CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 5, No. 3, 2011 Chemistry

Volodymyr Mizyuk and Volodymyr Shibanov

EFFECT OF SPECTRA RECORDING CONDITIONS ON THE EXAMPLE OF CHEMICAL SHIFTS CALCULATION IN CMR SPECTRA OF 1-PENTYLBENZOYLFORMATE

Ukrainian Academy of Printing, Lviv, Ukraine

Received: August 18, 2010 / Revised: November 25, 2010 / Accepted: January 30, 2011

© Mizyuk V., Shibanov V., 2011

Abstract. The concept of "compatible" and "incompatible" CMR spectra has been introduced. Application of compatibility increments (IC) allows to calculate the chemical shifts of C^2 and C^3 atoms of pentyloxyl fragment in 1-pentylbenzoylformate with a sufficiently good accuracy.

Keywords: CMR spectra, benzoates, benzoylformates, basic and differential spectral parameters, chemical shifts, additional increments, "compatible" and "incompatible" spectra.

1. Introduction

It has been shown [1] that using calculation methods [2] developed by us, attribution of signals in CMR spectra which are close by chemical shifts to C^2 and C^3 atoms of pentoxyl fragment of 1-pentanol esters, including 1-pentylbenzoate (I) at $d^C_i \sim 28$ ppm [3, 4] may be proved. We did not include the discussion of one more spectrum – pentylbenzoylformate (II) into [1] – because calculated values differ from experimental ones by ~ 0.3 ppm that is greater than admissible difference of 0.2 ppm[1]. CMR spectrum of 1-pentylbenzoylformate (II) is given in [3] with the aim of the confirmation of one of by-products structure extracted from reaction mixture at the synthesis of photoinitiator – 2,2-dipentyloxy-1-phenylethanone. It is also recorded in $CDCl_3$ but without accurate observance of concentration and temperature conditions. The reason is the absence of necessity to obtain table data of the basic spectral parameters d^C_i for 1-pentylbenzoylformate (II).[2]

[1] The choice of maximum permissible value of the difference between calculated and experimental values is arbitrary. We consider that it depends upon "repeatability" of the same spectra in various literature sources and should be equal to maximum permissible values of the difference between basic spectral parameters (δ^C_i) in spectra which are compatible (see below).

[2] Such spectra are usually called "routine" spectra.

1.1. Identification of "Spectra Compatibility" Criteria

It is convenient to characterize the difference between the values of the same basic [4] spectral parameter d^C_i for every *i*-type carbon nuclei in spectra A (d^A_i) and B (d^B_i) of the same substance by differential [4] spectral parameters $\Delta d_i^{A\text{-}B}$ calculated according to Eq. (1):

$$\Delta\delta^{A\text{-}B}_i = \delta^A_i - \delta^B_i \qquad (1)$$

It concerns both calculated $(\delta^C_i)_{calc.}$ and experimental $(\delta^C_i)_{exp.}$ values.

The coincidence of the experimental values of d^C_i values in spectra of different compounds given in different informational sources becomes possible only at high degree of spectra repeatability (for instance spectra A and B) of the same compound recorded by different authors under same conditions. Such spectra as well as sources where they are present we define as "compatible". The absolute values of $|\Delta\delta^{A\text{-}B}_i|$ parameters for "compatible" CMR spectra should tend to zero. However, they usually have values of 0.1–0.2 ppm. If such values considerably exceed the value of 0.2 ppm, then we consider such spectra as "incompatible". The concept of "compatibility" can be also extended to the same fragments of various substances spectra.

To our mind one of the possible reasons of such exceeding of assumed value of 0.2 ppm by $|\Delta\delta^{A\text{-}B}_i|$ parameter is the difference between recording conditions of the same substance spectra. The large differences usually occur in "incompatible" spectra, taken from "incompatible" sources.

According to the above logic, the value of 0.2 ppm is chosen as the maximum allowable absolute value of differences between calculated and experimental basic parameters δ^C_i (denominated as $|\Delta\delta^{A\text{-}B}_i|_{calc.}$). Thus the condition of "compatibility" between calculated and experimental values δ^C_i is formulated using the inequality $|\Delta\delta^{A\text{-}B}_i|_{calc} \leq 0.2$ ppm.

2. Experimental

CMR spectra for all I-VIII esters (except of II and VII spectra) were taken from two sources which are the most reliable to our mind – internet-site [5] and atlas of NMR spectra, Aldrich firm [6]. The data were obtained in deuterochloroform as a result of accurate physico-chemical investigations (fixed temperature and concentration). They usually are in good agreement with each other, *i.e.* admitted by us as "compatible".

This conclusion is usually impossible for "routine" spectra (also obtained in $CDCl_3$) which are given in the articles concerning the synthesis of new substances, for example, for the spectra of II and VII compounds described in [3]. It is a great probability that the basic spectral parameters δ^{C}_{i} present in them would be "incompatible" with δ^{C}_{i} values from [5] and [6].

To study the effect of CMR spectrum recording conditions on $\delta^{C,N}_{i}$ parameters (for each of the *i*-type carbon atoms in the compound N), we consider CMR spectra of 1-octanol esters (octylformate (III) taken from [6], octylacetate (IV) [6], two spectra octylbutyrate (V) [5, 6], octylbenzoate (VI) and octylbenzoylformate (VII) [3]) as the most informative example. The spectral data of related to esters octyltosylate (VIII) [5] are present for comparison.

$R\text{-}C(O)\text{-}O\text{-}C^1H_2\text{-}C^2H_2\text{-}C^3H_2\text{-}C^4H_2\text{-}C^5H_3$ where R = Ph- (I), Ph-C(O)- (II)
I, II

$R\text{-}C(O)\text{-}O\text{-}C^1H_2\text{-}C^2H_2\text{-}C^3H_2\text{-}C^4H_2\text{-}C^5H_2\text{-}C^6H_2\text{-}^{(\omega-1)}C^7H_2\text{-}^{(\omega)}C^8H_3$
III - VII
where R = H- (III), Me- (IV), Pr^n- (V), Ph- (VI), Ph-C(O)- (VII)

$p\text{-}CH_3\text{-}C_6H_4\text{-}S(O_2)\text{-}O\text{-}C^1H_2\text{-}C^2H_2\text{-}C^3H_2\text{-}C^4H_2\text{-}C^5H_2\text{-}C^6H_2\text{-}^{(\omega-1)}C^7H_2\text{-}^{(\omega)}C^8H_3$
VIII

The values of basic and some differential (as described below) spectral parameters are given in Tables 1 and 2.

3. Results and Discussion

As it has been shown in [2], in order to define a set of increments necessary for the calculation of the basic spectral parameters ($\delta^{C}_{calc.}$) we need the analysis of the spectra of the same class substances with the most long alkyl chains. For benzoate and benzoylformates classes the esters of *n*-octyl alcohol are homologues, for which reliable spectral data exist.

3.1. Analysis of 1-Octanol Esters CMR Spectra

The most detailed analysis was made for three spectra of most interesting to us substance – octylbenzoate (VI). Two of them were obtained in deuterochloroform and published in different sources [3, 5], and the third one is the CMR spectrum, obtained in deutero-metylenechloride as a solvent, and not published before. Table 1 represents values of basic (d^{C}_{i}) and differential spectral parameters of CMR spectra (taken in parentheses) for 13 types of octylbenzoate (VI) carbon atoms. Spectral parameters [$100\cdot\Delta\delta^{VI(n)-[5]}_{i}$] were chosen as differential ones. The basis for choice is given below.

3.1.1. Analysis of octylbenzoate (VI) CMR spectra

Fig. 1 shows listed in Table 1 differential parameters $\Delta\delta^{VI(n)}_{i}$, enlarged in 100 times (for the convenience of working with the whole numbers) and calculated for all i = 13 types of carbon atoms in the molecule (VI) in all three spectra.

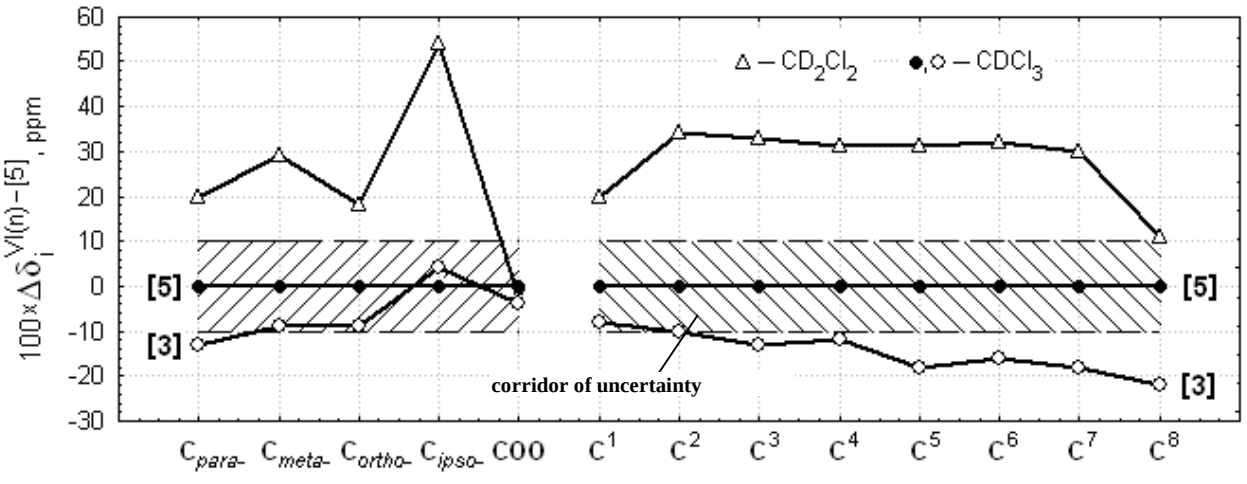

Fig. 1. Differential spectral parameters ($100\cdot\Delta\delta^{VI(n)-[5]}_{i}$) in CMR spectra of octylbenzoate (VI)

Table 1

Basic (δ^{C}_{i}) and differential spectral parameter ($100\cdot\Delta\delta^{VI(n)-[5]}_{i}$) of octylbenzoate (VI) CMR spectra, ppm

Source of information	Solvent	Carbon atom's type in (VI)												
		C*para*-	C*meta*-	C*orto*-	C*ipso*-	COO	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8
[5]	$CDCl_3$	132.74(0)	128.30(0)	129.56(0)	130.65(0)	166.59(0)	65.11(0)	28.82(0)	26.12(0)	29.26(0)	29.32(0)	31.86(0)	22.70(0)	14.10(0)
[3]	$CDCl_3$	132.61(-13)	128.21(-9)	129.47(-9)	130.69(+4)	166.55 (-4)	65.03(-8)	28.72(-10)	25.99(-13)	29.14(-12)	29.14(-18)	31.70(-16)	22.52(-18)	13.88(-22)
-	CD_2Cl_2	132.94(−20)	128.59(+29)	129.56(+18)	130.65(+54)	166.57 (-2)	65.31(+20)	29.16(+34)	26.45(+33)	29.57(+31)	29.63(+31)	32.18(+32)	23.00(+30)	14.21(+11)

Table 2

Basic (δ^{C}_{i}) and differential spectral parameters ($100\cdot\Delta\delta^{N-VI[5]}_{i}$) (in parentheses) in the CMR spectra of esters (III-VII) and tosylate (VIII) in $CDCl_3$, ppm

Subs-tance	Source of information	Carbon atom's type in VI						
		C^2	C^3	C^4	C^5	C^6	C^7	C^8
VI	[5]	28.82(0)	26.12(0)	29.26(0)	29.32(0)	31.86(0)	22.70(0)	14.10(0)
VI	[3]	28.72(-10)	25.99(-13)	29.14(-12)	29.14(-18)	31.70(-16)	22.52(-18)	13.88(-22)
III	[6]	28.61(-21)	25.91(-21)	29.23(-3)	29.23(-9)	31.85(-1)	22.71(+1)	14.10(0)
IV	[6]	28.69(-13)	25.98(-14)	29.21(-5)	29.26(-6)	31.83(-3)	22.66(-4)	14.06(-4)
V	[5]	28.82(0)	26.08(-4)	29.34(+8)	29.34(+2)	31.92(+6)	22.75(+5)	14.12(+2)
V	[6]	28.69(-13)	25.96(-16)	29.21(-5)	29.24(-8)	31.82(-4)	22.66(-4)	14.10(0)
VII	[3]	28.46(-36)	25.69(-43)	28.98(-28)	28.98(-34)	31.61(-25)	22.46(-24)	13.83(-27)
VIII	[5]	28.86(+4)	25.36(-76)	28.86(-40)	29.06(-26)	31.72(-14)	22.61(-9)	14.06(-4)

One can see the broken lines obtained by connection of plots representing Δd_i parameters for interconnected carbon atoms in the molecule (VI). Leftmost point is the value $\Delta\delta^{VI(n)}{}_p$ for *para*-carbon atom of the phenyl fragment, and at the rightmost one – the value $\Delta\delta^{VI(n)}{}_8$ for methyl – ω-carbon atom of octyloxyl group (OC-8).

The figure is plotting in such a way that spectrum (VI) taken from the most reliable source [5] is chosen as a main one. For this spectra we assumed all values of i = 13 types of $\Delta\delta^{VI[5]}{}_i$ parameters equal to zero, *i.e.* all 13 points in Fig. 1 are connected by a straight line with the ordinate equalling to zero.

The lower line represents the differential spectral parameters $\Delta\delta^{[3]-[5]}{}_i$, calculated by the same way from spectrum (VI) recorded in $CDCl_3$ but published in different works [3, 5]. For the spectrum of octylbenzoate (VI) taken from [3] and shown at the lower broken line, every i^{th} differential parameter $\Delta\delta^{VI[3]-[5]}{}_i$ is calculated from Eq. (1), where parameter $\delta^{VI[3]}{}_i$ is the minuend A and parameter $\delta^{VI[5]}{}_i$. is the subtrahend B.

Parameters $\Delta\delta^{solv.}{}_i = \delta^{MX}{}_i - \delta^{Ch}{}_i$, calculated from spectrum (VI) and recorded in deuteromethylenechloride and deuterochloroform [5] are represented at the upper line. Parameter $\Delta\delta^{solv}{}_i$ describes the difference between analogous values $d^C{}_i$ in spectra obtained in different solvents. On the top line in Fig. 1 all 13 points of $\Delta\delta^{solv.}{}_i$ parameters, calculated from Eq. (2) are connected:

$$\Delta\delta^{solv.}{}_i = \delta^{MX}{}_i - \delta^{Ch}{}_i \qquad (2)$$

Parameter $\delta^{MX}{}_i$ is a minuend and was obtained for the spectrum of benzoate (VI) in CD_2Cl_2 (as described above), and parameter $\delta^{Ch}{}_i$ is a subtrahend as parameter $\delta^{VI[5]}{}_i$ in the previous case, *i.e.* $\delta^{Ch}{}_i = \delta^{VI[5]}{}_i$. One can see from the symbols, the parameter $\Delta\delta^{solv.}{}_i$ is to compare the spectra, recorded in different solvents: deuteromethylenechloride (MX) and deuterochloroform.

One can see from Fig. 1 that for different types of carbon atoms i values of $\Delta\delta^{A-B}{}_i$ parameters are different. Thus, values of $\Delta d^{solv}{}_i$ parameters for all i atoms (except $\Delta d^{solv}{}_{COO}$ parameter) are positive, *i.e.* all signals (except $\Delta d^{MX}{}_{COO}$) obtained in CD_2Cl_2 spectrum are detected in a lower field, compared with the same signals obtained in $CDCl_3$ and given in [5]. Thus, the example of octylbenzoate (VI) CMR spectrum confirms our observations [7] concerning a lowfield shift (by ~ 0.2–0.3 ppm) of the single-type signals which occurs when the $CDCl_3$ solvent is changed for CD_2Cl_2.

It should be noted that for octylbenzoate (VI), for the majority of i = 13 types of carbon atoms parameter $\Delta\delta^{solv.}{}_i$ exceeds the value of +0.2 ppm. In particular, for octyloxyl fragment ($O–C_8H_{17}$) 6 medial parameters ($\Delta\delta^{solv.}{}_2 - \Delta\delta^{solv.}{}_7$) are approximately equal to +0.3 ppm, and only the extreme one has less value ($\Delta\delta^{solv.}{}_8$ = +0.1 ppm).

On the contrary, all $\Delta\delta^{[3]-[5]}{}_I$ parameters (except $\Delta\delta^{[5]-[3]}{}_{ipso}$-) have negative values, *i.e.* the majority of spectra plots from [3] is located under the zero line (spectrum plot in [5]). It means that in the spectrum given in [3] signals are detected in the upper field (except the signal of phenyl ring carbon *ipso*-atom) compared with the same signals from the spectrum given in [5] and the only positive parameter $\Delta\delta^{[3]-[5]}{}_{ipso}$ = +0.04 ppm has a small absolute value. Negative parameters $\Delta\delta^{[3]-[5]}{}_I$ of other three types of atoms (phenyl ring carbon atoms, carboxyl group atoms and octyl group C^1-C^4 atoms) have also small values (~ -0.1 ppm). And only for the last four carbon atoms of octyl group (C^5-C^8) the absolute value of $\Delta\delta^{[3]-[5]}{}_I$ negative parameters is essentially greater (0.16–0.22 ppm). The values of the most $\Delta\delta^{VI[3]-[5]}{}_i$ parameters depicted on the bottom line, on the contrary, are negative. 12 points of the spectral (VI) line from [3] (except the point C_{ipso}) are below the zero line. Thus, 12 different types of carbon atoms of the spectrum (VI) from [5] absorb in the lower field compared with the analogous atoms in the spectrum described in [3]. The majority of $\Delta\delta^{VI[3]-[5]}{}_i$ parameters [where i = *para*-, *metha*-, *orto*-carbon atoms of phenyl ring, carbalkoxyl group and atoms C^1-C^4 (i = 1, 2, 3, 4) of octyloxyl group) has a small absolute value (~ 0.1 ppm) and is situated in the below described "corridor of uncertainty". And only for the last four carbon atoms of octyloxyl group (C^5-C^8) the absolute value of negative parameters $|\Delta\delta^{VI[3]-[5]}{}_i|$ (i = 5, 6, 7, 8) is significantly higher (0.16–0.22 ppm).

3.1.2. Graphical analysis of esters (III-VIII) CMR spectra

Table 2 and Fig. 2 show the differential parameters $\Delta\delta^{N-VI[5]}{}_2 - \Delta\delta^{N-VI[5]}{}_8$, calculated from Eq. (1) for the compounds (III-VIII) (N = III-VIII).

The difference between spectral fragments of C^5-C^8 and C^1-C^4 atoms of octyl group in (VI) is especially obvious in Fig. 2, where $\Delta\delta^{[3]-[5]}{}_2 - \Delta\delta^{[3]-[5]}{}_8$ parameters are represented, as well as some other differential parameters of $\Delta d^{A-B}{}_i$ type from Eq. (1). In this figure in all cases spectrum No2 (subtrahend in Eq. (1)) is octylbenzoate (VI) spectrum recorded in $CDCl_3$ and given in [5]. The minuends in Eq. (1) are basic spectral parameters $d^C{}_i$ of octyl alcohol and organic acids esters: octylformate (III) [6], octylacetate (IV) [6], two spectra of octylbutyrate (V) [5, 6] and octylbenzoylformate (VII) [3]. Spectral data of octyltozylate (VIII) [5] are represented for the comparison.

The nature of acyl radicals R has a greater influence on the carbon atoms which are closer to the acyl fragment (C^1-C^4) in esters (III-VIII), than on outlying atoms of the chain (C^5-C^8). As a rule, the absolute values of parameters $|\Delta\delta^{N-VI[5]}{}_i|$ (i = 1–4) are higher than those of parameters $|\Delta\delta^{N-VI[5]}{}_i|$ (i = 5–8). For this reason further consideration does not include C^1 carbon atoms due to the significant differences between $\delta^C{}_1$ values in compounds (III-VIII).

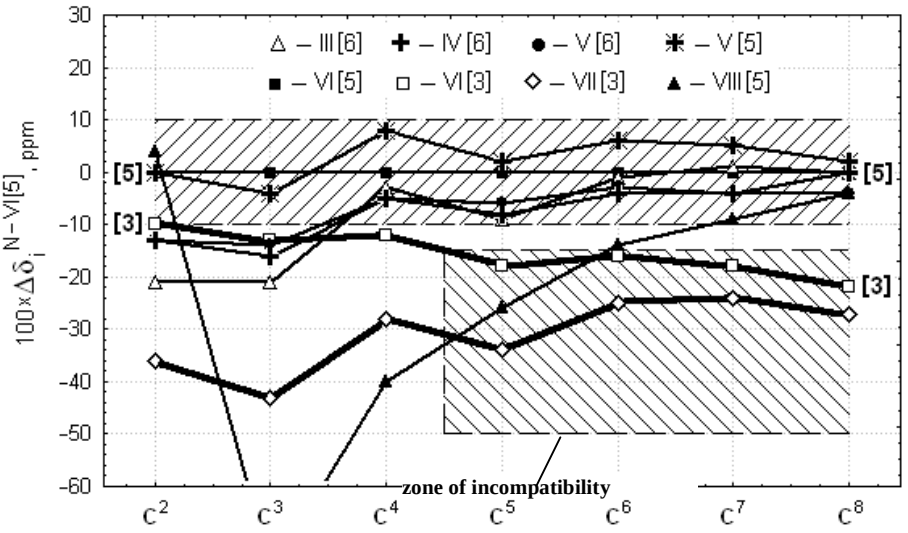

Fig. 2. Differential spectral parameters ($100{\cdot}\Delta\delta^{VI(n)-[5]}{}_i$) in CMR spectra of esters (III-VII) and tosylate (VIII) in $CDCl_3$

One can see from Fig. 2 that the absolute values of 20 differential spectral parameters $|\Delta\delta^{N-VI[5]}{}_4| - |\Delta\delta^{N-VI[5]}{}_8|$, calculated for C^4-C^8 atoms in the octyl esters of aliphatic acids (III-V) (N = III–V) are less or equal to 0.1 ppm. Their spectra are taken from the "compatible" sources [5, 6]. Plots corresponding to these parameters are situated in the area hatched at angle of 45° which we consider as a "corridor of uncertainty". The width of this corridor corresponds to the extreme error for "compatible" spectral parameters and equals to 0.2 ppm (by 0.1 ppm on both sides of thezero line[3]).

The arrangement of ($\Delta\delta^{N-VI[5]}{}_i$) parameter in the "corridor of uncertainty" means that it is impossible to determine its real difference from other analogous parameter also situated in this corridor, *i.e.* both parameters are indistinguishable within the measurement error. The examples are $\Delta\delta^{V[5,6]-VI[5]}{}_i$ (i = 4-8) values of both spectra of octylbutyrate (V) taken from "compatible" sources [5] and [6]. Hence, we can conclude that basic spectral parameters ($\delta^{C,N}{}_i$) taken from [5] and [6] practically coincide with any carbon atoms of the fragment C^5–C^8 in esters (III-V).

Octyltozylate (VIII) is a sulfoacid ester but not an ester. The arrangement of points on the octyltosylate (VIII) line, presented in Fig. 2, is explained by more significant influence of sulfonic group nature in tosylate (VIII) on the value of the chemical shifts of alkoxyl fragment carbon atoms, compared with the influence of the ester group in esters (III-VII). The absolute value of $\Delta\delta^{VIII-VI[5]}{}_2 - \Delta\delta^{VIII-VI[5]}{}_6$ parameters decreases as we move towards the "methyl" end of the alkyl fragment, gradually approaching to the "corridor of uncertainty". And only $\Delta\delta^{VIII-VI[5]}{}_7$ and $\Delta\delta^{VIII-VI[5]}{}_8$ parameters which are the farest from the tosyl group of C^7 and C^8 atoms, are located in this "corridor".

3.1.3. Peculiarities of graphic images of esters VI and VII CMR spectra, given in [3]

In Fig. 2 the points of $\Delta\delta^{N-VI[5]}{}_i$ parameters of substances VI and VII are connected by thick lines. Considering the line connecting $\Delta\delta^{VI[3]-[5]}{}_i$ (i = 2-8) parameters of the octylbenzoate (VI) spectrum taken from [3], the difference between points of C^5–C^8 atoms fragment and that of C^2–C^4 atoms fragment, located near the "corridor of uncertainty" is obvious. The similar situation is observed for $\Delta\delta^{VII[3]-VI[5]}{}_5$–$\Delta\delta^{VII[3]-VI[5]}{}_8$ parameters of C^5–C^8 atoms fragment in the octylbenzoylformiate (VII) spectrum.

In contrast to the esters (III-V), where almost all values of $|\Delta\delta^{N-VI[5]}{}_i|$ parameters are in the "corridor of uncertainty", in the octylbenzoate (VI) spectrum [3] as we move towards the "methyl" end of the chain, the absolute values of $|\Delta\delta^{VI[3]-[5]}{}_i|$ parameters increase, approaching to the values of 0.16-0.27 ppm if i = 6–8[4]. And for the octylbenzoylformiate (VII) spectrum the whole line connecting the points of $\Delta\delta^{VII[3]-VI[5]}{}_i$ (i = 2–8), parameters

[3] Actually the value of 0.1 ppm is a half of allowable error accepted by us. It means that three parameters of four ($\Delta\delta^{VI[3]-[5]}{}_5$, $\Delta\delta^{VI[3]-[5]}{}_6$ and $\Delta\delta^{VI[3]-[5]}{}_7$) do not exceed the limits. Only the parameter $\Delta\delta^{VI[3]-[5]}{}_8$ = 0.22 ppm exceeds the accepted admissible value of spectral data "compatibility".

[4] The most impressive difference between given in Fig. 2 lines of ester (III-V) and VIII on the one hand, and esters (VI) [3] on the other hand, is an asymptotic approximation of the first ones and receding of the second ones from the zero line (*i.e.* $\Delta\delta^{VI[5]-VI[5]}{}_i$ parameters, see above) as we move to the "methyl" end of the alkyl chain.

is located much farther (below) the "corridor of uncertainty".

3.1.4. The "compatibility" criteria of esters (III-VIII) CMR spectra

Similarly to the introduction of the shaded at the angle of 45^0 area near the zero line (the "corridor of uncertainty"), let us hatch with perpendicular shading (at the angle of 315^0) the area in the lower right corner of the firgure. We named it as "zone of incompatibility" of $\Delta\delta^{N\text{-}VI[5]}{}_i$ (i = 5–8) spectral parameters for the C^5–C^8 atoms fragment of the octyl chain. The arrangement of mentioned parameters of octylbenzoate (VI) spectrum given in [3] defines the "incompatibility" of involved sources of information: [3] – on the one hand, and [5, 6] – on the other hand.

As we move along the alkyl chain to its "methyl" end ($i \rightarrow \omega$), the arrangement of $\Delta\delta^{N\text{-}VI[5]}{}_i$ parameter in the "corridor of uncertainty" (or near it) is the main criterion of spectra "compatibility", to our mind, and hence, sources "compatibility'' as well. On the contrary, the receding from the mentioned "corridor" and arrangement in the "zone of incompatibility" (*e.g.*, for octylbenzoate VI spectrum [3]) indicates probable "incompatibility" both spectra and sources of information. All mentioned above argues the conclusion about the compatibility of CMR spectra given in "compatible sources" [5, 6], and their "incompatibility" with "routine" spectra given in [3]. On the other hand it is possible that spectra of all esters given in [3] (including esters of 1-pentylbenzoate (I) and pentylbenzoylformate (II)), which are "incompatible" with the spectra from [5 and 6], may be "compatible" between each other.

3.2. Calculation of $d^{C,I}{}_i$ Basic Parameters in 1-Pentylbenzoate (I) CMR Spectrum

Taking into consideration the "compatibility" of informational source [3], it is advisable to calculate $(\delta^{II}{}_i)_{calc.}$ parameters in CMR spectrum of pentylbenzoylformate (II) on the example of its nearest analogue – 1-pentylbenzoate (I).

1-Pentylbenzoate (I) is a particular case of compounds of the general formula $CH_3(CH_2)_nX$ (n = 4, X = OBz). There is a calculation method [2] of $d^C{}_{i,calc.}$ basic spectral parameters using formula (3) taken from [1]:

$$\delta^C{}_{i.calc.} = \delta^C{}_{mid} + \Delta\delta^C{}_r + \Delta\delta^C{}_s \qquad (3)$$

The parameter $\delta^C{}_{mid}$ is a constant value equaled to 29.75 ppm. Parameters $\Delta\delta^C{}_r$ and $\Delta\delta^C{}_s$ are the set of increments necessary for calculation of $d^C{}_i$ values in $CH_3(CH_2)_nX$ compounds [2]. The increments for the molecule alkyl end are designated as $\Delta\delta^C{}_r$ and the increments for functionalized end are designated as $\Delta\delta^C{}_s$. The values of the first five increments from the set $\Delta\delta^C{}_r$ (r = 1–5) are the same for all classes of $CH_3(CH_2)_nX$ compounds and alkyl chains of different length. They are: $\Delta\delta^C{}_\omega$ = -15.65 ppm, $\Delta\delta^C{}_{\omega\text{-}1}$ = -7.00 ppm, $\Delta\delta^C{}_{\omega\text{-}2}$ = = +2.25 ppm, $\Delta\delta^C{}_{\omega\text{-}3}$ = -0.30 ppm, $\Delta\delta^C{}_{\omega\text{-}4}$ = -0.05 ppm, correspondingly. The set of increments $\Delta\delta^C{}_s$ is different for every substituent X and depends upon peculiarities of its chemical structure. The method is justified in [2].

3.2.1. Calculation of $\Delta\delta^C{}_s$ increments for benzoate class using octylbenzoate (VI) CMR spectra taken from different sources

Every s increment from the $\Delta\delta^C{}_s$ set for benzoate class is calculated using formula (4) derived from formula (3) and rounded to the nearest value divisible by 0.05 ppm:

$$\Delta\delta^C{}_s = \delta^C{}_i - \delta^C{}_{mid} - \Delta\delta^C{}_r \qquad (4)$$

In order to increase the calculations accuracy we use spectral data of alkylbenzoates with the longest alkyl chains. Octylbenzoate (VI) is such a compound in both [3] and [5]. Values of the $\Delta\delta^C{}_s$ increments set for the benzoate class based on spectral data of the compound (VI) given in [5] are given in [1]. Taking mentioned facts into account this set is admitted as a "compatible" one and marked by the italic type in Table 3.

All necessary spectral parameters are given in Table 3 for the illustration of calculation of "non-compatible" set of $\Delta\delta^C{}_s$ increments using CMR spectrum of octylbenzoate (VI) given in [3]. The $\Delta\Delta\delta^C{}_s$ differential parameters, *i.e.* $(\Delta\delta^C{}_s)_{comp.}$- $(\Delta\delta^C{}_s)_{nonc.}$. are also given there.

Table 3

Spectral parameters necessary for calculation of $\Delta\delta^C{}_s$ increments by formula (4) for benzoates class using CMR spectrum of octylbenzoate (VI) given in [3]

Calculation for atom	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8
Parameter $\delta^C{}_{mid}$	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75
Parameter $\Delta\delta^C{}_r$	0.00	0.00	0.00	-0.05	-0.30	+2.25	-7.00	-15.65
Basic spectral parameter $\delta^C{}_i$ from [3]	65.03	28.72	25.99	29.14	29.14	31.70	22.52	13.88
Rounded calculated parameter $\Delta\delta^C{}_s$ from "non-compatible" set	+35.30	-1.05	-3.75	-0.55	-0.30	-0.30	-0.25	-0.20
Rounded calculated parameter $\Delta\delta^C{}_s$ given in [1], *i.e.* "compatible" set	*+35.35*	*-0.95*	*-3.65*	*-0.40*	*-0.15*	*-0.15*	*-0.05*	*0.00*
Difference $\Delta\Delta\delta^C{}_s$ of $\Delta\delta^C{}_s$ values from "compatible" and "non-compatible" sets	*+0.05*	*+0.10*	*+0.10*	*+0.15*	*+0.15*	*+0.15*	*+0.20*	*+0.20*

3.2.2. Comparison of $\Delta\delta^C_s$ increments for benzoates class calculated from spectral data of octylbenzoate (VI) taken from [3] and [5]

One can see from Table 3 that values of all 8 increments $\Delta\delta^C_s$ from "non-compatible" set are less than corresponding values from the "compatible" set. At the same time the difference between them (*i.e.* $\Delta\Delta\delta^C_s$) increases as moving toward the "methyl end" of the chain (i→ω). As it was mentioned above, for the calculation of every set of $\Delta\delta^C_s$ parameters the formula (4) was used. Two (δ^C_{mid} and $\Delta\delta^C_r$) from three parameters do not depend upon the source of the compound (VI) spectrum. And only one item is variable. It is d_i^C basic parameter of octylbenzoate taken from [3] or [5]. Thus, values of every 8 parameters $\Delta\Delta\delta^C_s$ given in Table 3 are equal *per se* to difference parameters $\Delta\delta^{VI[5]-[3]}_i$ given in Figs. 1 and 2 and rounded to the nearest value divisible by 0.05 ppm. These values are reciprocal to the mentioned above $\Delta\delta^{VI[3]-[5]}_i$ parameters.

It should also be noted that moving toward the "methyl end" of the chain from C^5 toward C^8 atom, the absolute values of $\Delta\Delta\delta^C_s$ parameters increase for these spectra achieving 0.16–0.27 ppm, and the line connecting them moves off the "corridor of uncertainty" of "compatible" set of $\Delta\delta^C_s$ parameters. To our mind the most simple and logical method of "compatible" and "non-compatible" sets unification is the introduction of additional "compatible" increment (CI) for C^5–C^8 atoms (i = 5–8) into "non-compatible" set. Such parameter should take into consideration the removal of two hatched area in Fig. 2, typical for C^5–C^8 atoms: (i) zone of incompatibility" from "non-compatible" set and (ii) "corridor of uncertainty" from "compatible" set, hatched with the opposite slope. It is advisable to admit at first approximation the identical averaged values of $\Delta\Delta\delta^C_s$ parameters equal to +0.20 ppm as the CI for all four atoms of the chain "methyl end" (C^{ω}, $C^{\omega-1}$, $C^{\omega-2}$ and $C^{\omega-3}$). This set is called as the "constant" one. For other carbon atoms of the alkyl chain (C^1–C^4) the CI is equal to zero.

The second possible variant of calculations is the usage of difference parameters $\Delta\delta^{VI[3]-[5]}_i$ (i = 5–8) as the CI. They are given in Fig. 1 and rounded to the nearest value divisible by 0.05 ppm. Such set of increments is called as a "variable" one and equals to: IC_{C5} = 0.15 ppm, IC_{C6} = 0,15 ppm, IC_{C7} = 0,2 ppm, IC_{C8} = 0 2 ppm.

3.2.3. Calculation of $d^I_{i,calc.}$ values and their comparison with experimental data [5] of 1-pentylbenzoate (I) CMR spectrum

We calculated three variants of $\delta^{C,I}_i$ parameters for pentylbenzoate (I) using "non-compatible" set of $\Delta\delta^C_s$ parameters. At the first variant (without taking into consideration the CI) d_i values are calculated by the formula (3); at the second and third variants (taking into consideration nonzero CI for C^{ω}, $C^{\omega-1}$, $C^{\omega-2}$ and $C^{\omega-3}$ atoms) – by the formula (5):

$$\delta^C_{i,calc.} = \delta^C_{mid} + \Delta\delta^C_r + \Delta\delta^C_s - \mathrm{CI} \qquad (5)$$

To illustrate the calculations of $\delta^{C,I}_i$ parameters for pentylbenzoate (I) using formula (5) all necessary parameters and obtained calculated values are given in Table 4, as well as other sets of $\delta^C_{i,calc.}$ parameters for pentylbenzoate (I), including calculated parameters from [1] given by the italic type. Experimental results from [3] are given in bold letters.

Table 4

Experimental ($\delta^{C,I}_{i,exp.}$) and calculated ($\delta^{C,I}_{i,calc.}$) parameters for pentylbenzoate (I) using formulas (3) and (5)

Calculation for atom	C^1	C^2	C^3	C^4	C^5
Experimental parameter $\delta^C_{.i,exp}$ ([5])	**65.12**	**28.58***	**28.32***	**22.41**	**13.94**
Calculated values $\delta^C_{i,calc.}$ Parameter $\delta^C_{.mid.}$	29.75	29.75	29.75	29.75	29.75
Parameter $\Delta\delta^C_r$	-0.05	-0.30	+2.25	-7.00	-15.65
Parameter $\Delta\delta^C_s$ from "compatible" set	+35.35	-1.95	-3.65	-0.40	-0.15
Parameter $\delta^C_{i,calc.}$, calculated from "compatible" set [1]	*65.05*	*28.50*	*28.35*	*22.35*	*13.95*
Calculated values $\delta^C_{i,calc.}$ Parameter $\Delta\delta^C_s$ from "non-compatible" set	+35.30	-1.05	-3.75	-0.55	-0.30
Parameter $\delta^C_{i,calc.}$, calc. by formula (3), *i.e.* without IC	65.00	28.40	28.25	22.20	13.80
Calculated values $\delta^C_{i,calc.}$ "constant" IC	0.00	+0.20	+0.20	+0.20	+0.20
Parameter $\delta^C_{i,calc.}$, calc. by formula (5), *i.e.* with constant IC	65.00	28.60	28.45	22.40	14.00
Calculated values $\delta^C_{i,calc.}$ "variable" IC	0.00	+0.15	+0.15	+0.20	+0.20
Parameter $\delta^C_{i,calc.}$, calc. by formula (5), *i.e.* with variable IC	65.00	28.55	28.40	22.40	14.00

Table 5

The differences between calculated and experimental $\delta^{C,I}_i$ values for pentylbenzoate (I)

The differences between calc. and exp. parameters δ^C_i for atom nuclei	C^1	C^2	C^3	C^4	C^5	$100\Sigma\lvert\Delta\delta\rvert$
The differences $\Delta\delta_{i,calc.-exp.}$ between $\delta^C_{i,calc.}$ [1] and $\delta^C_{i,exp.}$	-0.07	-0.08	+0.03	-0.06	+0.01	25 (5.0)
The differences $\Delta\delta_{i,calc.-exp.}$ between $\delta^C_{i,calc.}$ (by formula (3)) and $\delta^C_{i,exp.}$	-0.12	-0.18	-0.07	-0.21	-0.14	72(14.4)
The differences $\Delta\delta_{i,calc.-exp.}$ between $\delta^C_{i,calc.}$ (by formula (5) with const. CI) and $\delta^C_{i,exp.}$	-0.12	+0.02	+0.13	-0.01	+0.06	34(6.8)
The differences $\Delta\delta_{i,calc.-exp.}$ between $\delta^C_{i,calc.}$ (by formula (5), with var. CI) and $\delta^C_{i,exp.}$	-0.12	-0.03	+0.08	-0.01	+0.06	30(6.0)

All 5 values of basic spectral parameters $\delta^{C,II.}_{i,calc.}$ for pentylbenzoate (I) calculated by both variants of the formula (5) using "non-compatible" set of $\Delta\delta^C_s$ increments and taking into consideration both types of the CI satisfactorily agree with experimental values $\delta^{C,II}_{..i.exp.}$. Table 5 shows the difference between the experimental ($\delta^C_{i.exp.}$) and calculated ($\delta^C_{i.calc.}$) values obtained using different variants of calculation, as well as total differences, which are described below.

Two parameters were chosen as the criteria for calculation method suitability: (i) the absolute value of the maximum difference between calculated and experimental parameters $\lvert\Delta\delta_{i,calc.-exp.}\rvert = \delta_{i,calc.} - \delta_{i,exp.}$ (the value of parameter $\lvert$max. $\delta_{i,calc.-exp.}\rvert$ must not exceed the assumed value of the experimental error equal to 0.2 ppm); and (ii) the sum of all absolute differences $\Delta\delta_{i,calc.-exp.}$ for five carbon atoms of pentyloxyl fragment multiplied by 100 and denoted as $100\Sigma\lvert\Delta\delta\rvert$. The average values (in parentheses) for a single atom are given in Table 5. Obviously, the average value should not exceed 20 (corresponding to the value $\delta_{i,calc.-exp.}$ = 0.2 ppm). The value is lower, the calculation method is more suitable.

Taking into consideration these criteria, we estimate the calculation methods as follows. The method using "non-compatible" set of δ^C_i parameters taken from [3] and calculated by the formula (3), *i.e.* without CI, is the worst. The value of parameter $\lvert$max.$\delta_{i,calc.-exp.}\rvert$ = 0.21 slightly exceeds the assumed value of 0.20 ppm. The second criterion is worse ($100\Sigma\lvert\Delta\delta\rvert$ = 72, the average value is 14.4).

As it was expected, the best was the method using the "compatible" set of δ^C_i parameters taken from [5]. The parameter $\lvert$max.$\Delta\delta_{i,calc.-exp.}\rvert$ = 0.08; $100\Sigma\lvert\Delta\delta\rvert$ = 25, the average value is of 5.0. The results using calculated by the formula (5) using "non-compatible" set of δ^C_i parameters taken from [3] are close for both versions of CI. The parameter $\lvert$max.$\Delta\delta_{i,calc.-exp}\rvert$ in both cases does not exceed 0.13 ppm. Using CI constant values the parameter $100\Sigma\lvert\Delta\delta\rvert$ is equal to 34 (on the average by less than 0.07 ppm for each carbon atoms of pentyloxyl fragment), and using the variable set of CI – 30 (on the average of 0.06 ppm).

Hence we may conclude that in spite of the approximation of CI values, the calculation method, using "non-compatible" set of δ^C_i parameters (both versions of the formula (5)) is much better correlated with experimental data than that by formula (3), *i.e.* without CI. The calculation by the formula (5) may effectively help to attribute signals in "non-compatible" CMR spectra.

3.3. Calculation of $d^{C,II}_i$ Values of 1-Pentylbenzoylformate (II) CMR Spectrum and Comparison of Calculated and Experimental Parameters Taken from [3]

Spectral parameters $d^{C,II}_i$ of pentylbenzoylformate (II) were taken from "routine" spectrum [3] which do not agree with spectra taken from [5, 6]. Therefore, it should be advisable to use for calculations the variant with the "non-compatible" set of $\Delta\delta^C_s$ increments and the formula (5) with both types of CI.

3.3.1. Calculation of ' non-compatible÷ set of $\Delta\delta^C_s$ increments for benzoylformates from octylbenzoylformate (VII) CMR spectra [3]

"Non-compatible" set of $\Delta\delta^C_s$ increments for benzoylformates is calculated from available spectrum of the most long-chain ester of this class – octylbenzoylformate (VII). The values d^{VII}_i (i = 2–8) are given in Table 2, value δ^{VII}_1 = 66.20 ppm is taken from [3]. Using these data we receive the "non-compatible" set by the formula (4), which includes rounded values of $\Delta\delta^C_s$ increments: $\Delta\delta^C_1$= +36.45, $\Delta\delta^C_2$ = -1.30, $\Delta\delta^C_3$ = -4.05, $\Delta\delta^C_4$ = -0.70, $\Delta\delta^C_5$ = -0.45, $\Delta\delta^C_6$ = -0.40, $\Delta\delta^C_7$ = -0.30, $\Delta\delta^C_8$ = -0.25 ppm.

The closeness of $\Delta\delta^C_s$ increments for benzoates and benzoylformates C^6–C^8 atoms (s = 6–8) should be noted. Since, as it was mentioned above, for the calculation of $\Delta\delta^C_s$ parameters formula (4) was used, where the variable item is only the spectral data d_i of octylbenzoate (VI) and octylbenzoylformate (VII), the difference between them is equal to the distance between corresponding plots on thick lines represented in Fig. 2. These difference parameters in

both cases are rounded to the nearest value divisible by 0.05 ppm and selected as a "variable" set of CI.

3.3.2. Calculation of $d^{C,II}_i$ Values and Comparison with Experimental Data [3] of 1-Pentylbenzoylformate (II) CMR Spectrum

The $d^{C,II}_i$ values for 1-pentylbenzoylformate (VII) are calculated by formulas (3) and (5), the same as it is for 1-pentylbenzoate (I). As it was mentioned above, CI parameters from the "variable" set for C^1–C^5 atoms should be selected as following: IC_{C1} = 0.00, IC_{C2} = -0.15, IC_{C3} = -0.10, IC_{C4} = -0.05 and IC_{C5} = -0.05 ppm. The values of CI constant parameters for C^2–C^5 atoms are selected as equal to their average values, *i.e.* -0.10 ppm. Table 6 represents $\delta^{C,II}_i$ experimental parameters for pentylbenzoylformate (II) taken from [3] (bold type) and $\Delta\delta_{i,calc.-exp.}$ parameters characterizing the difference between calculated and experimental $\delta^{C,II}_i$ values calculated by different methods.

Table 6

Calculated and experimental $\delta^{C,II}_i$ values for 1-pentylbenzoylformate (II)

Calculated values $\delta^{C,II}_{i,calc.}$	C^1	C^2	C^3	C^4	C^5	$100\Sigma\lvert\Delta\delta\rvert$
Experimental parameter $\delta^{C,II}_{.i,exp}$ ([3])	66.13	27.90	27.65	22.00	13.66	25 (5.0)
The differences $\Delta\delta_{i,calc.-exp.}$ between $\delta^C_{i,calc.}$ (by formula (3)) and $\delta^C_{i,exp}$	+0.02	+0.25	+0.30	+0.05	-0.01	63(12.6)
The differences $\Delta\delta_{i,calc.-exp.}$ beteen. $\delta^C_{i,calc.}$ (by formula (5), with const. CI) and $\delta^C_{i,exp.}$	+0.02	+0.15	+0.20	-0.05	-0.11	53(10.6)
The differences $\Delta\delta_{i,calc.-exp.}$ beetw. $\delta^C_{i,calc.}$ (by formula (5), with var. CI) and $\delta^C_{i,exp.}$	+0.02	+0.10	+0.20	0.00	-0.06	38(7.6)

One can see from Table 6 that parameters $\delta^{C,II}_{calc,i}$ calculated by the formula (5) for the compound (II) are in better agreement with experimental parameters $\delta^{C,II}_{exp,i}$ than $\delta^{C,II}_{calc,i}$ values calculated by the formula (3).

The value of parameter $\lvert\max.\Delta\delta_{i,calc.-exp.}\rvert$ = 0.30 calculated by the formula (3) substantially exceeds the permissible value of 0.20 ppm. Correspondence by the second criterion is bad too: $100\Sigma\lvert\Delta\delta\rvert$ = 63, average value is 12.6. The better results were received using the formula (5). The value of the parameter $\lvert\max.\Delta\delta_{i,calc.-exp.}\rvert$ = = 0.20 in both cases is equal to the permissible one; $100\Sigma\lvert\Delta\delta\rvert$ = 53, the average value is 10.6 when using constant CI and 38 (on average by less than 0.08 ppm), if we use the variable set of CI.

The same as in the case with pentylbenzoate (I), calculations by the formula (5) using the "variable" set of CI gives better results than the version with the "constant" set.

In the best calculation method the values of calculated parameters for C^2 ($\Delta\delta_{2,calc.-exp.}$ = 0.15 ppm) and C^3 ($\Delta\delta_{3,calc.-exp.}$ = 0.20 ppm) atoms do not exceed the maximum permissible value $|\max.\Delta\delta_{i,calc.-exp}|$ = 0.20 ppm. Therefore, by analogy with conclusions presented in [1] it is more logical to attribute signals at 27.90 ppm and 27.65 ppm in the compound (II) spectrum to the adsorption of C^2 ($\delta^{II}_{2,calc.}$ = 28.00 ppm) and C^3 ($\delta^{II}_{3,calc.}$ = =27.85 ppm) atoms correspondingly. The value of $\Delta\delta^{II}_{2-3}$ differential parameter obtained from the mentioned calculated parameters (28.00 – 27.85 = +0.15 ppm) satisfactorily corresponds to $\Delta\delta^{II}_{2-3}$ value calculated using experimental data [3] (27.90 – 27.65 = +0.25 ppm) which is general for all esters of 1-pentanol [1].

The opposite attribution of experimental signals at 27.90 and 27.65 ppm to C^3 and C^2 atoms correspondingly worsens the accordance of the latter signal (27.65 ppm) to the calculated value ($\delta^{I.}_{2,calc.}$ = 28.00 ppm). At the same time the differential parameter ($\Delta\delta_{2,calc.-exp.}$ = +0.35 ppm) exceeds the maximum permissible value of 0.20 ppm. Although such attribution of signals for C^3 atom leads to the good agreement between calculated ($\delta^{II}_{3,calc.}$ = = 27.85 ppm) and experimental ($\delta^{II}_{2,exp.}$ = 27.90 ppm) data the calculated differential parameter $\Delta\delta^{II}_{2-3}$ changes its sign: (27.85 – 28.00 = -0.15 ppm). And on the basis of the changing sign it was recommended in [1] to change the author's signal attribution to C^2 and C^3 atoms [5] in the pentylformate CMR spectrum.

Thus, an improved calculation method of pentylbenzoylformate (II) CMR spectrum using the additivity principle of chemical shifts increments reduces a permissible level of differences between calculated and experimental d^C_i parameters and reasonably allows to attribute both signals in the area of 27–28 ppm presented in the spectrum [3] to the adsorption of C^2 and C^3 atoms of the pentyloxyl group.

4. Conclusions

The improvement of the described earlier [1] calculation method of CMR spectra *via* introduction of additional "compatible" increment (CI) allows to use "non-compatible" spectra to calculate sets of $\Delta\delta^C_s$ increments. At the same time the difference between calculated and experimental parameters does not exceed maximum permissible values accepted by us.

Acknowledgements

This work was performed within the national project "Determination of the general regularities defining the values of chemical shifts in ^{1}H NMR and CMR spectra depending on the chemical structure of organic substances". Theme № B 802-2010. We express our gratitude to the National Institute of Advanced Science and Technology (SDBS Web://riodb 01.ibase.aist.go. jp/sdbs) for CMR data used in this article.

References

[1] Mizyuk V., Shybanov V.: Chem. & Chem. Techn., 2010, **4**, 171.
[2] Mizyuk V., Marshalok I. and Shybanov V.: XI conference "Lviv Chemistry Readings", Conferences theses O24, 2009.
[3] Shybanov V., Mizyuk V. and Kobryn L.: Voprosy Khimii i Khim. Techn., 2005, **5**, 51.
[4] Mizyuk V. and Shybanov V.: Chem. & Chem. Techn., 2008, **2**, 249.
[5] http://www.aist.go.jp.
[6] Aldrich/ACD Library of FT NMR Spectra (Pro) Data Base Window.
[7] Mizyuk V., Shybanov V. and Marshalok I.: Rus. J. Org. Chem., 1994, **30**, 601.

ВПЛИВ УМОВ ЗАПИСУ СПЕКТРІВ НА ПРИКЛАДІ РОЗРАХУНКУ ХІМІЧНИХ ЗСУВІВ В СПЕКТРАХ ЯМР ^{13}С 1-ПЕНТИЛБЕНЗОЇЛФОРМІАТУ

Анотація. *Введено поняття "сумісних" і "несумісних" ЯМР спектрів. Застосування "інкрементів узгодження" дало можливість з достатньою точністю розрахувати хімічні зсуви атомів C^2 і C^3 пентилоксильного фрагменту в 1-пентилбензоїлформіаті.*

Ключові слова: *ЯМР^{13}С спектри, бензоат, бензоїлформіат, базові і диференційні спектральні параметри, хімічні зсуви.*