchar} = \Delta\Delta\delta_{5-2}^{IIIa-d} = 0.08$ ppm.

As was expected the value of parameter ($\Delta\delta_{5-2}^{IIa} = 2.65$ ppm) for short-chain methylbenzoate is significantly higher and the value of parameter ($\Delta\delta_{5-2}^{IIb} = 2.18$ ppm) is still high and considerably close to the value of characteristic parameter ($\Delta\delta_{5-2}^{IIchar} = 2.11$ ppm). The value of parameter ($\Delta\delta_{5-2}^{IIc} = 2.12$ ppm) of average-chain propylbenzoate (IIc) is practically the same as ($\Delta\delta_{5-2}^{IIchar} = 2.11$ ppm) and is within the above-mentioned interval $\Delta\Delta\delta_{5-2}^{IIchar} = 0.08$ ppm.

One can see from Fig. 2 that other two "phenyl" parameters $\Delta\delta_{2-3}^{IIx}$ and $\Delta\delta_{2-4}^{IIx}$ have the same ratio between short-, average- and long-chain compounds.

However, the forth informative parameter $\Delta\delta_{1-2}^{IIx}$, so called "benzoyl" parameter, which is not presented in Fig. 2, behaves in another way. In such a case not only expected value of parameter ($\Delta\delta_{1-2}^{IIc} = 35.93$ ppm) for propylbenzoate (IIIc) but even value of parameter ($\Delta\delta_{1-2}^{IIb=} = 35.92$ ppm) for ethylbenzoate (IIb) is located in the widest interval $\Delta\Delta\delta_{1-2}^{IIchar} = 0.17$ ppm (from 35.81 to 35.98 ppm) among all $\Delta\Delta\delta_{i-j}^{Nx-y}$ intervals. This situation is analogous to that of non-informative parameter $\Delta\delta_{3-4}^{Nx}$ presented in Fig. 2.

We may explain the misfit between the observed and the expected values of parameter $\Delta\delta_{1-2}^{IIb}$ in the following way. Probably, the behavior of basic parameter δ_1^{Nx} for carboxyl carbon atom C-1 with regard to the influence of alkyl group structure differs from the behavior of basic parameters δ_j^{Nx} (j = 2–5) for carbon atoms of phenyl ring (C-2–C-5). Therefore, the behaviour of corresponding

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[3] When the wider interval does not merge the narrower one (e.g. for parameter $\Delta\delta_{3-4}^{Nx.}$, N = II,III), the characteristic interval $\Delta\Delta\delta_{3-4}^{IIchar.}$ is calculated as difference between two extremum of parameters $\Delta\delta_{3-4}^{IIi}$ and $\Delta\delta_{3-4}^{IIIj}$: $\Delta\Delta\delta_{i-j}^{Nx-y} = \Delta\delta_{i-j}^{Nx} - \Delta\delta_{i-j}^{Ny}$. One of extreme value belongs to the compound IIx ($\Delta\delta_{3-4}^{IIg.} = 1.27$ ppm) and the second one – to the compound IIIy ($\Delta\delta_{3-4}^{IIId} = 1.21$ ppm). Therefore, $\Delta\Delta\delta_{3-4}^{IIchar} = 0.06$ ppm and $\Delta\delta_{3-4}^{IIchar} = 1.24$ ppm.

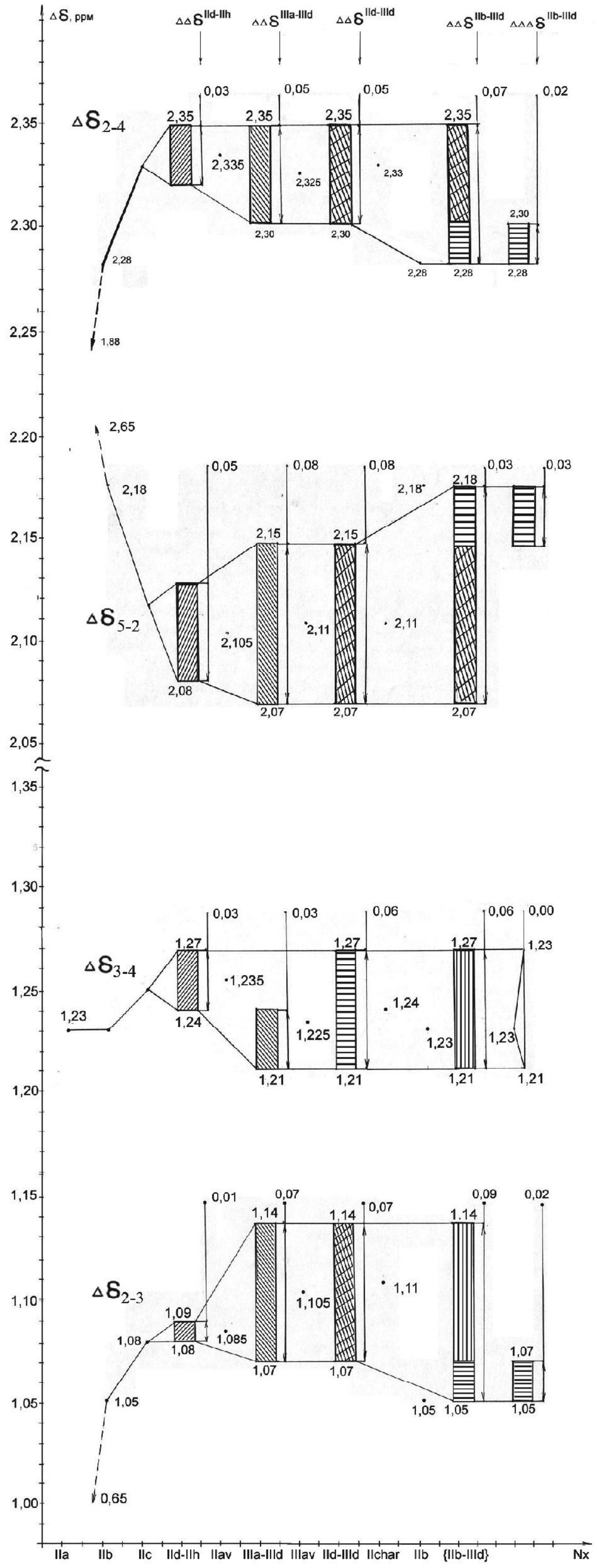

Fig. 2. The change of some differential parameters $\Delta\delta_{i-j}^{Nx}$ (i, j = 1–5) in the row IIa→IIb→IIc→$\mathrm{II_{av}}$→$\mathrm{III_{av}}$→$\mathrm{II_{char}}$→(IIb–$\mathrm{II_{char}}$). Intervals of $\Delta\delta$ diffusive parameters are marked as hatched parallelepipeds

differential parameter $\Delta\delta_{1-2}^{IIx}$ differs too and its use advisability is doubtful.

However, another explanation may take place, ***e.g.*** incommensurability of absolute values of differential parameters $\Delta\delta_{1-2}^{IIx} \sim 36$ ppm from the one side and values of interval parameters ($\Delta\Delta\delta_{1-2}^{IIb-IIchar} = \Delta\delta_{1-2}^{IIb} - \Delta\delta_{1-2}^{IIchar} = 36.92 - 39.895 = 0.025$ ppm) – from the other. The ratio between these values is more than 1000:1. Taking into account the accuracy of our investigations, it is not quite correct to compare the mentioned values because even minimum measuring error for the parameter δ_i^{Nx} may be determinative.

Due to the small width of intervals $\Delta\Delta\delta_{i-j}^{IIchar}$ calculated for long-chain primary alkylbenzoates, as well as contiguity of values $\Delta\delta_{i-j}^{IIchar}$ and $\Delta\delta_{i-j}^{IIb}$ (parameter of intermediate ethylbenzoate), involvement of the latter value in calculations insignificantly increases the width of new intervals. Thus, value of “united” interval parameter $\Delta\Delta\delta_{5-2}^{IIb-IIId}$, involving parameter $\Delta\delta_{5-2}^{IIb}$ increases only by 0.03 ppm (from $\Delta\Delta\delta_{5-2}^{IIchar} = 0.08$ to $\Delta\Delta\delta_{5-2}^{IIb-IIId} = 0.11$ ppm). Let us denominate this value as $\Delta\Delta\Delta\delta_{5-2}^{IIb-IIId}$ parameter. In the same way we denominate the width increase from 0.07 to 0.09 ppm of parameter $\Delta\Delta\delta_{2-3}^{IIb-IIId}$ as $\Delta\Delta\Delta\delta_{2-3}^{IIb-IIId} = 0.02$ ppm and width increase from 0.04 to 0.07 ppm of parameter $\Delta\Delta\delta_{2-4}^{IIb-IIId}$ as $\Delta\Delta\Delta\delta_{2-4}^{IIb-IIId} = 0.03$ ppm. The similar increase from 0.03 to 0.04 ppm is observed for non-informative parameter $\Delta\Delta\delta_{5-4}^{IIb-IIId}$ (parameter $\Delta\Delta\Delta\delta_{5-4}^{IIb-IIId} = 0.01$ ppm). At the same time the width of non-informative parameter $\Delta\Delta\delta_{3-4}^{IIb-IIId}$ is constant and equal to 0.06 ppm (analogously to the informative parameter $\Delta\Delta\delta_{1-2}^{IIb-IIId} = 0.17$ ppm).

As mentioned above, all operations carried out with 4 of 6 differential parameters $\Delta\delta_{i-j}^{Nx}$, which are typical for primary benzoates (II and III) in the row IIb→IIc→IIav→IIIav→IIchar, are represented in Fig. 2. We examined three informative parameters $\Delta\delta_{2-3}^{Nx}$, $\Delta\delta_{2-4}^{Nx}$ and $\Delta\delta_{5-2}^{Nx}$, and one non-informative parameter $\Delta\delta_{3-4}^{Nx}$. Parameters $\Delta\delta_{1-2}^{Nx}$ and $\Delta\delta_{5-4}^{Nx}$ were excluded by the following reasons. Involvement of parameter $\Delta\delta_{1-2}^{Nx}$ requires 10 time scale change which renders the diagram not visual. Moreover, involvement of both parameters will not result in the appearance of new information because their behaviors are similar to the other ones represented in the diagram.

4. Conclusions

The comparison of differential parameters $\Delta\delta_{i-j}^{N}$ for long-chain linear alkylbenzoates (IId–IIh) with corresponding values of intermediate by the alkyl chain length ethyl (IIb) and propyl (IIc) homologes allows concluding that the behavior of propylbenzoate corresponds to long-chain compounds behavior and ethylbenzoate behavior is intermediate between the above-mentioned compounds and short-chain methylbenzoate. However, ethylbenzoate behavior is closer to long-chain homologes.

The list of characteristic differential parameters for typical primary (long-chain), secondary and tertiary alkylbenzoates, as well as cycloalkylbenzoates (IV_{cycl}) is presented below.

For parameter $\Delta\delta_{5-2}^{N}$ we assumed following values (with accuracy of 0.05 ppm): $\Delta\delta_{5-2}^{IIchar} = 2.10$ ppm, $\Delta\delta_{5-2}^{IVchar} = 1.60$ ppm, $\Delta\delta_{5-2}^{Vchar} = 0.25$ ppm, $\Delta\delta_{5-2}^{(IV\ cycl)\ char} = 1.30$ ppm.

For parameter $\Delta\delta_{2-3}^{N}$: $\Delta\delta_{2-3}^{IIchar} = 1.10$ ppm, $\Delta\delta_{2-3}^{IVchar} = 1.50$ ppm, $\Delta\delta_{2.3}^{Vchar} = 2.70$ ppm, $\Delta\delta_{2-3}^{(IVcycl)\ char} = 1.70$ ppm.

For parameter $\Delta\delta_{2-4}^{N}$: $\Delta\delta_{2-4}^{IIchar} = 2.35$ ppm, $\Delta\delta_{2-4}^{IVchar} = 2.75$ ppm, $\Delta\delta_{2-4}^{Vchar} = 4.00$ ppm, $\Delta\delta_{2-4}^{(IVcycl)\ char} = 3.00$ ppm.

For parameter $\Delta\delta_{1-2}^{N}$: $\Delta\delta_{1-2}^{IIchar} = 35.90$ ppm, $\Delta\delta_{1-2}^{IVchar} = 35.05$ ppm, $\Delta\delta_{1-2}^{Vchar} = 33.55$ ppm, $\Delta\delta_{1-2}^{(IVcycl)\ char} = 34.65$ ppm.

For parameter $\Delta\delta_{3-4}^{N}$: $\Delta\delta_{3-4}^{IIchar} = 1.25$ ppm, $\Delta\delta_{3-4}^{IVchar} = 1.25$ ppm, $\Delta\delta_{3-4}^{Vchar} = 1.30$ ppm, $\Delta\delta_{2-3}^{(IVcycl)\ char} = 1.30$ ppm.

For parameter $\Delta\delta_{5-4}^{N}$: $\Delta\delta_{5-4}^{IIchar} = 4.40$ ppm, $\Delta\delta_{5-4}^{IVchar} = 4.40$ ppm, $\Delta\delta_{5-4}^{Vchar} = 4.25$ ppm, $\Delta\delta_{5-4}^{(IVcycl)\ char} = 4.35$ ppm.

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ОСОБЛИВОСТІ СПЕКТРІВ ЯМР ^{13}С БЕНЗОЙНОЇ КИСЛОТИ І НАСИЧЕНИХ АЛКІЛБЕНЗОАТІВ. II. ВИЯВЛЕННЯ ЗАКОНОМІРНИХ ВІДМІННОСТЕЙ У СПЕКТРАХ БЕНЗОЇЛЬНОГО ФРАГМЕНТУ АЛКІЛБЕНЗОАТІВ, ПОХІДНИХ ПЕРВИННИХ, ВТОРИННИХ І ТРЕТИННИХ СПИРТІВ

Анотація. *Для ряду первинних, вторинних і третинних алкілбензоатів розраховано деякі диференційні спектральні параметри* $\Delta\delta^C$*, які є різницею між двома базовими спектральними параметрами – значеннями* δ^C *у спектрах ЯМР* ^{13}*С. На прикладі вирішення конкретної спектральної задачі для первинних алкілбензоатів показано ефективність використання диференційних спектральних параметрів.*

Ключові слова: *спектри ЯМР* ^{13}*С, первинні, вторинні і третинні алкілбензоати, базові та диференційні (спектральні) параметри.*