

DEPENDENCE OF SPECTRAL PARAMETERS IN ^1H AND ^{13}C NMR SPECTRA OF AROMATIC COMPOUNDS UPON SUBSTITUENT SPATIAL-STRUCTURAL PECULIARITIES

XIV*. Study of the effect of substituent R nature in phenylsulfones derivatives PhSO_2R on the chemical shifts of phenyl ring protons in NMR ^1H spectra

Volodymyr L. Mizyuk

Ukrainian Academy of Printing, Lviv, Ukraine, e-mail: vlm46@mail.ru

Abstract

At the explanation of the spectra peculiarities of phenylsulfones by general formula $\text{C}_6\text{H}_5\text{SO}_2\text{R}$ the arguments in favour of intramolecular effect of functional groups position in the fragment R through the spatial on the value of phenyl protons chemical shifts δ_i^{H} have been adduced.

Key words: NMR ^1H spectra of phenylsulfones by general formula $\text{C}_6\text{H}_5\text{SO}_2\text{R}$, basic (δ_i^{H}) and differential ($\Delta\delta_i^{\text{H}}$) spectral parameters, main and auxiliary compounds, “threshold” differential parameters, intramolecular effect through the spatial.

I. Introduction

It has been shown [1-4] that basic spectral parameters (chemical shifts δ^{H}) of all three types of hydrogen atom nuclei (δ_j^{H}) comprising the phenyl fragment in para-substituted alkylbenzenes in NMR ^1H spectra neatly depend upon volume space occupied by alkyl substituent in the definite part of alkyl chain. Thus, if the change of alkyl substituent volume resulting as alkyl chain branching takes place at α -carbon atom, the mentioned above changes of δ values are called as α -effect. If the branching takes place at β -atom, it means β -effect.

In para-substituted alkylbenzenes [4] changes of δ_j^{H} values (where j denotes the type of hydrogen atoms in phenyl fragment—ortho- or meta-) taking place at volume increase (branching of alkyl chain) at its α -carbon atom are called as “protonic volumetric α -effects”. These effects are subdivided into ortho- α -effect and meta- α -effect. Protonic β -effects are classified in a similar way. Such classification developed for the peculiarities of NMR ^1H spectra of para-substituted alkylbenzenes has an universal mean and may be used for NMR spectra of other classes of aromatic compounds.

* Part 13 – see ref. [3].

II. Subject of investigations

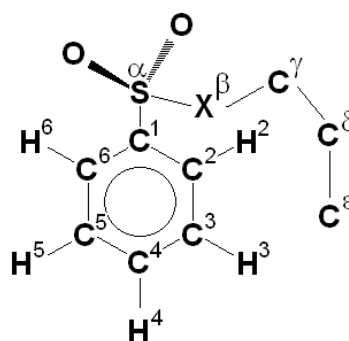
The subjects of present investigations are peculiarities of NMR ^1H spectra of phenylsulfones derivatives ($\text{X} = \text{C}$) by general formula $\text{C}_6\text{H}_5\text{SO}_2\text{R}$, where R means (substituted) alkyl or aryl groups, and other substituents R containing heteroatoms at the addition point to $\text{C}_6\text{H}_5\text{SO}_2$ - fragment, e.g. $\text{X} =$ haloid atoms (Cl), alkylamino ($\text{NR}^{\text{I}}\text{R}^{\text{II}}$) and alkoxygroups (OR^{III}). Thus, the general formula $\text{C}_6\text{H}_5\text{SO}_2\text{R}$ unites such classes of compounds (**1-29**, structural

formulae are given in table), which are different from the chemical point of view: phenylsulfone acid ($C_6H_5SO_2H$), sulfones ($C_6H_5SO_2Alk$ and $C_6H_5SO_2Ar$), benzenesulfonic acid ($C_6H_5SO_2OH$), its esters ($C_6H_5SO_2OAlk$ and $C_6H_5SO_2OAr$), amides, haloidanhydrades, etc. But for our purpose these structural peculiarities are not principal, thereby spectra of all mentioned compounds are considered together, though they are divided into two types (main and auxiliary).

Sulfones (**1-21**) by general formula $C_6H_5SO_2C(Y)(Y^I)(Y^{II})$ we used as main objects. The “sulfonic” fragment $C-S(O_2)-C$ must be obligatory present in them. For comparison we used spectra of auxiliary compounds (**22-29**) containing $C-S(O_2)-Het(Z)(Z^I)$ fragment (where $X =$ “Het”; and symbol “Het” means—O, N, Cl, etc. heteroatom).

The choice of phenylsulfones derivatives $C_6H_5SO_2R$ as objects of NMR 1H spectra investigations is based on following. There are a lot of spectral data in the literature we used (see below) in order one can see the definite regular dependencies between the structure and properties (in our case: the effect of substituent R nature on the change of δ^H_j values of phenyl fragment atom nuclei).

Fig. 1



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The second argument is the peculiarity of spatial arrangement of long alkyl chain of substituent R relative to phenyl ring. Fig. 1 shows that if sulfur atom is placed in the center of conventional tetrahedron, the four joint substituents (two oxygen atoms, C-1 atom of phenyl ring and C or Het atom of R group) are arranged in its corners. Actually, tetrahedron plotted in such a manner cannot be regular because of the different length of atomic bonds and different angles between corresponding atomic bonds which are differ from required values (109.5°). Nevertheless, the existence of $C_6H_5SO_2R$ molecule conformation (as depicted in Fig. 1), where phenyl group and alkyl chain of substituent R are arranged in the space as a semi-loop, is possible. At the same time the approach of H-2, H-3 and may be H-4 atoms of phenyl ring with outlying carbonic atoms (C^γ , C^δ , C^ϵ) of the substituent alkyl chain takes place. The possibility of mentioned atoms effect on each other through the space is appeared leading to the change of investigated basic spectral parameters δ^H .

III. Investigation procedure

For the comparison of spectral parameters of various compounds we use the accepted earlier [1-4] approach based on the virtual division of investigated molecule into two fragments: “invariable” and “variable”. We study the change of spectral parameters (both basic and differential ones) taking place in the part of “invariable” fragment under the influence of the “variable” fragment (substituent R) structural change. After this we compare differential spectral parameters ($\Delta\delta_j^H$) of atom nuclei of phenyl ring which is a component of “invariable” fragment.

Since the differential parameters indicate the quantitative estimation of mentioned in [1-4] α - and β -effects in NMR 1H and ^{13}C spectra of alkylbenzenes, in this work we carefully analyze just differential parameters $\Delta\delta_j^H$.

The fragment $C_6H_5-S^{\alpha}O_2-C^{\beta}-$ is chosen as “invariable” one for main compounds and three “variable” substituents “Y” at β -carbon atom are denoted as $(-Y)$, $(-Y^I)$ and $(-Y^{II})$. Analogously, $C_6H_5-S^{\alpha}O_2-Het^{\beta}-$ is used as “invariable” fragment for auxiliary compounds and $(-Z)$ и $(-Z^I)$ are denoted as “variable” substituents at a heteroatom. Their amount (0, 1 or 2) depend upon heteroatom valency.

IV. Experimental data

IV.1. Basic spectral parameters $\delta_j^{H,N(i)}$

Symbols. Basic spectral parameters of phenylsulfone derivatives $C_6H_5SO_2R$ are denoted as $\delta_j^{H,N(i)}$. First symbol in superscript means spectrum type (“H” – protonic NMR), then number of the substance (N) and then substituent type (i). The subscript “j” means atom position in phenyl ring, e.g. “o” for ortho-hydrogen atoms (H-2 and H-6), etc. In some cases there is also Ref. number in the superscript.

Sources of spectral information. The spectral data sources were chosen taking into account their reliability and compatibility, criteria of which were examined earlier in [1, 4, 5]. We used values $\delta_j^{H,N(i)}$, obtained in deuteriochloroform as a solvent, and presented in the reference books [6, 7]. Spectra obtained in other solvents (e.g. in DMSO- d_6) are examined in this work only in exceptional cases, which are specified. The usage of $CDCl_3$ as a solvent is determined by significant dependence of δ^C and δ^H values upon solvent nature. Comparing relatively small changes of δ^H basic spectral parameters taking place due to the supposed spatial interaction between molecule fragments, it is impossible to take into account greater changes caused by the solvent differed by nature.

IV.2. Basic “protonic” spectral parameters $\delta_j^{H,N(i)}$

The structure of Table and symbols in it. All NMR 1H spectral data are presented in Table 1. Every cell of the table has two $\delta_j^{H,N(i)}$ values: the upper numeral means δ parameter taken from [7], i.e. $\delta_j^{H,N(i)[7]}$; and lower numeral – the same parameter $\delta_j^{H,N(i)[6]}$, taken from [6]. If some numeral is absent, dash is instead. NMR 1H data taken from [7] are presented by ordinary type, and data from [6] – by bold type. Values of basic spectral parameters $\delta_j^{H,N(i)[6]}$ taken from [6] and obtained at the instrument 90 MHz are in square brackets and obtained at the instrument 400 MHz – without them. In some cases Ref. [6] gives two different values of the same parameters $\delta_j^{H,N(i)[6]}$: (i) obtained at the instrument with 90 MHz frequency and (ii) obtained at the instrument with high frequency of 400 MHz. In Table (as well as during calculations of differential parameters $\Delta\delta_j^{H,N(i)[6]}$) we use only that value obtained at high frequency instrument and do not cite parameter $[\delta_j^{H,N(i)[6]}]$. We use parameter $[\delta_j^{H,N(i)[6]}]$ forcedly for calculations of differential parameters $\Delta\delta_j^{H,N(i)[6]}$ only in a case when “high frequency” parameter $\delta_j^{H,N(i)[6]}$ is absent in [6].

Ref. [6] presents author’s attribution of NMR 1H spectra signals to the corresponding values $\delta_j^{H,N(i)}$ for two ortho-, two meta- and one para-protons. Since the signal attributions are absent in [7] we made them by ourselves analogously to the data from [6]. In some cases such attributions are difficult due to the closeness of $\delta_o^{H,N(i)}$, $\delta_m^{H,N(i)}$ and $\delta_p^{H,N(i)}$ values (differed by 0.1 ppm). In Ref. [6] mentioned attributions are marked with special superscript symbols, i.e. authors assume that they may be exchanged. We don’t consider such cases when we calculate differential spectral parameters.

Usually values of $\delta_j^{H,N(i)[6]}$, given in [6] and parameters $\delta_j^{H,N(i)[7]}$, attributed by us from the spectra given in [7], are in good agreement. The divergence between them is rarely exceeds 0.020 ppm. The latter value we assume as experimental average possible error, i.e. at the determination of $\delta_j^{H,N(i)}$ parameters.

IV.3. Differential spectral parameters $\Delta\delta_o^{H,N(i)}$

$\Delta\delta_j^{H,N(i)}$ differential parameters are calculated using formula (1) given in [3]:

$$\Delta\delta_j^{H,N(i)} = \delta_j^{H,N(i)} - \delta_j^{H,N(0)} \quad (1)$$

where $\delta_j^{H,N(i)}$ – investigated basic parameter in $C_6H_5SO_2R$ compounds with substituent R ($R \neq Me$), and $\delta_j^{H,N(0)}$ “zero” parameters are chemical shifts of nuclei of aryl atom hydrogen in “standard” compound. Phenylmethylsulfone $C_6H_5SO_2CH_3$ containing methyl group as a fragment R was chosen to be a “standard” compound.

Symbols in Table. “Direct” differential parameters. It is desirable to choose minuend ($\delta_j^{H,N(i)}$) and subtrahend ($\delta_j^{H,N(0)}$) in formula (1) from the same source: either [6] or [7]. Such differential parameters $\Delta\delta_j^{H,N(i)[7]}$ and $\Delta\delta_j^{H,N(i)[6]}$ we symbolically call as “direct” ones. The same as for basic spectral parameters (δ^H), every cell of differential parameter ($\Delta\delta^H$) has two numerals: the upper one is $\Delta\delta^{H[7]}$ parameter obtained by calculations using data from [7]; the lower one is the same parameter $\Delta\delta^{H[6]}$, using data from [6]. If numerals are absent, there is dash or value of “cross” parameter (see below). The values of “direct” parameters $\Delta\delta$ (the same as for basic parameters δ) are without brackets; the upper value $\Delta\delta^{[7]}$ is presented by ordinary type and $\Delta\delta^{[6]}$ – by bold type.

“Cross” differential parameters. In those cases when $\delta_j^{H,N(i)}$ basic parameter is absent in [6] or [7] but it presents in other source, we calculate so called “cross” differential parameters in order to increase statistical quantity of data. “Cross” parameters are situated in a cell instead of missing values of “direct” parameter and denoted by bold type in parentheses. For example, “cross” parameter may be calculated by formula ($\Delta\delta_o^{H,N(i)}$) = $\delta_o^{H,N(i)[6]} - \delta_o^{H,N(0)[7]}$, or, on the contrary, by formula: ($\Delta\delta_m^{H,N(i)}$) = $\delta_m^{H,N(i)[7]} - \delta_m^{H,N(0)[6]}$.

Calculating differential spectral parameters ($\Delta\delta^H$) and discussing the results we prefer “direct” parameters $\Delta\delta_o^{H,N(i)[7]}$, obtained using data [7] than $\Delta\delta_j^{H,N(i)[6]}$ from [6]. Such preference is determined by the possibility to control author’s attribution of $\delta_j^{H,N(i)[7]}$ signals (given in [7]) by the scale enlargement of spectrum interesting area. Thus we can diminish risk of errors perhaps made by authors [6].

Since we assume that reliability and accuracy of “direct” differential parameters (both $\Delta\delta_j^{H,N(i)[7]}$ and $\Delta\delta_j^{H,N(i)[6]}$) are higher than those of “cross” parameters $\Delta\delta_j^{H,N(i)}$, their values are given in the tables only due to the impossibility of calculation of “direct” differential parameters in both informational sources because of the data lack.

IV.4. Classification of R substituents. Meaning of “i” symbol

Every R substituent consists of alkyl chain of various length, in which functional group is “built-in” at the definite point. We assume the following classification of R substituents.

Substituent type we denote by above-mentioned symbol “i” consisting of two parts. Greek letter pointing the position of functional group in alkyl chain is the first component. This position is determined by that atom (or group of atoms, as for instance, sulfonic group SO_2 is depicts as “ α ”) in the chain, which functional group is attached to. In the case when multiple bond (C-C, C-N or C-O) is a functional group, the Greek letter means the carbon atom nearest to sulfonic fragment.

The second component of the symbol “i” is a numeral designated the type of functional group. We introduce following numbers of functional groups occurred in compounds **1-29**. The numeration is based on the numbers increase in periodic table of that functional group atom which is attached to the corresponding atom of alkyl chain (or to the sulfone fragment $-S^{\alpha}O_2-$) in substituent R. First 5 numbers are assigned to “carbon” functional groups. In following 5 numbers corresponding heteroatom is an attached atom.

1 – double bond C=C

- 2 – triple bond C≡C
- 3 – aryl group (phenyl or substituted into the nucleus phenyl groups)
- 4 – triple bond C≡N (nitrile group)
- 5 – double bond C=O (in our case it is carboxylic group and its derivatives: COOH, COOR, including ortho-esteric functional group (OR)₃)
- 6 – alkylamine group (NR^IR^{II})
- 7 – alkoxy group OR (OAlk, as well as cyclic tetrahydropyranyl fragment – THP)
- 8 – alkylthio group (SR^I)
- 9 – alkylsulfonic group (SO₂R^I)
- 10 – haloid atom

Numeral “0” means hydrogen atom of uttermost carbon atom in alkyl chain of substituent R. This group does not contain functional substituent.

IV.5. Spectral parameters

The table presents values of three basic spectral parameters $\delta_j^{H,N(i)}$ taken from [6] and [7] and calculated on their bases differential spectral parameters $\Delta\delta_j^{H,N(i)}$ for the compounds (1–29). Values of both parameters ($\delta_o^{H,N(i)}$ and $\Delta\delta_o^{H,N(i)}$) are given with the accuracy of 0.001 ppm.

Table

Values of basic ($\delta_j^{H,N(i)}$) and differential ($\Delta\delta_o^{H,N(i)}$) spectral parameters of 1-29 compounds

No. of compounds	Substituent R	Symbol “i”	Compound formula	$\delta_o^{H,N(i)}$	$\Delta\delta_o^{H,N(i)} = \delta_o^{H,N(i)} - \delta_o^{H,N(0)}$	$\Delta_m^{H,N(i)}$	$\Delta\delta_m^{H,N(i)} = \delta_m^{H,N(i)} - \delta_m^{H,N(0)}$	$\Delta_p^{H,N(i)}$	$\Delta\delta_p^{H,N(i)} = \delta_p^{H,N(i)} - \delta_p^{H,N(0)}$
1	C ₆ H ₅	α_3	C ₆ H ₅ -SO ₂ -C ₆ H ₅	7.950 -	0.000 (+0.007)	7.490 -	-0.090 (-0.120)	7.550 -	-0.120 (-0.100)
2	(o-NH ₂)C ₆ H ₄	α_3	C ₆ H ₅ -SO ₂ -C ₆ H ₄ (o-NH ₂)	7.910 -	-0.040 (-0.033)	7.440 -	-0.140 (-0.170)	7.520 -	-0.150 (-0.130)
3	CH ₃	β_0	C ₆ H ₅ -SO ₂ -CH ₃	7.950 [7.943]	0.000 0.000	7.580 [7.610]	0.000 0.000	7.670 [7.650]	0.000 0.000
4	CH=CH ₂	β_1	C ₆ H ₅ -SO ₂ -CH=CH ₂	7.895 -	-0.055 (-0.048)	7.550 -	-0.030 (-0.060)	7.640 -	-0.030 (-0.010)
5	CH ₂ -(o-CH ₃)C ₆ H ₄	β_3	C ₆ H ₅ -SO ₂ -CH ₂ -(o-CH ₃)C ₆ H ₄	7.640 -	-0.310 (-0.303)	7.440 -	-0.140 (-0.170)	7.610 -	-0.060 (-0.040)
6	CH ₂ -(o-CH ₂ Br)C ₆ H ₄	β_3	C ₆ H ₅ -SO ₂ -CH ₂ -(o-CH ₂ Br)C ₆ H ₄	7.715 -	-0.235 (-0.228)	7.490 -	-0.090 (-0.120)	7.640 -	-0.030 (-0.010)
7	2-THP	β_7	C ₆ H ₅ -SO ₂ -CH[(-CH ₂) ₄ -O-]	7.920 -	-0.030 (-0.023)	7.550 -	-0.030 (-0.060)	7.670 -	0.000 (+0.020)
8	CH ₂ -S-CH ₃	β_8	C ₆ H ₅ -SO ₂ -CH ₂ -S-CH ₃	7.965 -	+0.015 (+0.022)	7.580 -	0.000 (-0.030)	7.680 -	+0.010 (+0.030)
9	CH ₂ -SO ₂ -C ₆ H ₅	β_9	C ₆ H ₅ -SO ₂ -CH ₂ -SO ₂ -C ₆ H ₅	7.940 -	-0.010 (-0.003)	7.560 -	-0.020 (-0.050)	7.690 -	+0.020 (+0.040)

10	CH ₂ Cl	β10	C ₆ H ₅ -SO ₂ - CH ₂ Cl	7.980 7.983	+0.030 +0.040	7.620 7.622	+0.040 +0.012	7.740 7.734	+0.070 +0.084
11	CH ₂ Br	β10	C ₆ H ₅ -SO ₂ - CH ₂ Br	7.985 -	+0.035 (+0.042)	7.620 -	+0.040 (+0.012)	7.730 -	+0.060 (+0.080)
12	CH ₂ -CH ₃	γ0	C ₆ H ₅ -SO ₂ - CH ₂ -CH ₃	- 7.917	(-0.033) -0.026	- 7.585	(+0.005) -0.025	- 7.667	(-0.003) +0.017
13	CH ₂ -CH=CH ₂	γ1	C ₆ H ₅ -SO ₂ - CH ₂ - CH=CH ₂	7.875 7.878	-0.075 -0.065	7.555 7.560	-0.025 -0.050	7.650 7.650	-0.020 0.000
14	CH ₂ -C≡CH	γ2	C ₆ H ₅ -SO ₂ - CH ₂ -C≡CH	7.940 -	-0.010 (-0.003)	7.570 -	-0.010 (-0.040)	7.680 -	+0.010 (+0.030)
15	CH ₂ C≡N	γ4	C ₆ H ₅ -SO ₂ - CH ₂ -C≡N	8.030 8.039	+0.080 +0.096	7.650 7.666	+0.070 +0.056	7.780 7.785	+0.110 +0.135
16	CH ₂ -COOCH ₃	γ5	C ₆ H ₅ -SO ₂ - CH ₂ - COOCH ₃	7.950 -	0.000 (+0.007)	7.590 -	+0.010 -0.020	7.700 -	+0.030 (+0.050)
17	CH ₂ -CH ₂ -OH	γ7	C ₆ H ₅ -SO ₂ - CH ₂ -CH ₂ -OH	7.925 -	-0.025 (-0.018)	7.580 -	0.000 (-0.030)	7.680 -	+0.010 (+0.030)
18	CH=CH-SO ₂ - C ₆ H ₅	γ9,β1	Z-C ₆ H ₅ -SO ₂ - CH=CH- SO ₂ -C ₆ H ₅	8.025 -	+0.075 (+0.082)	7.570 -	-0.010 (-0.040)	7.690 -	+0.020 (+0.040)
19	CH ₂ -CH ₂ -C≡N	δ4	C ₆ H ₅ -SO ₂ - CH ₂ -CH ₂ - C≡N	7.955 -	+0.005 (+0.012)	7.700 -	+0.120 (+0.090)	7.800 -	+0.130 (+0.150)
20	CH ₂ -CH ₂ - C(OCH ₃) ₃	δ5	C ₆ H ₅ -SO ₂ - CH ₂ -CH ₂ - C(OCH ₃) ₃	7.930 -	-0.020 (-0.013)	7.580 -	0.000 (-0.030)	7.670 -	0.000 (+0.020)
21	CH ₂ -CH ₂ - COOH	δ5	C ₆ H ₅ -SO ₂ - CH ₂ -CH ₂ - COOH	7.905 -	-0.045 (-0.038)	7.630 -	+0.050 (+0.020)	7.720 -	+0.050 (+0.070)
22	NH ₂	α6	C ₆ H ₅ -SO ₂ - NH ₂	- [7.851]	(-0.099) -0.092	- [7.580]	(0.000) -0.030	- [7.58]	(-0.090) -0.070
23	NHCH ₃	α6	C ₆ H ₅ -SO ₂ - NHCH ₃	- [7.862]	(-0.088) -0.081	- -	- -	- -	- -
24	NHC ₄ H ₉ ⁿ	α6	C ₆ H ₅ -SO ₂ - NHC ₄ H ₉ ⁿ	- [7.890]	(-0.060) -0.053	- -	- -	- -	- -
25	OCH ₃	α7	C ₆ H ₅ -SO ₂ - OCH ₃	- -	- -	- -	- -	- -	- -
26	O-CH ₂ -CH ₃	α7	C ₆ H ₅ -SO ₂ - O-CH ₂ -CH ₃	- [7.900]	(-0.050) -0.043	- -	- -	- -	- -
27	O-C ₄ H ₉ ⁿ	α7	C ₆ H ₅ -SO ₂ - O-C ₄ H ₉ ⁿ	- [7.920]	(-0.030) -0.023	- -	- -	- -	- -
28	O-CH ₂ -C(CH ₃) ₃	α7	C ₆ H ₅ -SO ₂ -O- CH ₂ -C(CH ₃) ₃	- 7.913	(-0.037) -0.030	- 7.559	(-0.021) -0.051	- 7.646	(-0.024) -0.004
29	Cl	α10	C ₆ H ₅ -SO ₂ -Cl	8.045 [8.033]	+0.095 +0.090	7.630 -	+0.050 (+0.020)	7.630 -	-0.040 (-0.020)

V. Results and Discussion

V.1. Discussion of differential spectral parameters of 1-29 compounds

The main compounds used for the comparison of differential spectral parameters are compounds **1-21** having “sulfonic” fragment $\text{Ph-S}^{\alpha}\text{O}_2\text{-C}^{\beta}$ -, i.e. ($X = \text{C}$) in the molecule. These compounds are situated in the Table as functional group in the substituent R receding from the sulfonic fragment in alkyl chain (i.e. from α - до δ -) and as number of substituent type increasing. Then auxiliary components **22-29** ($X = \text{Het}$) used for comparison are situated. They are derivatives of phenylsulfonic acids and contain $\text{S}^{\alpha}\text{O}_2\text{-Het}^{\beta}$ fragment instead of $\text{S}^{\alpha}\text{O}_2\text{-C}^{\beta}$.

As it was mentioned above, phenylmethylsulfone $\text{C}_6\text{H}_5\text{-S}^{\alpha}\text{O}_2\text{-C}^{\beta}\text{H}_3$ (**3**) was chosen as a standard compound for comparison of spectral data for all compounds **1-29**. Given in [6] and [7] basic spectral parameters $\delta_j^{\text{H},3(\beta^0)}$ only partially differ between each other, except parameter δ_m^{H} (see below). The closeness of values of phenylmethylsulfone corresponding basic parameters $\delta_j^{\text{H},3(\beta^0)[6]}$ and $\delta_j^{\text{H},3(\beta^0)[7]}$ which are subtrahends in formula (1) essentially increases the accuracy of “cross” differential parameters ($\Delta\delta_j^{\text{H},\text{N}(i)}$) and makes them especially useful for comparative studies.

V.1.2. The introduction of differential parameters “threshold” values

Taking into account the postulated value of experimental error (0.020 ppm) we accept the definite “threshold” value for absolute values of differential parameters. This “threshold” value is introduced with the aim of definition of those compounds, which difference between differential parameters $\Delta\delta_j^{\text{H},\text{N}(i)}$ we consider to be “significant”, i.e. specified by the effect of differences in the substituent R structure, not by experimental error.

For “protonic” parameters $\Delta\delta_j^{\text{H},\text{N}(i)}$ the value of 0.050 ppm we chose as “threshold” value. It is in 2.5 times higher than assumed experimental error. All mentioned in the Table cases of crossing (or equality) of “threshold” differential parameters $\Delta\delta_j^{\text{H},\text{N}(i)}$ are listed below.

For the convenience of $\Delta\delta_j^{\text{H},\text{N}(i)}$ discussion we accept following semi-quantitative scale with corresponding symbols.

1. Comparatively small “threshold crossing”. The absolute value of $\Delta\delta_j^{\text{H},\text{N}(i)}$ parameter is within the range from $|0.050 \text{ ppm}|$ to $|0.065 \text{ ppm}|$. Depending upon the sign of $\Delta\delta_j^{\text{H},\text{N}(i)}$ parameter to denote the “small crossing” we introduce symbols “+” and “-” given by bold type and greater size. Symbol “+” means the shifts of basic spectral parameter $\delta_j^{\text{H},\text{N}(i)}$ of investigated compound N toward the low field compared with $\delta_j^{\text{H},3(\beta^0)}$ parameter of phenylmethylsulfone **3**, chosen as a standard. Correspondingly, symbol “-” indicates the shift toward high field.

2. Mean “threshold crossing”. The interval of $\Delta\delta_j^{\text{H},\text{N}(i)}$ parameters is from $|0.065 \text{ ppm}|$ to $|0.100 \text{ ppm}|$. Symbols: “++” or “--”.

3. Great “threshold crossing”. The interval of $\Delta\delta_j^{\text{H},\text{N}(i)}$ parameters is from $|0.100 \text{ ppm}|$ to $|0.200 \text{ ppm}|$. Symbols: “+++” or “---”.

4. Very great “threshold crossing”. The interval of $\Delta\delta_j^{\text{H},\text{N}(i)}$ parameters is higher than $|0.200 \text{ ppm}|$. Symbols: “++++” or “----”.

V.1.3. Ortho-protons H-2 and H-6

Table 1 shows following cases of crossing (equality) of “threshold” values by both rounded values of differential parameters $\Delta\delta_o^{\text{H},\text{N}(i)[6]}$ and $\Delta\delta_o^{\text{H},\text{N}(i)[7]}$. Let us examine them as alkyl chain lengthening in the substituent R. Taking into account all mentioned above, we'll consider first of all the values of “direct” differential parameters and then values of “cross” parameters. The latter we consider as “reliable” because the difference between parameters $\delta_m^{\text{H},3(\beta^0)[7]} = 7.950 \text{ ppm}$ and $[\delta_m^{\text{H},3(\beta^0)[6]}] = [7.943] \text{ ppm}$ is only 0.007 ppm. This difference is smaller than the

estimated value of experimental error (0.020 ppm). Therefore, such difference between subtrahends in formula (1) only slightly affects the value of “cross” parameter.

V.1.3.1. The set of main compounds (1-21)

1. Phenylvinylsulfone **4**. $\Delta\delta_o^{H,4(\beta^1)} = -0.055$ ppm and **(-0.048)** ppm; “--“.
2. Phenyl-[(2-methyl)phenyl]methylsulfone **5**. $\Delta\delta_o^{H,5(\beta^3)} = -0.310$ ppm and **(-0.303)** ppm; “----“.
3. Phenyl-[(2-bromomethyl)phenyl]methylsulfone **6**. $\Delta\delta_o^{H,6(\beta^3)} = -0.235$ ppm and **(-0.228)** ppm; “----“.
4. Phenylallylsulfone **13**. $\Delta\delta_o^{H,13(\gamma^1)} = -0.075$ ppm and **-0.065** ppm; “--“.
5. Phenyl(cyano)methylsulfone **15**. $\Delta\delta_o^{H,15(\gamma^4)} = +0.080$ ppm and **+0.096** ppm; “++“.
6. Cis-1,2-di(phenylsulfon)ethane **18**. $\Delta\delta_o^{H,18(\gamma^9,\beta^1)} = +0.075$ ppm and **+0.082** ppm; “++“.

V.1.3.2. The set of auxiliary compounds (22-29)

1. Phenylsulfonamide **22**. $\Delta\delta_o^{H,22(\alpha^6)} = (-0.099)$ ppm and **-0.092** ppm; “--“.
2. Phenyl(N-methyl)sulfonamide **23**. $\Delta\delta_o^{H,23(\alpha^6)} = (-0.088)$ and **-0.081** ppm; “--“.
3. Phenyl(N-buthyl)sulfonamide **24**. $\Delta\delta_o^{H,24(\alpha^6)} = (-0.060)$ ppm and **-0.053** ppm; “--“.
4. Phenylsulfochloride **29**. $\Delta\delta_o^{H,29(\alpha^{10})} = +0.095$ ppm and **+0.090** ppm; “++“.

It is possible that $\Delta\delta_o^{H,N(i)}$ parameter of ethylphenylsulfonate **26** also may be referred to the parameters crossing the “threshold”: $\Delta\delta_o^{H,26(\alpha^7)} = (-0.050)$ ppm and **-0.043** ppm; “--“.

V.1.4. Meta-protons H-3 and H-5

The values of δ_m^H basic spectral parameters of phenylmethylsulfone **3**, taken from [6] and [7] considerably differ between each other. The value of basic parameter $\delta_m^{H,3[6]}$ for **3** in [6] was obtained at the low frequency (90 MHz) instrument. It is equal to **[7.610]** ppm. The triplet signal in NMR¹H spectrum [7], which we attributed to the meta-protons absorption, i.e. basic parameter $\delta_m^{H,3(\beta^0)[7]} = 7.580$ ppm was obtained using high frequency instrument (300 MHz). Therefore we consider the latter value more reliable compared with ($[\delta_m^{H,3(\beta^0)[6]}] = [7.610]$ ppm). The difference between absolute values of $\delta_m^{H,3(\beta^0)[7]}$ and $[\delta_m^{H,3(\beta^0)[6]}]$ equaled to 0.030 ppm is in 1.5 times higher than the estimated value of experimental error. It means that values of “cross” differential parameters ($\Delta\delta_m^{H,N(i)}$) are practically unreliable. Moreover, the considerable difference between “direct” differential parameters $\Delta\delta_m^{H,N(i)[7]}$ and $\Delta\delta_m^{H,N(i)[6]}$ seems to be very possible. Therefore, we took into consideration this fact during the selection of cases when differential parameters $\Delta\delta_m^{H,N(i)}$ crosses (or equals to) the “threshold” value ($|0.050$ ppm) and registered those cases when only $\Delta\delta_m^{H,N(i)[7]}$ parameter crosses it. In mentioned cases (compounds **4**, **7**, **9**, **13**) we did not take into consideration the crossing of “threshold” value by $\Delta\delta_m^{H,N(i)[6]}$ parameter, especially if the latter one is “cross” parameter, i.e. ($\Delta\delta_m^{H,N(i)[6]}$).

The cases when differential parameters $\Delta\delta_m^{H,N(i)}$ crosses (or equals to) the “threshold” value are listed below. There is also an example of compound **13**, when $\Delta\delta_m^{H,N(i)[7]}$ is such a parameter and ($\Delta\delta_m^{H,N(i)[6]}$) “cross” parameter is not.

V.1.4.1. The set of main components (1-21)

1. Diphenylsulfone **1**. $\Delta\delta_m^{H,1(\alpha^3)} = -0.090$ ppm and **(-0.120)** ppm; “--“.
2. Phenyl-[(2-amino)phenyl]sulfone **2**. $\Delta\delta_m^{H,2(\alpha^3)} = -0.140$ ppm and **(-0.170)** ppm; “--“.
3. Phenyl-[(2-methyl)phenyl]methylsulfone **5**. $\Delta\delta_m^{H,5(\beta^3)} = -0.140$ ppm and **(-0.170)** ppm; “--“.

4. Phenyl-[(2-bromomethyl)phenyl]methylsulfone **6**. $\Delta\delta_m^{H,6(\beta 3)} = -0.090$ ppm and **(-0.120)** ppm; “--”.
5. Phenyl(cyano)methylsulfone **15**. $\Delta\delta_m^{H,15(\gamma 4)} = +0.070$ ppm and **+0.056** ppm; “++”.
6. Phenyl(β -cyano)ethylsulfone **19**. $\Delta\delta_m^{H,19(\delta 4)} = +0.120$ ppm and **+0.090** ppm; “+++”.
7. β -(Phenylsulfonyl)propionic acid **21**. $\Delta\delta_m^{H,19(\delta 5)} = +0.050$ ppm and **(+0.020)** ppm; “+”.

V.1.4.2. The set of auxiliary components (22-29)

In the Table there are δ_m^H and δ_p^H values for only three compounds – **22**, **28** and **29**. Data for other compounds (**23-27**) are absent. The reason is that signals caused by absorption of meta- and para-protons are very close and sometimes overlapped unlike δ_o^H values for ortho-protons. Therefore the reliable assignment of such signals is difficult. In [6] the discrete values of multiplet signals for protons of both types are absent; instead there is an interval of δ^H values, in which both multiplets are situated. We also were not able to reliably attribute the centers of corresponding multiplet signals in spectra given in [7]. The crossing of “threshold” value was found only for phenylsulfochloride **29**.

1. Phenylsulfochloride **29**. $\Delta\delta_m^{H,29(\alpha 10)} = +0.050$ ppm and **(+0.020)** ppm; “+”.

It is also possible that $\Delta\delta_m^H$ value for neopentyl phenylsulfonate may be referred to the parameters crossing “threshold” value (in spite of the above mentioned about the reliability of $\Delta\delta_m^{H,N(i)[6]}$ parameters): $\Delta\delta_m^{H,28(\alpha 7)} = (-0.021)$ ppm and **-0.051** ppm; “-”.

V.1.5. Para-protons H-4

The values of δ_p^H basic spectral parameters of phenylmethylsulfone **3**, taken from [6] and [7] differ between each other by estimated value of experimental error (0.020 ppm). The value of basic parameter for **3** in [6] ($[\delta_m^{H,3(\beta 0)[6]}] = [7.650]$ ppm) is obtained at the instrument with the frequency of 90 MHz and the same value of $\delta_m^{H,3(\beta 0)[7]}$ parameter equals to 7.670 ppm. Taking into account the above-mentioned reasons the latter value is accepted as more reliable.

During the selection of cases when differential parameters $\Delta\delta_p^{H,N(i)}$ crosses (or equals to) the “threshold” value ($|0.050$ ppm) we indicate below only those when $\Delta\delta_m^{H,N(i)[7]}$ parameter crosses it, the same as in a case with meta-protons. In some cases, analogously to meta-protons, we observe the “threshold crossing” by only one of two $\Delta\delta_p^{H,N(i)}$ parameters.

V.1.5.1. The set of main compounds (1-21)

1. Diphenylsulfone **1**. $\Delta\delta_p^{H,1(\alpha 3)} = -0.120$ ppm and **(-0.100)** ppm; “---”.
2. Phenyl-[2(-amino)phenyl]sulfone **2**. $\Delta\delta_p^{H,2(\alpha 3)} = -0.150$ ppm and **(-0.130)** ppm; “---”.
3. Phenyl-[(2-methyl)phenyl]methylsulfone **5**. $\Delta\delta_p^{H,5(\beta 3)} = -0.060$ ppm and **(-0.040)** ppm; “--”.
4. Phenylchloromethylsulfone **10**. $\Delta\delta_p^{H,10(\beta 10)} = +0.070$ ppm and **+0.084** ppm; “++”.
5. Phenylbromomethylsulfone **11**. $\Delta\delta_p^{H,11(\beta 10)} = +0.060$ ppm and **(+0.080)** ppm; “++”.
6. Phenyl(cyano)methylsulfone **15**. $\Delta\delta_p^{H,15(\gamma 4)} = +0.110$ ppm and **+0.135** ppm; “+++”.
7. Phenyl(β -cyano)ethylsulfone **19**. $\Delta\delta_p^{H,19(\delta 4)} = +0.130$ ppm and **(+0.150)** ppm; “+++”.
8. β -(Phenylsulfonyl)propionic acid **21**. $\Delta\delta_p^{H,19(\delta 5)} = +0.050$ ppm and **(+0.070)** ppm; “+”.

It is possible that $\Delta\delta_p^H$ value for methylphenylsulfoacetate **16** may be referred to the parameters crossing “threshold” value (in spite of the above mentioned about the reliability of $\Delta\delta_p^{H,N(i)[6]}$ parameters): $\Delta\delta_p^{H,16(\gamma 5)} = +0.030$ ppm and **(+0.050)** ppm; “+”.

V.1.5.2. The set of auxiliary components (22-29)

The table presents values of only three compounds – **22**, **28** and **29**, but data for **23-27** compounds are absent. The “threshold crossing” is observed only for phenylsulfonamide **22**.

1. Phenylsulfonamide **22**. $\Delta\delta_p^{H,22(\alpha 6)}$ (-0.090) ppm and -0.070 ppm; “--”.

V.2. The possible dependence between “threshold crossing” by $\Delta\delta_j^{H,N(i)}$ differential spectral parameters for 1-29 compounds and the structure of fragment R

V.2.1. The set of main compounds 1-21

Let us see the tendency of “threshold crossing” by absolute values of $\Delta\delta_j^{H,N(i)}$ differential parameters in the set of main (“sulfone”) compounds **1-21** depending upon the type of functional group in the fragment R. One can see from above-mentioned data that different types of functional groups differently change $\Delta\delta_j^{H,N(i)}$ parameters for protons arranged in different positions of phenyl ring.

V.2.1.1. Functional groups in α -position (compounds 1 and 2)

V.2.1.1.1. Ortho-protons – absence

The absence of above-mentioned “threshold crossing” by $\Delta\delta_o^{H,N(i)}$ parameters in phenylarylsulfones **1** and **2** may indicate the ortho-protons of phenyl fragment in them are insensitive to the action of aryl group being in α -position in the chain (i.e. connected with sulfur atom of sulfonic group).

V.2.1.1. 2. Meta-protons: **1** (“---”); **2** (“---”).

V.2.1.1. 3. Para-protons: **1** (“---”); **2** (“---”).

At the same time a great “threshold crossing” by $\Delta\delta_m^{H,N(i)}$ and $\Delta\delta_p^{H,N(i)}$ parameters denoted by “---” symbol is observed for meta- and para-protons. Hence, we may conclude that geometric arrangement of aryl and phenyl rings favor the effect of system of aryl ring 6 π -electrons on meta- and para-protons of phenyl ring. Moreover, values of para-parameters $\Delta\delta_p^{H,N(i)}$ slightly higher than those of meta-parameters $\Delta\delta_m^{H,N(i)}$. Perhaps, the greatest effect of the system of aryl ring 6 π -electrons directs just on the proton of para-hydrogen atom, especially in compound **2**, where ortho-aniline fragment is an aryl group.

V.2.1.2. Functional groups in β -position (compounds 3-11)

V.2.1.2.1. Ortho-protons: **4** (“-”); **5** (“----”); **6** (“----”).

The different situation is observed in the compounds with β -position of functional groups joint in aryl chain (**3-11**). For ortho-protons there is only small (“-”) “threshold crossing” by $\Delta\delta_o^{H,4(\beta 1)}$ parameters for vinylsulfone **4** and very great (“----”) crossing for β -arylsulfones (benzyl sulfones) **5** and **6**. The absolute values of such parameters are maximum ones among all values given in this work.

In compound **4** the double bond C=C is a functional group, and in compounds **5** and **6** – system of aryl ring 6 π -electrons. If other functional group which joint not to carbon atom, but to heteroatom (compounds **7-11**, types of functional groups 7, 8, 9, 10, 11), is connected with β -carbon atom, then it is obvious that any functional group has not so strong effect on ortho-protons to overcome of their chemical shifts the “threshold”. Therefore we may assume that the effect of heteroatom in β -position on ortho-protons of phenyl ring is weaker than the effect on it

of a single C=C double bond and especially the effect of the system of C=C double bonds in aryl group arranged in β -position of the fragment R.

V.2.1.2.2. Meta-protons: 5 (“---”); 6 (“---”).
V.2.1.2.3. Para-protons: 5 (“-”); 10 (“++”); 11 (“++”).

The greater absolute values of $\Delta\delta_m^{H,5}$ and $\Delta\delta_m^{H,6}$ compared with $\Delta\delta_m^{H,4}$ parameter should be noted. For $\Delta\delta_m^{H,4}$ parameter the “threshold crossing” is registered only at “unreliable” cross parameter ($\Delta\delta_m^{H,4}$). Thus, we did not include it to the list of parameters crossed the “threshold”. It seems that double bond C=C in vinylsulfone **4** does not “achieves” neither meta-, nor para-protons of phenyl ring. The absence of “threshold crossing” by corresponding meta- ($\Delta\delta_m^{H,4(\beta^1)}$) and para- ($\Delta\delta_p^{H,4(\beta^1)}$) parameters confirms this fact. The effect of system of aryl ring 6 π -electrons is greater, because mentioned “threshold” is crossed by both meta- ($\Delta\delta_m^{H,5(\beta^3)}$) and para- ($\Delta\delta_p^{H,5(\beta^3)}$) parameters of benzyl sulfone **5**, as well as by meta-parameter $\Delta\delta_m^{H,6(\beta^3)}$ of benzyl sulfone **6**. It should be noted that ortho-tolyl group in the compound **5** has greater influence on all types of phenyl protons: ortho-, meta- and para- compared with ortho-brommethylphenyl group in the compound **6**. The para-parameter $\Delta\delta_p^{H,6(\beta^3)}$ was not able to cross the “threshold”. Perhaps, the arrangement of para-hydrogen atom in phenyl ring is very far from sphere of influence of the system of aryl ring 6 π -electrons in ortho-brommethylphenyl fragment of compound **6**. This fact is confirmed by the decrease of parameters $\Delta\delta_p^{H,5(\beta^3)}$ and $\Delta\delta_p^{H,6(\beta^3)}$ absolute values compared with corresponding parameters $\Delta\delta_m^{H,5(\beta^3)}$ and $\Delta\delta_m^{H,6(\beta^3)}$.

For para-protons the “threshold crossing” by $\Delta\delta_p^{H,N(i)}$ parameters in the group of β -sulfones is also observed for the compounds **10** and **11** having haloid atoms of β_{10} type as functional groups. The absolute values of such crossing are admitted as mean values using our classification and equal to ~ 0.070 ppm. It should be noted also that the effect of β -haloidmethyl groups in sulfones **10** and **11** on the absorption of phenyl ring ortho- and meta-protons is insufficient to cross the mentioned “threshold”.

V.2.1.3. Functional groups in γ -position (compounds 13-18)

V.2.1.3.1. Ortho-protons: 13 (“-”); 15 (“++”); 18 (“++”).

For ortho-protons the “threshold crossing” by differential parameters $\Delta\delta_o^{H,N(i)}$ absolute values takes place in three cases: in allylsulfone **13**, in nitrile-containing sulfone **15** and in the compound **18**, in which the fragment R contains 2 functional groups simultaneously. The double bond C=C is the functional group in the compound **13**, and nitrile group – in the compound **15**. Both functional groups are joint to γ -carbon atom of the fragment R chain. Since we consider the compound **18** as bifunctionally-substituted one, interpretation of factors causing the effect of its fragment R on ortho-protons chemical shifts of phenylsulfonic fragment is difficult and was not done.

Let us note that the value of “threshold crossing” in all mentioned γ -compounds is mean value using our classification. These values are higher than those for β -vinylsulfone **4**, but in three times less than values for β -arylsulfones **5** and **6**.

V.2.1.3.2. Meta-protons: 15 (“++”).

V.2.1.3.3. Para-protons: 15 (“+++”).

For meta-protons among γ -sulfones the “threshold crossing” by $\Delta\delta_m^{H,N(i)}$ parameters is observed only for nitrile-containing sulfone **15**. The absolute value of such crossing is classified as mean value. Absolute values of parameter $\Delta\delta_m^{H,15(\gamma^4)}$ is less then abovementioned absolute values of $\Delta\delta_m^{H,N(i)}$ of compounds **1**, **2**, **5** and **6**.

For para-protons among γ -sulfones the “threshold crossing” by $\Delta\delta_p^{H,N(i)}$ parameters is also observed only for nitrile-containing sulfone **15**. Moreover, it is the highest by absolute value among γ -sulfones. Parameter $\Delta\delta_p^{H,15(\gamma^4)}$ exceeds value of 0.100 ppm and thus is situated in the category of “great threshold crossing”.

It should be stressed that γ -nitrile functional group in the compound **15** (type γ^4), as well as β -aryl group in benzyl sulfone **5** (β^3) are only two functional groups in the fragment R, for which “threshold crossing” is observed by all three differential parameters (ortho-, meta- and para-) for all 29 compounds.

V.2.1.4. Functional groups in δ -position (compounds 19-21)

V.2.1.4.1. Ortho-protons – absence

For ortho-protons among δ -sulfones the “threshold crossing” is not observed for any of three compounds **19-21**.

V.2.1.4.2. Meta-protons: **19** (“+++”); **21** (“+”).

V.2.1.4.3. Para-protons: **19** (“+++”); **21** (“+”).

For meta-protons among δ -sulfones the “threshold crossing” by $\Delta\delta_m^{H,N(i)}$ parameter is observed for two compounds: nitrile-containing sulfone **19** and acid **21**. The same situation is with $\Delta\delta_p^{H,N(i)}$ parameters for para-protons. The values of $\Delta\delta_m^{H,19(\delta^4)}$ and $\Delta\delta_p^{H,19(\delta^4)}$ parameters are great using our classification and exceed the value of 0.100 ppm. Corresponding parameters $\Delta\delta_m^{H,21(\delta^4)}$ and $\Delta\delta_p^{H,21(\delta^4)}$ are less by absolute values and we determined them as “comparatively small”.

It should be stressed that NMR¹H spectrum of the compound **19** given in [7] was obtained in the solution of hexadeuteriodimethylsulfoxide (DMSO-d₆), and the spectrum of the compound **21** – in the mixture of solvents (CDCl₃+DMSO-d₆) [7]. As it was mentioned above, this condition calls in question all conclusions concerning differential spectral parameters of the compounds **19** and **21**.

V.2.2. The set of auxiliary compounds 22-29

V.2.2.1. Ortho-protons: **22** (“--”); **23** (“--”); **24** (“-”); **29** (“++”).

It is found that “threshold crossing” by absolute values of $\Delta\delta_o^{H,N(\alpha^6)}$ parameters for ortho-protons in all phenylarylsulfonamides **22-24** and $\Delta\delta_o^{H,29(\alpha^{10})}$ for sulfochloride **29** are “comparatively small” (compound **24**) or “mean” using our classification. As it was mentioned above, benzenesulfonamide **22** spectrum was obtained in DMSO-d₆. Therefore, if parameter $\Delta\delta_o^{H,22(\alpha^6)}$ on the one hand and parameters $\Delta\delta_o^{H,23(\alpha^6)}$ and $\Delta\delta_o^{H,24(\alpha^6)}$ on the other hand are commensurable with each other, (what indicates only the insignificant effect of the difference in the nature of solvents in which NMR ¹H spectra were obtained), the fact of “threshold crossing” by ortho-parameter $\Delta\delta_o^{H,22}$ will not be discussed.

Perhaps, the decisive factor of observed “threshold crossing” by $\Delta\delta_o^{H,N(i)}$ parameters in sulfonamides **22-24** is the effect of nitrogen amide atom on the ortho-protons, because this phenomenon is not observed for sulfoesters **25-28**. Probably, ortho-protons of phenyl fragment of the latter compounds are insensitive to the effect of oxygen atom of sulfoester group which is in α -position (i.e. connected with sulfur atom of sulfonic group), the same as for sulfonamides.

V.2.2.2. Meta-protons: **29** (“+”).

V.2.2.3. Para-protons: **22** (“--”).

Differential parameters for meta- and para-protons (as it was mentioned above) were calculated only for 3 auxiliary compounds: sulfonamide **22**, sulfoester **28** and benzenesulfochloride **29**. The fact that NMR¹H spectrum of benzene sulfonamide **22** was obtained in DMSO-d₆ does not allow to consider this only one case, when para-parameter of auxiliary compound crosses the “threshold”.

We consider it is inexpediently to analyze fully these differential spectral parameters because parameters of only two compounds (**28** and **29**) take part in the comparison. Moreover, values of their meta- and para-parameters do not cross abovementioned “threshold” (value $\Delta\delta_m^{H,29(\alpha^{10})} = +0.050$ ppm equals to the assumed value of “threshold”).

V.3. Discussion of signs of $\Delta\delta_o^{H,N(i)}$ parameters, absolute values of which “cross the threshold” by value of 0.050 ppm

During the earlier discussion of $\Delta\delta_o^{H,N(i)}$ differential parameters we did not pay attention to the sign of parameters and considered only their absolute values. In this section we try to connect the type of functional substituent in the fragment R for all compounds **1-29** with the sign of “crossed the threshold” differential parameter.

Let us note that among such functional groups in main compounds (**1-21**) there are double bond C=C (type 1), aryl group (type 3) and triple bond C≡N in nitrile group (type 4). Carboxyl group (type 5) in the compound **21** (meta- and para-protons, but NMR¹H spectrum was obtained in the mixture of CDCl₃+DMSO-d₆ [7]) and haloid atoms (type 10, para-protons in the compounds **10** and **11**) are mentioned episodically. Parameters of ortho-protons in bifunctionally-substituted (type 1 and 9) fragment R of the compound **18**, are without comments, as it was mentioned above.

We classify “crossed the threshold” differential parameters $\Delta\delta_o^{H,N(i)}$ by numbers (types) of their functional groups and examine signs of these parameters in every case for three types of functional groups: C=C, Ar and C≡N.

V.3.1. Double bond C=C (type 1).

It is observed in compounds **4** (β 1) and **13** (γ 1). In the compound **4** β - and γ -atoms of fragment R alkyl chain are connected by C=C bond. In the compound **13** it is arranged in γ - δ position of the fragment R. There are only two cases of “threshold crossing” in compounds of type 1 and both of them are for ortho-protons with the sign “-”. For meta- and para-protons in the compounds with double bond C=C we do not observe any “threshold crossing”.

Thus, for both compounds – vinylsulfone **4** and allylsulfone **13** – the slight shift of $\delta_o^{H,N(1)}$ basic spectral parameters to the high field is typical only for ortho-protons.

V.3.2. Aryl groups (type 3).

They are observed in the compounds **1** (α 3), **2** (α 3), **5** (β 3) and **6** (β 3). In the compounds **1** and **2** aryl group is in α -position, and in the compounds **5** and **6** – in β -position of the fragment R. There are following cases of “threshold crossing” in the compounds of type 3.

In α -compounds **1** and **2** any “threshold crossing” by ortho-protons is not observed; “threshold crossing” by meta- and para-protons has negative sign “---”. In β -compounds **5** and **6** parameters of all three proton types (except para-proton in **6**) also have negative values “----”, “--” and “-”. At the same time both values of “non-crossed the threshold” parameter $\Delta\delta_p^{H,6(\beta^3)[7]} = -0.030$ ppm and $(\Delta\delta_p^{H,6(\beta^3)[6]}) = -0.010$ ppm also have negative sign too.

Thus, for both types of compounds – α -compounds **1** and **2** and β -compounds **5** and **6**, for all three types of protons (ortho-, meta- and para-) the great (sometimes very great) shift to the high field of $\delta_j^{H,N(3)}$ basic spectral parameters is typical.

V.3.3. Nitrile group, triple bond C≡N (type 4).

It is observed in the compounds **15** (γ^4) and **19** (δ^4). In the compound **15** γ -C and δ -N atoms of the fragment R alkyl chain are bonded with C≡N bond. In the compound **19** it is arranged in δ - ε -position of the fragment R. Unfortunately, since authors [7] used hexadeuteriodimethylsulfoxide instead of deuteriochloroform as a solvent at the obtaining of NMR¹H spectrum for the compound **19**, we cannot admit the comparison of its differential parameters as a correct result. However, as it was mentioned above, for other cases it is possible that the change of differential parameters connected with the change of a solvent, is negligible and does not distort the results. Taking this fact into account we'll discuss the compound **19** nevertheless.

As it was mentioned above, "threshold crossing" is observed for all three parameters $\Delta\delta_j^{H,15(\gamma^4)}$ in the compound **15**, as well as for two parameters $\Delta\delta_m^{H,19(\delta^4)}$ and $\Delta\delta_p^{H,19(\gamma^4)}$ in the compound **19**. All mentioned parameters have positive signs ("++") for ortho- and meta-protons in **15**, ("+++") for meta-protons in **19** and for para-protons of both compounds.

Thus, for both nitrilesulfones **15** and **19** mean or great shift toward low field of all three basic spectral parameters $\delta_j^{H,N(4)}$ (except parameter $\Delta\delta_m^{H,19(\delta^4)} = +0.005$ ppm and $(\Delta\delta_m^{H,19(\delta^4)}) = +0.012$ ppm) is typical.

Generalizing all results we can make following conclusions:

1. Double bond C=C or aryl group (which also may be considered as a system of three conjugated double bonds C=C) suitably arranged in the fragment R of arylsulfones by general formula C₆H₅SO₂R **cause the upfield shift** of the basic spectral parameters δ_j^H of all three types of phenyl ring protons (ortho-, meta- and para-) compared with the value of corresponding parameters $\delta_j^{H,3(\beta^0)}$ of phenylmethylsulfone **3** which has not functional group in the fragment R and so selected as a standard.
2. Triple bond C≡N in the nitrile group suitably arranged in the fragment R of arylsulfones by general formula C₆H₅SO₂R **causes the downfield shift** of the basic spectral parameters δ_j^H of all three types of phenyl ring protons (ortho-, meta- and para-) compared with the value of corresponding parameters $\delta_j^{H,3(\beta^0)}$ of phenylmethylsulfone **3** which has not functional group in the fragment R and so selected as a standard.
3. The presence of other examined functional groups in the fragment R of arylsulfones by general formula C₆H₅SO₂R does not lead to the identically interpretive results.

V.4. Discussion of the effect of functional group position in the fragment R alkyl chain on the value of differential parameters $\Delta\delta_o^{H,N(i)}$, absolute values of which "cross the threshold" of 0.050 ppm

This problem was partially discussed above when we examined "threshold crossing" by $\Delta\delta_j^{H,N(i)}$ parameters. Here we present some more results.

1. It is interesting to compare the absolute values of differential parameters $\Delta\delta_m^{H,N(i)}$ and $\Delta\delta_p^{H,N(i)}$ for the components **1** and **2** (with α -position of aryl groups in the fragment R) with the compounds **5** and **6**, where aryl rings (as the functional groups in the fragment R) are connected 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 higher in the case of compounds **1** and **2**. If we take into consideration that in the case of ortho-parameters there is an opposite situation, i.e. absolute values are higher for the compounds **5** and **6**, then we may assume the following. Aryl ring of benzyl group in the compounds **5** and **6** which arrangement is farther by one methylene group from the phenyl ring affects the nuclei of

closer arranged hydrogen atoms in this phenyl ring, i.e. mainly on ortho- and meta-protons. Such effect on para-protons is weaker. On the opposite, if aryl rings (the fragment R) in phenylarylsulfones **1** and **2** are directly connected with sulfone fragment (without auxiliary methylene group) they may affect only far nuclei of hydrogen atoms in phenyl ring, i.e. mainly meta- and para-protons. Ortho-protons, probably, are too close to the main effect direction of the system of aryl ring 6 π -electrons and therefore are situated “out of its reach”.

2. The same observations may be done for those cases when multiple bonds C=C or C \equiv N are functional groups in the fragment R of arylsulfones C₆H₅SO₂R. However, in such cases the opposite connection with the position of functional group in the fragment R is observed. Multiple bonds (C=C in β - γ position in **4** and C \equiv N bond in γ - δ position in **15**) which are closer arranged to the sulfonic fragment affects in a greater degree the nuclei of ortho- and meta-hydrogen atoms which are closer arranged in phenyl ring. The far multiple bonds (C=C in γ - δ position in **13** and C \equiv N bond in δ - ϵ position in **19**) affects in a greater degree the nuclei of meta- and para-hydrogen atoms which are far arranged in phenyl ring. Thus, the lengthening of the fragment R alkyl chain by one methylene group displaces the “focus” of the greatest effect of multiple bonds on hydrogen atoms which are the most far arranged from sulfonic fragment in para- (or meta-) positions of arylsulfones phenyl ring.
3. The absence of great and very great values of differential parameters $\Delta\delta_j^{H,N(i)}$ using our classification for the auxiliary compounds **22-29** (phenylsulfonic acid derivatives) indirectly confirms the correctness of our assumption concerning the main effect of intramolecular interaction between functional group in the fragment R with phenyl ring on the values of phenyl protons chemical shifts. This explanation is more probable than that concerning the effect of nature of atom in α -position (carbon atom or heteroatom).

VI. Conclusions

At the explanation of the spectra peculiarities of phenylsulfones by general formula C₆H₅SO₂R the arguments in favour of intramolecular effect through the spatial positions of functional groups in the fragment R of C₆H₅SO₂R molecule on the value of phenyl protons chemical shifts have been adduced [8].

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