STUDY OF THE INFLUENCE OF SUBSTITUENT R NATURE IN PHENYLSULFONES DERIVATIVES PhSO₂R ON THE CHEMICAL SHIFTS OF PHENYL RING PROTONS IN NMR ¹H SPECTRA

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Received: June 07, 2011 / Revised: June 20, 2011 / Accepted: September 08, 2011

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Abstract. At the explanation of the spectra peculiarities of phenylsulfones of the general formula C₆H₅SO₂R the arguments in favour of intramolecular influence through the space of functional groups situated in fragment R on the value of phenyl protons chemical shifts δₚ have been adduced.

Keywords: NMR ¹H spectrum, phenylsulfone, basic spectral parameter, differential spectral parameters, “threshold”, intramolecular influence, space.

Introduction

It has been shown [1-3] that in NMR ¹H spectra the basic spectral parameters (chemical shifts δₖ) of all three types of hydrogen atoms nuclei (δₖ) composing the aromatic fragment in monoalkylbenzenes and para-substituted alkylbenzenes depend upon the volume of the space occupied by alkyl substituent in a definite place of alkyl chain. Thus, if the changes of alkyl substituent volume, which result from alkyl chain branching, take place near α-carbon atom, the above-mentioned changes in δ values are called α-effect; if the branching takes place near β-atom – β-effect is observed.

In para-substituted alkylbenzenes [3] the changes in δₖ values (where j is the type of hydrogen atoms in phenyl fragment – ortho- or meta-) observed at the volume increase (alkyl chain branching) near its α-carbon atom are called “proton volumetric α-effects”. These effects are divided into ortho-α-effect and meta-α-effect. Proton β-effects are classified and called in the same way. To our mind, the mentioned classification may be universally applicable and used for NMR spectra of other aromatic compounds.

While studying the dependencies of the basic spectral parameters (δₖ) in NMR ¹H spectra of monosubstituted benzenes upon substituent’s σ constants [4, 5] we paid attention to the anomalously large shift of δₚ values of some C₆H₅SO₂R sulfone derivatives to the low field¹. Thus, the aim of the present paper is the study of peculiarities of NMR ¹H spectra of phenylsulfone derivatives 1–29 of the general formula C₆H₅SO₂R [6]. Unsubstituted and substituted alkyl and aryl groups as well as other substituents containing heteroatoms in the point of addition to C₆H₅SO₂-, for example haloid atoms (Cl), alkylamino- (NR²R³) and alkoxygroups (OR⁴), are marked by the “R” symbol. Thus, the general formula C₆H₅SO₂R unites compounds which are different from the chemical point of view: sulfones (C₆H₅SO₂Alk and C₆H₅SO₂Ar), benzene sulfonic acid ethers (C₆H₅SO₂OAл and C₆H₅SO₂OAг), its amides, haloidanhydrides, and other similar compounds. However, for our purpose these structural differences are inessential, therefore spectra of all the above mentioned compounds are examined together, being divided into two types (main and auxiliary).

¹ The existence of linear dependence of para-protons chemical shift in monosubstituted benzenes PhX upon the X substituent constants, e.g. Hammet constants, was proved earlier [4]. According to the constant values, methylsulfonic group (X = –SO₂Me, σ = 0.72) together with nitrogroup (X = NO₂, σ = 0.79) are the most electron-withdrawing substituents X. The values of δₚ basic spectral parameters of Ph-SO₂Me phenylmethylysulfone, taken from different literature sources (δₚ = 7.650 ppm, δₚ = 7.670 ppm, see below) and nitrobenzene (δₚ = 7.710 ppm), were the most low-field parameters among all 26 monosubstituted benzenes PhX. However the careful analysis of the data given in [9] show that values of δₚ basic spectral parameters of some phenylalkylsulfones Ph-SO₂R are even higher than 7.71 ppm for nitrobenzene. If we assume that electron-withdrawing ability of the substituent X (alkylsulfogroup –SO₂R in our case) is the only factor affecting the δₚ value, then Hammet constant may achieve the value of 0.90 for the same substituents in Ph-SO₂R. Such conclusion contradicts the common sense, because the exchange of methyl group for alkyl one during the transfer of phenylmethylsulfone to phenylalkylsulfones cannot cause such a significant shift of δₚ signal to the low field overlapping the effect of nitrogroup, which is more electron-withdrawing. To our mind, the presence of additional factor affecting the chemical shift of para-protons in Ph-SO₂R is more probable. Therefore, we investigated this assumption.
2. Experimental

2.1. Objects

The main investigated objects were unsubstituted and substituted into alkyl fragment alkylsulfones 1–21 of the general formula \( \text{C}_6\text{H}_5\text{SO}_2\text{C}(\text{Y}^1)(\text{Y}^2)(\text{Y}^3) \), which necessarily contain “sulfone” fragment \( \text{C-S-C} \). The spectra of auxiliary compounds 22–29, containing \( \text{C-S-Het(Y}^1\text{)(Y}^2\text{)} \) fragment (where “Het” denotes O, N, Cl and other heteroatoms) were used for comparison. The used literature sources contain sufficient amount of spectral data allowing to trace the structure/property regular dependencies (in our case the influence of substituent \( R \) structure on changes of phenyl fragment \( \delta^H \) values).

The second argument is peculiarities of spatial arrangement of \( R \) substituent relative to phenyl ring in compounds \( \text{C}_6\text{H}_5\text{SO}_2\text{R} \text{1-21} \) with sufficiently long alkyl chain. Fig. 1 shows that if sulphur atom is situated in the centre of conditional tetrahedron, then 4 adjoined substituents (two oxygen atoms, phenyl ring C-1 atom and X-atom (C-atom or Het of R group)) will be in its corners. Generally, such tetrahedron does not need to be a regular one because of the different lengths of atomic bonds and angles between corresponding atomic bonds differing from the required value (\( -109.5^\circ \)). However, we assume the existence of \( \text{C}_6\text{H}_5\text{SO}_2\text{R} \) molecule conformation, where phenyl group and alkyl chain of \( R \) fragment are situated in the space as a half-loop depicted in Fig. 1. The spatial approaching between H-2, H-3 and probably H-4 phenyl ring with outlying carbon atoms (\( C^\prime, C^\beta, C^\varepsilon \), etc.) of the \( R \) fragment alkyl chain takes place. The interference of the mentioned atoms through the space becomes possible and we may expect the change of the studied spectral parameters.

![Phenylsulfone derivatives 1-29](image)

**Fig. 1.** Phenylsulfone derivatives 1-29

2.2. Procedure

The previously accepted approach [1-3], based on the virtual division of investigated molecule into two fragments – “invariable” and “variable” one – is used for the comparison of spectral parameters of different compounds. The changes in differential spectral parameters (see below) which take place in the investigated part of the “invariable” fragment under the influence of the changing structure of the “variable” fragment (substituent \( R \)) are examined.

The fragment \( \text{C}_6\text{H}_5\text{S}^\alpha\text{O}_2\text{C}^\beta \), in the main compounds 1–21 is chosen as the “invariable” one and three “variable” substituents at \( \beta \)-carbon atom are denoted as \( (\text{Y}^1) \), \( (\text{Y}^2) \) and \( (\text{Y}^3) \). Similarly, the \( \text{C}_6\text{H}_5\text{S}^\alpha\text{O}_2\text{Het}^\gamma \) is an “invariable” fragment and “variable” substituents at heteroatom (Het) are denoted as \( (\text{Y}^1) \) and \( (\text{Y}^2) \) for the comparative auxiliary compounds 22–29. Their amount depends on heteroatom valency.

3. Results and Discussion

3.1. Basic Spectral Parameters

3.1.1. Introduced symbols and information sources

Basic spectral parameters in NMR \( ^1\text{H} \) spectra of \( \text{C}_6\text{H}_5\text{SO}_2\text{R} \) phenylsulfone derivatives are denoted as \( \delta^{\text{H[N(i)]}} \). The superscript symbols mean: (i) type of NMR spectrum (\( H \)); (ii) number of compounds (\( N \)); (iii) type of \( R \) substituent (\( i \)). In some cases references number is indicated as well. Subscript symbol (\( j \)) was discussed above.

The sources of spectral data were chosen on the assumption of their reliability and compatibility, whose criteria were discussed earlier [7]. We used \( \delta^{\text{H[N(i)]}} \) values obtained in deuterochloroform and given in Refs. [8, 9]. Spectra obtained in other solvents (e.g. DMSO-d6) were used only in separate cases, which were specified. CDCl3 use as a solvent is dictated by considerable dependence of \( \delta^H \) values upon the solvent nature. When comparing relatively small changes in \( \delta^H \) basic spectral parameters resulting from probable spatial interaction between molecule fragments, it is impossible to take into account greater changes, which may be caused by the use of solvents different by their nature.

3.1.2. Signals attribution in the spectra

The author’s signals attribution of NMR \( ^1\text{H} \) spectra to the corresponding values \( \delta^{\text{H[N(i)]}} \) for two ortho-, two meta- and one para-protons is given in [8] in all cases. Since in [9] the signals attribution is absent, it was made by us. Usually values of \( \delta^{\text{H[N(i)]}} \) parameters given in [8] and \( \delta^{\text{H[N(i)]}} \) parameters attributed by us using spectra presented in [9] are in a good agreement and the difference between them rarely exceeds 0.020 ppm. The latter is assumed as an average possible experimental error, i.e. \( \delta^{\text{H[N(i)]}} \) parameters determination.

In some cases simple attribution of the mentioned signals is difficult due to the closeness of \( \delta^{\text{H[N(i)]}} \) and
δ^H,N(i) parameters differing by 0.1 ppm. The authors of such signals attribution [8] assume that the mentioned ones may trade places. For those cases (compounds 23–27) we did not calculate differential parameters and put dashes in the Table.

Basic spectral parameters δ^H,N(i) given in [8] were obtained using instruments with different working frequency: 90 and 400 MHz. In order to calculate the differential parameters, in the cases when both values of δ^H,N(i) are given in [8] and they are different, we used δ^H,N(i)[8] parameter obtained by the high-frequency instrument. “Low-frequency” parameter was forcedly used only in the absence of “high-frequency” parameter.

3.2. Differential Spectral Parameters Δδ^H,N(i)

Since the differential parameters indicate the quantitative estimation of α- and β-effects in NMR^1H and ^13C spectra of alkylbenzenes mentioned in [1-3], in this work we carefully analyze just Δδ^H,j differential parameters.

Differential parameters Δδ^H,N(i) were calculated in accordance with the formula (1) given in [2]:

Δδ^H,N(i) = δ^H,N(i) - δ^H,N(0)

(1)

where δ^H,N(i) is studied basic parameter in C_6H_5SO_2R compounds with the substituent R (R ≠ Me), and “zero” parameters δ^H,N(0) are chemical shifts of nuclei of hydrogen aryl atoms in the “standard” compound C_6H_5SO_2CH_3, containing methyl group as R fragment.

3.2.1. Introduced symbols

Values of Δδ^H,N(i) differential spectral parameters are represented in the Table. Every cell of the Table has two values of Δδ^H,N(i) differential parameter given as a fraction: numerator is the value calculated by formula (1) using δ^H,N(i)[9] basic parameters taken from [9] and denominator is the same parameter but calculated using parameter δ^H,N(0)[8]. The numerator is presented in common type and denominator – in bold type; both numerals are given without parentheses.

In the cases when values of δ^H,N(i) basic parameter are absent in [8] or [9] it is impossible to calculate the value of corresponding differential parameter. To increase the statistic amount of data we calculated so-called “crossed” differential parameter. It is calculated with simultaneous use of different sources ([8] and [9]) and placed in the cell instead of lacking value. “Crossed” differential parameters are presented in bold type in parentheses. For example, “crossed” parameter may be calculated by formula: Δδ^H,N(i) = δ^H,N(i)[8] - δ^H,N(0)[9] or vice versa: Δδ^H,N(i) = δ^H,N(i)[9] - δ^H,N(0)[8].

Discussing the results we preferred Δδ^H,N(i)[9] parameters compared with those of Δδ^H,N(i)[8]. Such preference is determined by the possibility to control the author’s attribution of δ^H,N(i) signals by scale enlargement of that part of the spectrum we are interested in. Thus, we decrease the risk of errors possibly committed by the authors [8].

Whereas we assume that accuracy and reliability of both differential parameters Δδ^H,N(i)[9] and Δδ^H,N(i)[8] are considerably higher than those of corresponding “crossed” parameters Δδ^H,N(i), as well as taking into account that “crossed” parameters are given because of calculation impossibility of corresponding differential parameters, their own worth is low. If the value of “crossed” differential parameter does not practically differ from the second parameter in the cell (i.e. Δδ^H,N(i)[9] or Δδ^H,N(i)[8]), the “crossed” parameter serves only for the confirmation of the latter value. If not, we do not take them into consideration.

3.2.2. Classification of R substituents.

Meaning of “i” symbol

Let us accept the following classification of R substituents for all 1–29 compounds. The type of substituent we denote by symbol “i” (see above), consisting of two parts. The first part is a Greek letter indicating the position of the functional group in the alkyl chain. For compounds 1–21 such position is determined by the number of carbon atom in the chain which functional group is attached to (Fig. 1). In the case when multiple bond (C–C) is a functional group, the nearest to the sulfonic fragment carbon atom is denoted by this letter. All auxiliary compounds 22–29 relate to α-type, since carbon chain in R fragment is absent in them and functional group (which is, in fact, the R fragment) is attached to the sulfur atom in –SO_2– group.

The second part of “i” symbol is a numeral denoting the type of functional group. Let us introduce the following numbers of functional groups types for 1–29 compounds. The number depends upon the position of the functional group atom attached to the alkyl chain in the substituent R (or to the sulfonic fragment –SO_2– for 22–29 compounds) in the periodic table. The first five numbers are assigned to “carbon” functional groups, the next five – to corresponding heteroatoms.

1 – double bond C=C
2 – triple bond C≡C
3 – aryl group (phenyl group or phenyl groups substituted into nucleus)
4 – triple bond C=N (nitrite group)
5 – double bond C=O (in our case it is carboxyl group and its derivatives: COOH, COOR, including ortho-etheric functional group (OR),)
6 – alkyamine group (NR^1H)
7 – alkoxy group OR (OH and cyclic tetrahydropyranyl fragment – THP)
8 – alkylthiol group (SR₂)
9 – alkylsulfonyl group (SO₂R₁)
10 – haloid atom

Number “0” denotes the hydrogen atom at the most outlaying carbon atom in the alkyl chain of R substituent, because functional group is absent in such compounds.

3.3. Table of Spectral Parameters

In the Table there are only values of three differential spectral parameters \( \Delta \delta_j^{HN(0)} \) for compounds 1–29; they were calculated by the formula (1). The values of basic spectral parameters \( \delta_j^{HN(0)} \) (except \( \delta_0^{HN(0)} \)) are minuends in formula (1) and are not presented in the Table. They may be calculated by addition of corresponding differential parameter (given in the Table) and subtrahend – parameter \( \delta_j^{HN(0)} \).

The values of both parameter types (\( \delta_j^{HN(0)} \) and \( \Delta \delta_j^{HN(0)} \)) are given with the accuracy of 0.001 ppm. Below are the parameters \( \delta_j^{HN(0)} \), used as the subtrahends in the formula (1) and taken from [8] and [9]: \( \delta_0^{HN(0)} = 7.943 \) ppm; \( \delta_o^{HN(0)[9]} = 7.950 \) ppm; \( \delta_m^{HN(0)[8]} = 7.610 \) ppm; \( \delta_m^{HN(0)[9]} = 7.580 \) ppm; \( \delta_p^{HN(0)[8]} = 7.650 \) ppm and \( \delta_p^{HN(0)[9]} = 7.670 \) ppm. The parameters \( \delta_j^{HN(0)[9]} \) were obtained using low-frequency instrument. Therefore, as was mentioned above, parameters \( \delta_j^{HN(0)[9]} \) obtained using high-frequency instrument of 300 MHz seem to be more reliable. The greatest difference between the similar parameters is equal to 0.030 ppm for meta-protons. This value is half as much again as our estimated value of the experimental error, which makes “crossed” differential parameters (\( \Delta \delta_j^{HN(0)} \)) doubtfull. The same, just to a lesser degree, refers to para-protons. The difference between \( \delta_j^{HN(0)[8]} \) and \( \delta_j^{HN(0)[9]} \) is equal to the value of the experimental error. Only for ortho-protons (\( \Delta \delta_j^{HN(0)} \)) the “crossed” differential parameters may be considered as reliable values, because the difference between \( \delta_j^{HN(0)[8]} \) and \( \delta_j^{HN(0)[9]} \) is equal to 0.007 ppm, which is three times less than the experimental error.

After every three columns with the values of \( \Delta \delta_j^{HN(0)} \) there are columns with the estimation of relative value of differential parameters, which will be discussed in detail below.

<table>
<thead>
<tr>
<th>No. of compounds</th>
<th>Compound formula</th>
<th>Substituent symbol “r”</th>
<th>( \Delta \delta_j^{HN(0)} ) parameter</th>
<th>Relative value of ( \Delta \delta_j^{HN(0)} )</th>
<th>Relative value of ( \Delta \delta_j^{HN(0)} )</th>
<th>Relative value of ( \Delta \delta_j^{HN(0)} )</th>
<th>Relative value of ( \Delta \delta_j^{HN(0)} )</th>
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<tr>
<td>1</td>
<td>C₆H₄–SO₂–C₆H₅</td>
<td>α3</td>
<td>0.000 (+0.007)</td>
<td>-0.090 (--0.120)</td>
<td>-0.120 (--0.100)</td>
<td>-0.120 (--0.100)</td>
<td>-0.120 (--0.100)</td>
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<td>2</td>
<td>C₆H₄–SO₂–C₆H₅</td>
<td>α3</td>
<td>-0.040 (--0.033)</td>
<td>-0.140 (--0.170)</td>
<td>-0.150 (--0.130)</td>
<td>-0.150 (--0.130)</td>
<td>-0.150 (--0.130)</td>
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<tr>
<td>3</td>
<td>C₆H₄–SO₂–CH₃</td>
<td>β0</td>
<td>0.000 0.000</td>
<td>0.000 0.000</td>
<td>0.000 0.000</td>
<td>0.000 0.000</td>
<td>0.000 0.000</td>
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<td>4</td>
<td>C₆H₄–SO₂–CH=CH₂</td>
<td>β1</td>
<td>-0.055 (--0.048)</td>
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<td>-0.030 (--0.010)</td>
<td>-0.030 (--0.010)</td>
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<td>5</td>
<td>C₆H₄–SO₂–C₅H₅</td>
<td>β3</td>
<td>-0.310 (--0.303)</td>
<td>-0.140 (--0.170)</td>
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<td>-0.140 (--0.170)</td>
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<td>β9</td>
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<td>-0.020 (--0.050)</td>
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<td>+0.020 (+0.040)</td>
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<td>C₆H₄–SO₂–C₆H₅Cl</td>
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<td>+0.030 (+0.040)</td>
<td>+0.040 (+0.012)</td>
<td>+0.070 (+0.084)</td>
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Study of the Influence of Substituent R Nature in Phenylsulfones Derivatives PhSO₂R on the... 139

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<td>- - -0.025 -0.050</td>
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<td>-0.010 (-0.040)</td>
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<td>γ4</td>
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<td>+ + +0.070 +0.056</td>
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<td>δ5</td>
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<td>0.000 (-0.030)</td>
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<td>C₆H₅–SO₂–CH₂–CH₂– COOH</td>
<td>δ5</td>
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<td>C₆H₅–SO₂–NH₂</td>
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<td>- - (0.000) -0.030</td>
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<td>- - -</td>
<td>- - -</td>
<td></td>
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<tr>
<td>25</td>
<td>C₆H₅–SO₂–OCH₃</td>
<td>α7</td>
<td>- - -</td>
<td>- - -</td>
<td>- - -</td>
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<tr>
<td>26</td>
<td>C₆H₅–SO₂–O–CH₂– CH₃</td>
<td>α7</td>
<td>(-0.050) -0.043</td>
<td>- - -</td>
<td>- - -</td>
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<tr>
<td>27</td>
<td>C₆H₅–SO₂–O–C₆H₅</td>
<td>α7</td>
<td>(-0.030) -0.023</td>
<td>- - -</td>
<td>- - -</td>
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<tr>
<td>28</td>
<td>C₆H₅–SO₂–O–CH₂– C(CH₃)₃</td>
<td>α7</td>
<td>(-0.037) -0.030</td>
<td>(-0.021) -0.051</td>
<td>(-0.024) -0.004</td>
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<tr>
<td>29</td>
<td>C₆H₅–SO₂–Cl</td>
<td>α10</td>
<td>+0.095 +0.090</td>
<td>++ +0.050 (+0.020)</td>
<td>+ + +0.040 (+0.020)</td>
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</table>

2-THP – 2-Tetrahydropyranyl fragment
3.4. Classification of Differential Spectral Parameters for Compounds 1-29

The main compounds 1–21 are listed in the Table in the order of functional group in the substituent R moving away from sulfonic fragment in the alkyl chain (i.e. from α- to δ-) and substituent type number increase. The auxiliary compounds 22–29 with the values “i” from α6 to α10 are situated below.

3.4.1. Introduction

of the notion of “threshold” values of differential parameters

Taking into account the postulated value of the experimental error (0.020 ppm) we accepted a definite “threshold” value for absolute magnitudes of differential parameter. The notion of “threshold” value is introduced with the aim to determine those compounds for which the parameter. The notion of “threshold” value is introduced with the aim to determine those compounds for which the parameter is “significant”, i.e. stipulated not by the experimental errors but by the influence of the differences in the substituent R structure.

For “protonic” parameters \( \Delta \delta_{i}^{HN} \) the value of 0.050 ppm is chosen as a “threshold” one. This value is 2.5 times higher than the accepted experimental error. At the determination of “threshold value exceeding” the value of \( \Delta \delta_{i}^{HN} \) parameters is rounded to the nearest values which are divisible by 0.005 ppm. Such cases of exceeding (or equality) of “threshold values” are presented in the Table in the columns next to the column of \( \Delta \delta_{i}^{HN} \) parameter. In other cases (when there is no exceeding) there are no denotations in the Table.

Let us introduce a semi-quantitative scale of exceeding (or equality) of \( \Delta \delta_{i}^{HN} \) parameters “threshold” values and corresponding symbols for each of the 4 types of “exceeding”.

1. Relatively small “threshold exceeding”. The absolute value of \( \Delta \delta_{i}^{HN} \) parameters is within the range from |0.050 ppm| to |0.065 ppm|. Depending upon the sign of \( \Delta \delta_{i}^{HN} \) parameter symbols “+” (for the positive values) and “−” (for the negative values) are introduced by bold type.

2. Medium “threshold exceeding”. The range of parameters is from |0.065 ppm| to |0.100 ppm|. Symbols “++” or “−−”.

3. Large “threshold exceeding”. The range of \( \Delta \delta_{i}^{HN} \) parameters is from |0.100 ppm| to |0.200 ppm|. Symbols “+++” or “−−−”.

4. Huge “threshold exceeding”. The value of \( \Delta \delta_{i}^{HN} \) parameters is above |0.200 ppm|. Symbols “++++” or “−−−−”.

3.5. Possible Relationship between “Threshold Exceeding” of 1–29 Compounds and R Fragment Structure

Let us observe the tendency of “threshold exceeding” by the absolute values of \( \Delta \delta_{i}^{HN} \) differential parameters in the set of the main compounds 1-21 depending upon the type of functional group in the R fragment. One can see from the Table that different types of functional groups “i” lead to the different changes by sign and magnitude in \( \Delta \delta_{i}^{HN} \) parameters for protons in different “j” positions of phenyl ring.

3.5.1. Functional groups in α-position (compounds 1 and 2)

In compounds 1 and 2 the alkyl chain in the R substituent is absent. Functional group (in our case aryl group) is the R substituent. It is directly connected with the C6H5SO2 fragment. That is why phenylarylsulfones 1 and 2 are compounds of α-type by definition.

In both compounds 1 and 2 the “threshold exceeding” by \( \Delta \delta_{o}^{HN} \) parameters of ortho-protons is absent. At the same time for meta- and para-protons there is a large negative “threshold exceeding” by \( \Delta \delta_{m}^{HN} \) and \( \Delta \delta_{p}^{HN} \) parameters (“−−−−”).

3.5.2. Functional groups in β-position (compounds 3–11)

A different situation is observed for the compounds with β-position of functional groups in the alkyl chain (3–11). Let us divide them into 2 parts depending on the nature of functional groups contained in the R substituent.

For the compounds where double bond C=C (compound 4) and the system of 6 π-electrons of aryl ring (compounds 5 and 6) are functional groups, there is small negative (“−−”) “threshold exceeding” by \( \Delta \delta_{o}^{HN} \) parameter for vinylsulfone 4 and huge (“−−−−−−”) “threshold exceeding” by β-arylsulfones (benzylsulfones) 5 and 6. The absolute values of the latter parameters are the maximum ones among all investigated values.

For meta-protons in the compounds 5 and 6 the negative values of \( \Delta \delta_{m}^{HS(β)} \) and \( \Delta \delta_{m}^{HS(β)} \) parameters are less, though they are large according to our classification. For para-protons the mentioned parameters are even less, because only one parameter \( \Delta \delta_{p}^{HS(β)} \) demonstrates “low” negative “threshold exceeding” for the compound 5.

In case when the functional group is connected with β-carbon atom of the alkyl chain in the compounds 7–11 and the group begins with a heteroatom (the types of functional groups are denoted as β7, β8, β9 and β10), none of the functional groups affects ortho- and meta-protons sufficiently strong to initiate exceeding of the
“threshold”. Therefore we may suppose that the effect of heteroatom in β-position of the R fragment on ortho- and meta-protons of phenyl ring in the compounds 7–11 is weaker than the effect of C=O double bond and especially the system of C=C double bonds in aryl group bound with β-carbon atom of the alkyl chain.

At the same time for para-protons the “threshold exceeding” was discovered for two compounds – 10 and 11 containing haloid atoms (type 10) as functional groups. The values of “threshold exceeding” for \( \Delta \delta^\beta_{19(10)} \) and \( \Delta \delta^\beta_{11(11)} \) parameters are positive and medium (approximately +0.070 ppm). A similar difference is also observed between the compounds 4–6 on the one part and 7–11 – on the other part.

3.5.3. Functional groups in γ-position (compounds 13–18)

As it was mentioned above, cis-di(phenylsulfonyl)ethylene 18 contains two functional groups at the same time and therefore it will not be examined. The rest 5 compounds (13–17) have 5 different types of functional groups in γ-position (or attached to γ-carbon atom of the chain, see Fig. 1). One can see from the Table that those functional groups are: C=C double bond in 13 (γ1), C=O triple bond in 14 (γ2), C≡N triple bond in 15 (γ4), COOME carbethoxyl group in 16 (γ5) and OH (γ7) hydroxyl group in 17.

The “threshold exceeding” is observed only in two cases. For allylphenylsulfonyl 13 the medium negative value of \( \Delta \delta^\gamma_{13(13)} \) parameter is observed. For nitrile 15 the “threshold exceeding” was found for all three types of protons. All of them have positive values from medium to large.

For ortho-protons “exceeding” by its absolute value is greater than that for β vinylsulfonyl 4, but three times less than huge values for β-arylsulfonyl 5 and 6.

γ-Nitrile functional group in the compound 15 (γ4 type) together with β-aryl group in benzyl sulfone 5 (β3) are only two functional groups in the R fragment for all studied 29 compounds, for which the “threshold exceeding” by all three differential parameters (ortho-, meta- and para-) is observed.

3.5.4. Functional groups in δ-position (compounds 19–21)

In three compounds (19–21) there are three different functional groups. All of them are in δ-position of the alkyl chain: C≡N triple bond in 19 (δ4), C(OMe)\(_2\) orthoetheric group in 20 (δ5) and COOH carboxylic group in 21 (δ5).

It should be noted that NMR \(^1\text{H}\) spectrum of the compound 19 was obtained in hexadeuteriodimethylsulfoxide (DMSO-\(d_6\)) and the spectrum of the compound 21 – in the mixture of CDCl\(_3\)+ DMSO-\(d_6\) [6]. As it was mentioned above, this fact calls in question all conclusions concerning differential spectral parameters of the compounds 19 and 21. Therefore, large positive values of “threshold exceeding” for meta- and para-protons in nitrile-containing sulfone 19 have no independent value. However, it is advisable to examine them together with the others, keeping in mind their defect. All the mentioned above for the compound 19 is valid for the small positive “threshold exceeding” of meta- and para-protons of sulfone-containing acid 21.

3.5.5. Auxiliary compounds 22–29 with functional groups in α-position

One can see from the Table that “threshold exceeding” is observed only for ortho-protons for the compounds 22–29, because values of two parameters \( \Delta \delta^\alpha_{22–29} = 0.051 \) ppm and \( \Delta \delta^\alpha_{22–29} = 0.050 \) ppm among meta- and para-protons are on the verge of such “exceeding”. Therefore they will not be discussed here. The negative values of “threshold exceeding” (\( \Delta \delta^\alpha_{11(11)} \) parameter) for ortho-protons in all three phenylarylsulfamides 22–24, as well as the positive value in sulfochloride 29 are “low” (compound 24) or “medium” by our classification. As it was mentioned above, benzene sulfamide spectrum was obtained in DMSO-\(d_6\). It is the reason why “threshold exceeding” by its ortho-parameter \( \Delta \delta^\alpha_{22–24} \) will not be discussed, though parameters \( \Delta \delta^\alpha_{11(11)} \) on the one part, and \( \Delta \delta^\alpha_{11(11)} \) together with \( \Delta \delta^\alpha_{11(11)} \) on the other part are comparable. It may indicate only insignificant effect of differences in the nature of solvents used for NMR \(^1\text{H}\) spectra.

The possible determinative of the observed “threshold exceeding” by \( \Delta \delta^\alpha_{11(11)} \) parameters in sulfamides 22–24 (α6) is the influence of nitrogen amide atom on ortho-protons, because there is no “threshold exceeding” for sulfoesters. Perhaps, ortho-protons of phenyl fragment are “inert” to the oxygen atom of sulfoesteric group.

3.6. Effect of Functional Group Position on the Magnitude and Sign of \( \Delta \delta^\alpha_{1,1(11)} \) Differential Parameters

The double bond C=C (type 1), aryl group (type 3) and triple bond C≡N in the nitrile group (type 4) are among functional groups generating “threshold exceeding” in the main compounds 1–21. Carboxyl group (type 5, meta- and para-protons in the compound 21, though NMR \(^1\text{H}\) spectrum was obtained in CDCl\(_3\)+DMSO-\(d_6\) [6]) and haloid atoms (type 10, para-protons in the compounds 10 and 11) are noted.
episodically. The parameters of ortho-protons (type 1 and 9) in bifunctionally substituted R fragment (compound 18) are not discussed. No “threshold exceeding” is observed for the following functional groups: triple bond C≡C (type 2); alkoxyl group OR (OH and cyclic tetrahydropyranyl fragment – THP, type 7) and alkylthiol group (SR, type 8).

Let us group \( \Delta d^{H,N(1)} \) differential parameters which overcome the “threshold exceeding” on the basis of functional groups (C=C, Ar, C≡N) numbers (types) and consider the signs of these parameters.

1. The double bond C=C in the compounds 4 (β1) and 13 (γ1). β- and γ-Atoms of the alkyl chain are bound by C≡C bond in the compound 4; in the compound 13 the bond is in ϒ-δ position of the R fragment. For the compounds of type 1 only two cases of “threshold exceeding” were observed. Both of them are for ortho-protons and both of them have negative values. Parameter \( \delta o^{H,N(1)} \) has a small value (“–”) and parameter \( \delta o^{H,13(1)} \) – a medium one (“––”). “Threshold exceeding” for meta- and para-protons in the compounds with double bond C≡C was not observed.

Thus, for the both compounds – vinylsulfone 4 and allylsulfone 13 – small or medium shift to the high field of \( \delta o^{H,N(1)} \) basic spectral parameters is typical only of ortho-protons. The value of shift increases as C≡C bond moves off from sulfonic group.

2. Aryl groups found in the compounds 1 (α3), 2 (α3), 5 (β3) and 6 (β3). In the compounds 1 and 2 the aryl group is in α-position and in the compounds 5 and 6 – in β-position of the R fragment. There is no “threshold exceeding” by ortho-protons in the compounds 1 and 2; and negative “exceeding” by meta- and para-protons are large (“–––”). The compounds 5 and 6 have huge negative “exceeding” (“–––”) by ortho-protons, which diminishes to large (“––”) and medium (“–”) values for meta-protons and small (“–”) value for para-proton \( \Delta d^{H,15(3)} \) = -0.060 ppm. It should be noted that two other para-parameters (\( \Delta d^{H,16}[5]^9 \) and \( \Delta d^{H,16}[6][8] \) which do not “exceed threshold”) also have negative sign and do not “exceed threshold” as well. Hence, they are not discussed.

Thus, for both types of compounds – α-compounds 1 and 2 and β-compounds 5 and 6 the large (sometimes huge) shift to the high field of \( \delta o^{H,N(1)} \) basic spectral parameters is typical of all three types of protons, especially for ortho-protons in 6.

3. The functional group containing triple bond C≡N (nitrile) is observed only in the compounds 15 (γ4) and 19 (δ4). In the compound 15 γ-C and δ-N atoms of the alkyl chain is bound by C≡N bond; in the compound 19 it is in δ-ε position. Due to the use of hexadeuteriodimethylsulfoxide as a solvent instead of deuterochloroform in the compound 19 [6], the results of its differential parameters comparison cannot be accepted as absolutely corrected. However, as it was mentioned above for the compounds 22–25, it is possible that the change of differential parameters connected with the solvent exchange is not large and does not distort the principal results. Therefore the nitrile compound 19 still should be discussed.

“Threshold exceeding” is observed for all three parameters \( \Delta d^{H,15(4)} \) in the compound 15, as well as two parameters \( \Delta d^{H,19(4)} \) and \( \Delta d^{H,19(4)} \) in the compound 19. All the mentioned parameters are positive and have values “++” for ortho- and meta-protons in the compound 15 and “++++” for meta-protons in 19 and para-protons in both compounds.

Thus, medium or large shift to the low field of all three basic spectral parameters \( \Delta d^{H,19(4)} \) (except ortho-protons in 19) is typical of both nitrilesulfones 15 and 19.

4. Conclusions

1. The double bond C≡C or aryl group (which may be considered as the system consisting of three conjugate double bonds C≡C) situated correspondingly in the fragment R of arylsulfones of the general formula \( \text{C}_n\text{H}_2\text{SO}-\text{R} \) causes the shift of the basic spectral parameters \( \Delta \delta j \) of all three types of phenyl ring protons to the high field, compared with the value of corresponding parameters \( \delta j^{H,19(4)} \) of etalon phenylmethane sulfone 3 without functional groups.

2. The triple bond C≡N in nitrile group situated correspondingly in the fragment R of arylsulfones of the general formula \( \text{C}_n\text{H}_3\text{SO}-\text{R} \) causes the shift of the basic spectral parameters \( \Delta \delta j \) of all three types of phenyl ring protons to the low field, compared with the value of corresponding parameters \( \delta j^{H,19(4)} \) of etalon phenylmethane sulfone 3.

3. The presence of other studied functional groups in the fragment R of arylsulfones of the general formula \( \text{C}_n\text{H}_3\text{SO}-\text{R} \) does not lead to uniquely interpretive results.

4. It is interesting to compare the absolute values of differential parameters \( \Delta \delta m^{19(4)} \) and \( \Delta \delta p^{19(4)} \) in the compounds 1 and 2 with α-position of aryl groups in the fragment R and those in the compounds 5 and 6, where aryl rings (as functional groups in the fragment R) are bound with β-carbon atom of the chain. The values of meta-parameters in all 4 compounds are practically the same and the values of para-parameters are greater in the case of the compounds 1 and 2. If we take into consideration that in the case of ortho-parameters the opposite situation is observed (i.e. the absolute values are greater for the parameters in the compounds 5 and 6), we may assume the following: aryl ring of the benzyl group in the compounds 5 and 6 is situated one methylene group further from the phenyl ring of phenylsulfonic fragment.
(spectra of which we study). It has a stronger influence on the nuclei of hydrogen atoms situated closer, i.e. mainly on ortho- and meta-protons. Its influence on para-protons is weaker. On the contrary, if aryl rings in the fragment $R$ in phenylarylsulfones 1 and 2 are directly connected with sulfonic fragment (without additional methylene group, the same as in 5 and 6), then they may spatially affect only outlying nuclei of hydrogen atoms in the phenyl ring, i.e. meta- and para-protons.

In that case ortho-protons are apparently too close to the main direction of the substituent influence (system of 6 $\pi$-electrons of aryl ring), therefore they are “beyond reach”.

5. The same results can be observed in the cases when multiple bonds C=C or C≡N are functional groups in the fragment $R$. However, there is an opposite influence upon functional group position in the fragment $R$. Multiple bonds (C=C in $\beta$-$\gamma$ position for 4 and C≡N in $\gamma$-$\delta$ position for 15) which are closer to the $C_6H_5SO_2R$ fragment, affect the closer situated nuclei of ortho- and meta-hydrogen atoms in the phenyl ring in a greater degree, while more outlaying bonds (C=C in $\gamma$-$\delta$ position for 13 and C≡N in $\delta$-$\epsilon$ position for 15) in a greater degree affect more outlaying nuclei of meta- and para-protons. Thus, the elongation of alkyl chain by one methylene group shifts the “focus” of the greatest influence of multiple bonds to more outlaying hydrogen atoms in para- (or meta-positions) of phenyl ring in the $C_6H_5SO_2R$ fragment.

6. The absence of large and huge (according to the accepted classification) values of chemical shifts in $^1H$ 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

[8] www.aist.go.jp

Acknowledgements

This work was performed within the national project “Determination of the general regularities defining the values of chemical shifts in $^1H$ NMR and CMR spectra depending on the chemical structure of organic substances”. Theme № B 802-2010.