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RESEARCH ARTICLE

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Effect of charged and *ortho* substituents on ^{17}O NMR chemical shifts of substituted phenyl tosylates in DMSO

Vilve Nummert | Mare Piirsalu | Lauri Toom | Tõnu Kesvatera | Ivo Leito | Ilmar A. Koppel

Institute of Chemistry, University of Tartu, Tartu, Estonia

Correspondence
Mare Piirsalu, Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia.
Email: mare.piirsalu@ut.ee

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Abstract

The ^{17}O nuclear magnetic resonance chemical shifts for 31 *ortho*-substituted, *para*-substituted, and *meta*-substituted phenyl esters of 4-methylbenzenesulfonic acid (phenyl tosylates, $4\text{-}CH_3\text{-}C_6H_4SO_2OC_6H_4\text{-}X$) with the neutral and charged substituents in phenoxy part were measured in DMSO-d_6 at 50°C. The chemical shifts, $\delta(^{17}O)$, of the sulfonyl (SO_2) and single-bonded phenoxy (O—Ph) oxygens for *para* and *meta* derivatives in the case of neutral substituents showed a good correlation with the Taft σ_I and $\sigma°_R$ substituent constants. The influence of the *ortho* substituents on the $\delta(^{17}O)$ chemical shifts of the sulfonyl oxygens and single-bonded phenoxy oxygens was found to be described well with the Charton equation: $\delta(^{17}O)_{ortho} = \delta(^{17}O)_H + \rho_I\,\sigma_I + \rho_R\sigma°_R + \delta E^B_s$ when the data treatment was performed separately for electron-donating $+R$ substituents and electron-withdrawing $-R$ substituents. The substituent constants, $\sigma°_{X\pm}$, for the charged substituents ($4\text{-}N^+(CH_3)_3I^-$, $3\text{-}N^+(CH_3)_3I^-$, $2\text{-}N^+(CH_3)_3I^-$, $4\text{-}COO^-N^+Bu_4$, $3\text{-}COO^-N^+Bu_4$, $2\text{-}COO^-N^+Bu_4$) calculated from the $\delta(^{17}O)$ chemical shifts for phenyl tosylates in DMSO prove that in DMSO, the compounds involving charged substituents are predominantly in ion pair form and not dissociated into free ions. The same conclusion was drawn recently from the carbonyl IR stretching frequencies, ν_{CO}, and the carbonyl carbon ^{13}C chemical shifts for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4\text{-}X$, in DMSO. It was shown that for ion pairs of the charged substituents in DMSO and concentrated aqueous salt solution, the same substituent constant, $\sigma°_{X\pm}$, could be used.

KEYWORDS

^{17}O NMR in phenyl tosylates, charged substituents, correlation equations, *ortho* effect, substituent effects

1 | INTRODUCTION

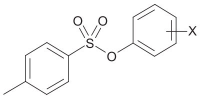
The effects of the charged substituents on different processes in the nonaqueous solutions have been studied considerably less as compared with the neutral substituents. Because the effects of the charged substituents were found to be dependent on the solvent effects and the processes considered, the points for the charged substituents in correlations with the Hammett equation usually deviate and are often excluded from the correlations. It has been found[1,2] that in aqueous solutions, the charged substituents have dualistic behavior. In diluted aqueous solutions, the charged substituents were considered to be completely ionized and an electrostatic Coulombic term, δ^B,[3] should be taken into account besides the polar influence of substituents described by the Hammett equation. For processes containing ionic substituents in the diluted aqueous solutions, an extended Hammett equation (Equation 1) could be used[1]

$$\Delta = \rho\sigma^L + \delta^B \tag{1}$$

In Equation 1 for neutral substituents, σ^L is a "normal" σ value, and for charged substituents, σ^L is the σ value without electrostatic term, ie, the σ value for dipoles equal to that for ion pairs. In the concentrated aqueous salt solutions, the molecules involving charged substituents were found to behave as ion pairs form where the electrostatic Coulombic term, δ^B,[3] turns zero, and the influence of the charged substituents is determined by the substituent constant σ^L values for ion pairs only.[1,2] The σ values for charged substituents estimated from the processes considered prove whether the charged substituents in this medium are in ion pairs form or they are dissociated into the free ions and the σ value contains an electrostatic component as well.

Recently,[4] we estimated the substituent constants, $\sigma°_{X\pm}$, for charged substituents (X = 3-$N^+(CH_3)_3I^-$, 4-$N^+(CH_3)_3I^-$, 4-$SO_3^-Na^+$, 3-$COO^-N^+Bu_4$, 4-$COO^-N^+Bu_4$, 3-$O^-N^+Bu_4$, 4-$O^-N^+Bu_4$, 2-$N^+(CH_3)_3I^-$) for DMSO solution on the basis of the infrared stretching frequencies, ν_{CO}, and the carbonyl carbon nuclear magnetic resonance (NMR) chemical shifts, δ_{CO}, for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, in DMSO. The substituent constants for charged substituents, $\sigma°_{\pm}$, for DMSO coincided well with the substituent constants of ion pairs reported by Hoefnagel and Wepster[1] for aqueous solutions and those estimated from the log k values of the alkaline hydrolysis of esters in aqueous 4.4 M NaCl solution at 50°C.[2,4]

In the present work, we measured the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, of the sulfonyl (SO_2) oxygen and single-bonded phenoxy oxygen (O-Ph) in 31 *ortho*-substituted, *meta*-substituted, and *para*-substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X,



containing the neutral substituents and the charged substituents (3-$N^+(CH_3)_3I^-$, 4-$N^+(CH_3)_3I^-$, 2-$N^+(CH_3)_3I^-$, 3-$COO^-N^+Bu_4$, 4-$COO^-N^+Bu_4$, 2-$COO^-N^+Bu_4$) in DMSO.

Previously,[5] the influence of substituent effects on the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, of the sulfonyl (SO_2) oxygen and single-bonded phenoxy (PhO) oxygen in substituted phenyl tosylates has been studied in the case of neutral (uncharged) substituents in CH_3CN. In the present paper, DMSO was used as solvent because the solubility of phenyl tosylates with charged substituents in CH_3CN is too low for recording the ^{17}O NMR spectra.

The main goal of this work was the re-evaluation of the substituent constants for charged substituents, $\sigma°_{X\pm}$, using the chemical shifts, $\delta(^{17}O)$, of substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, in DMSO, and comparison of the $\sigma°_{X\pm}$ values obtained in the present work with those estimated recently[4] from the infrared stretching frequencies, ν_{CO}, and carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, for substituted phenyl benzoate series, $C_6H_5CO_2C_6H_4$-X, in DMSO.

Another goal of this work was to compare the substituent effects of electroneutral substituents on the chemical shifts, $\delta(^{17}O)$, of *ortho*-substituted, *para*-substituted, and *meta*-substituted phenyl tosylates in DMSO with the same substituent effects in CH_3CN.[5]

In esters of benzenesulfonic acids, the influence of *ortho*, *meta*, and *para* substituents on the chemical shifts, $\delta(^{17}O)$, has received considerably less attention as compared to oxygen ^{17}O chemical shifts in the phenyl esters of benzoic acids.[6–14] In the substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, the chemical shifts, $\delta(^{17}O)$, dependent on the *ortho*, *meta*, and *para* substituent effects in the case of electroneutral substituents has been studied in CH_3CN only.[5] To the best of our knowledge, data on the chemical shifts, $\delta(^{17}O)$, for substituted phenyl tosylates containing charged substituents in DMSO are absent in the literature. In the previous work,[5] the chemical shifts, $\delta(^{17}O)$, of the sulfonyl (SO_2) oxygen and single-bonded phenoxy (PhO) oxygen have been determined for 35 *ortho*-substituted, *para*-substituted, and *meta*-substituted phenyl tosylates (4-CH_3-$C_6H_4SO_2OC_6H_4$-X) in the case of electroneutral substituents in CH_3CN. The $\delta(^{17}O)$ values of the sulfonyl (SO_2) and single-bonded phenoxy (O—Ph) oxygens for *para* and *meta* derivatives showed a good correlation with the Taft equation using the σ_I and $\sigma°_R$ substituent constants. Introduction of the electron-withdrawing $-R$ *para* and *meta* substituents produced deshielding, while electron-donating $+R$ substituents caused the shielding effect on the sulfonyl (SO_2) and the single-bonded phenoxy oxygens.

In the previous works[4,6,7,15,16] in the case of electroneutral substituents in substituted phenyl and alkyl benzoates (X-$C_6H_4CO_2C_6H_5$, $C_6H_5CO_2C_6H_4$-X, $C_6H_5CO_2R$), thoroughly the inductive, resonance, and the steric effects of *ortho*, *para*, and *meta* substituents on the chemical shifts, $\delta(^{17}O)$, in CH_3CN, the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, in $CHCl_3$ and DMSO, as well as on the infrared stretching frequencies of the carbonyl group, ν_{CO}, in CCl_4 and DMSO have been studied. In esters of benzoic acid, the polar substituent effect on the carbonyl oxygen chemical shifts, $\delta(^{17}O)$, was found to be 3 to 4 times stronger as compared with the substituent effects in the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}. The chemical shifts, $\delta(^{17}O)$, in substituted phenyl tosylates and in phenyl benzoates as well as the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, in phenyl benzoates have been successfully correlated with the corresponding substituent effects in the infrared stretching frequencies of the sulfonyl group $\left[\Delta\nu_{so_2} = (\nu_{so_2})x - (\nu_{so_2})_H\right]$ and carbonyl group, $\Delta\nu_{CO}$ $[\Delta\nu_{CO} = (\nu_{CO})_X - (\nu_{CO})_H]$, as well as the rates of the alkaline hydrolysis $\Delta\log k$ values ($\Delta\log k = \log k_X - \log k_H$).[5–7,15–20]

2 | EXPERIMENTAL

2.1 | NMR measurements

In the present paper, the ^{17}O NMR spectra for 31 *ortho*-substituted, *meta*-substituted, and *para*-substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X (phenyl esters of 4-methylbenzenesulfonic acid), including electroneutral and charged substituents (X = H, 4-$N^+(CH_3)_3I^-$, 3-$N^+(CH_3)_3I^-$, 2-$N^+(CH_3)_3I^-$, 4-$COO^-N^+Bu_4$, 3-$COO^-N^+Bu_4$, 2-$COO^-N^+Bu_4$, 4-NO_2, 4-CN, 4-COOH, 4-F, 4-Br, 4-OCH_3, 4-OH, 3-NO_2, 3-COOH, 3-F, 3-Br, 3-NH_2, 2-NO_2, 2-CN, 2-CF_3, 2-COOH, 2-$COCH_3$, 2-COC_6H_5, 2-F, 2-Cl, 2-Br, 2-OCH_3, 2-CH_3, 2-$CH(CH_3)_2$), were recorded at natural abundance in DMSO-d_6 (see Table 1 and Supporting Information).

The ^{17}O NMR spectra were recorded on a Bruker Avance III 700 spectrometer equipped with 5-mm BBO probe (^{17}O frequency 94.9 MHz). Approximately 1 molal solution of *ortho*-substituted, *meta*-substituted, and *para*-substituted phenyl tosylates in 0.75 mL DMSO-d_6 (99.9 atom% D) was used. DMSO-d_6 was purchased from Sigma-Aldrich. Temperature of the ^{17}O NMR measurements was 50°C. The ^{17}O NMR chemical shifts were referenced to H_2O (δ = 0.0 ppm) in a sealed capillary placed inside each NMR tube.

Depending on the sample, about 0.6 to 4.6 million scans were acquired at the spectral width 21739 Hz, and its size was 2048 data points. The 11 microsecond exitation pulse with prescan delay of 64 microseconds and with the relaxation delay of 0 millisecond was applied. The acquisition time was 47 milliseconds. Data were processed with Bruker TopSpin 2.1 software package (Bruker BioSpin GmbH, Rheinstetten, Germany). During of the data processing, an exponential multiplication of the FID with LB factor value 10 and the zero filling up to 32768 data points were applied. For correction of the spectral baseline rolling, cubic spline baseline correction was applied also during the data processing. The linewidth of the measured ^{17}O spectral lines varied depending on the ^{17}O nucleus position (=O) in the tosylate. In the DMSO, the S=O oxygen line was 100 to 180 Hz wide. Linewidth for the water standard, without application of the exponential multiplication, was around 25 Hz. The error of the chemical shifts measured was estimated on the basis of repetitive measurements and was ±0.4 ppm.

When the ^{17}O NMR spectra for substituted phenyl tosylates were recorded on a Bruker Avance III 700 spectrometer in DMSO-d_6, the signals for both oxygens in the sulfonyl SO_2 group and single-bonded phenoxy O—Ph oxygen were detected.

In the beginning of this work, we recorded the ^{17}O NMR spectra at natural abundance in deuterated DMSO (DMSO-d_6) on a Bruker Avance II 200 spectrometer (Brucer BioSpin GmbH, Rheinstetten, Germany) equipped with 10-mm BBO probe (^{17}O frequency 27.13 MHz) for 44 *ortho*-substituted, *meta*-substituted, and *para*-substituted phenyl tosylates, including derivatives with electroneutral and charged substituents. Approximately 1 molal solution of *ortho*-substituted, *meta*-substituted, and *para*-substituted phenyl tosylates in mixture of DMSO (2 mL) and DMSO-d_6 (0.75 mL, 99.9 atom% D) was used. When ^{17}O NMR spectra for substituted phenyl tosylates were recorded on a Bruker Avance II 200 spectrometer, only signals for the sulfonyl (SO_2) oxygen were detected; the signals for the single-bonded phenoxy OPh oxygen line was not detected in the case of all tosylates studied (see Supporting Information). The $\delta(^{17}O)$ values obtained for 44 *ortho*-substituted, *meta*-substituted, and *para*-substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, using a Bruker Avance II 200 spectrometer are listed in Table S1; the results of the $\delta(^{17}O)$ data correlations with substituent constants are shown in Table S2.

For compound characterization, the ^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 700.1 or 200 MHz (^1H), 176.0 or 50.3 MHz (^{13}C), and 658.7 MHz (^{19}F), using Bruker Avance II 200 or Bruker Avance III 700 spectrometers. All these NMR measurements were carried out at 25°C. Chemical shifts (^1H and ^{13}C) were indirectly referenced to TMS via the residual solvent signal (DMSO-d_6, 2.50 and 349.52 ppm, respectively). ^{19}F chemical shifts were referenced to external $CFCl_3$ at 0.0 ppm. The NMR signals were assigned from HSQC, HMBC, NOESY, and TOCSY spectra. The reported ^{13}C NMR data correspond to the ^1H-decoupled ^{13}C NMR data.

2.2 | Synthesis of compounds

The preparation procedure and characteristics for the most *ortho*-substituted, *meta*-substituted, and *para*-

TABLE 1 The ^{17}O NMR chemical shifts, $\delta(^{17}O)$, of the sulfonyl oxygen and single-bonded phenoxy oxygen for *ortho*-substituted, *para*-substituted, and *meta*-substituted phenyl tosylates, $4\text{-}CH_3\text{-}C_6H_4SO_2OC_6H_4\text{-}X$ (X-substituted phenyl esters of 4-methyl-benzenesulfonic acid), in DMSO at 50°C

$\delta(^{17}O)$[a]				$\delta(^{13}C)$
Substituent	**S=O**	**OC_6H_4X**	**In substituent**	***ipso*-C_O**[b]
$4\text{-}CH_3\text{-}C_6H_4SO_2OC_6H_4\text{-}X$				
H	165.8	191.8		149.1 (150.7)
$4\text{-}NO_2$	167.8	197.1	576.2 (NO_2)	153.2 (155.6)
4-CN	167.7	197.6		152.0
$4\text{-}N^+(CH_3)_3I^-$	167.7	–		149.0 (151.2)
4-COOH	167.2	–	254.0 (COOH)	152.2 (154.1)
4-Br	165.9	191.4		148.2 (149.4)[c]
4-F	165.0	188.4		145.1
$4\text{-}OCH_3$	164.3	187.1	50.7 (OCH_3)	142.4 (144)
4-OH	164.1	–	88.0 (OH)	141.3 (142.8)
$4\text{-}COO^-N^+Bu_4$	164.9	182.8	282.8 ($COO^-N^+Bu_4$)	149.0 (150.6)
$3\text{-}NO_2$	167.0	193.8	577.7 (NO_2)	148.9
3-F	166.4	192.4		149.6
3-Br	166.6	193.2		149.4
$3\text{-}NH_2$	165.8	190.8		150.4
$3\text{-}N^+(CH_3)_3I^-$	167.1	–		149.2 (151.1)
3-COOH	165.9	–	265.8 (COOH)[d]	149.0 (150.6)
$3\text{-}COO^-N^+Bu_4$	165.5	–	283.1 ($COO^-N^+Bu_4$)	148.6 (149.9)
$2\text{-}NO_2$	167.5	184.4	608.1 (NO_2)	140.2
$2\text{-}N^+(CH_3)_3I^-$	174.6[e]	–		142.1
2-CN	168.3	194.3		149.4
2-F	165.9	177.2		136.1
2-Cl	167.4	189.1		144.8
2-Br	167.8	194.1		146.1
$2\text{-}CF_3$	169.9	185.6		146.3
$2\text{-}COCH_3$	166.6	188.5	580.4 ($COCH_3$)	145.9
$2\text{-}COC_6H_5$	167.0	–	563.4 (COC_6H_5)	145.8
2-COOH	166.2	–	267.7 (COOH)[d]	147.0
$2\text{-}COO^-N^+Bu_4$	170.4	182.7	305.8 ($COO^-N^+Bu_4$)	145.6
$2\text{-}OCH_3$	165.0	176.9	41.8 (OCH_3)	137.6
$2\text{-}CH_3$	165.9	187.3		147.7
$2\text{-}CH\ (CH_3)_2$	166.3	184.5		146.3

[a] Approximately 1 molal solution of *ortho*-substituted, *meta*-substituted, and *para*-substituted phenyl tosylates in DMSO-d_6 (0.75 mL) was used. ^{17}O NMR spectra were recorded on a Bruker Avance III 700 spectrometer.

[b] The $\delta(^{13}C)$ values for *ipso*-C_O carbon in substituted phenyl benzoates, $C_6H_5CO_2C_6H_4\text{-}X$, in DMSO-$d_6$ are shown in brackets.[6] (See Supporting Information).

[c] The $\delta(^{13}C)$ value of *ipso*-C_O for 4-cholophenyl benzoate.

[d] The $\delta(^{17}O)$ value in a mixture of DMSO and DMSO-d_6.

[e] Partly decomposes.

substituted phenyl esters of *para*-toluenesulfonic acid, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, used in the present work have been described previously.[5,21–27]

The phenyl esters of *para*-toluenesulfonic acid, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X (X = 4-Br, 3-Br, 3-F, 2,6-$(CH_3)_2$) were prepared by the addition of *p*-toluenesulfonyl chloride to the corresponding phenol in pyridine with stirring at 0°C (the Einhorn method[28]). 4-Bromophenyl 4-toluenesulfonate: m.p. 95°C to 96°C (Hazlet[29] m.p. 93°C-95°C). 3-Bromophenyl 4-toluenesulfonate: m.p. 61°C to 62°C (Hazlet[29] m.p. 55°C-57°C). 3-Fluorophenyl 4-toluenesulfonate: m.p. 55°C to 56°C (Stang and Anderson[30] m.p. 47.5°C-48.5°C). 2,6-Dimethylphenyl 4-toluenesulfonate: m.p. 53°C to 54°C (Rottendorf and Sternhell[31] m.p. 53.5°C, Table S1).

Tetrabutylammonium salts of the [(4-methylphenyl) sulfonyl]oxybenzoic acids (4-CH_3-$C_6H_4SO_2OC_6H_4$-X, X = 4-$COO^-N^+Bu_4$, 3-$COO^-N^+Bu_4$, 2-$COO^-N^+Bu_4$) were prepared similar to the synthesis of the tetrabutylammonium (benzoyloxy)benzoates.[4] The equimolar amount of tetrabutylammonium hydroxide in methanol was added dropwise to the [(4-methylphenyl) sulfonyl]oxybenzoic acid in ethanol with intensive stirring similar to preparation of the tetrabutylammonium (benzoyloxy)benzoates.[4] The solvent evaporated to dryness in vacuo. The tetrabutylammonium [(4-methylphenyl)sulfonyl]oxybenzoates were obtained as colorless very viscous liquids.

Purity of synthesized substituted phenyl 4-toluenesulfonates was confirmed by ^1H and ^{13}C NMR spectroscopy in deuterated DMSO at 25°C. ^1H and ^{13}C NMR spectra for all studied phenyl 4-toluenesulfonates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, are shown in Supporting Information. In the case of tetrabutylammonium [(4-methylphenyl)sulfonyl]oxybenzoates (4-CH_3-$C_6H_4SO_2OC_6H_4$-X, X = 2-$COO^-N^+Bu_4$, X = 3-$COO^-N^+Bu_4$, X = 4-$COO^-N^+Bu_4$) in ^1H NMR spectra, the band for H in COOH group (δ: 13.19, 13.33, and 13.22) was not detected (Supporting Information).

3 | DATA PROCESSING AND RESULTS

The values of the chemical shifts, $\delta(^{17}O)$, of the sulfonyl oxygen (SO_2) and single-bonded phenoxy oxygen (OPh) in *para*-substituted and *meta*-substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, listed in Table 1 were correlated according to the Taft Equations 2 and 3 using the inductive σ_I[32,33] and the resonance σ°_R ($\sigma^\circ_R = \sigma^\circ_p - \sigma_I$)[32,34] and Taft σ°[32,35] substituent constants. The data treatment with Equations 2 and 3 was performed separately for *para* and *meta* derivatives.

$$\delta(^{17}O) = \delta(^{17}O)_H + (\rho_I)\sigma_I + (\rho_R)\sigma^\circ_R \tag{2}$$

$$\delta(^{17}O) = \delta(^{17}O)_H + (\rho)\sigma^\circ \tag{3}$$

In the case of *ortho* derivatives, the following Charton equations were used[36]:

$$\delta(^{17}O)_{ortho} = \delta(^{17}O)_H + (\rho_I)_{ortho}\sigma_I + (\rho_R)_{ortho}\sigma^\circ_R + \delta_{ortho}E^B_s \tag{4}$$

$$\delta(^{17}O)_{ortho} = \delta(^{17}O)_H + (\rho_I)_{ortho}\sigma_I + (\rho_R)_{ortho}\sigma^\circ_R + \delta_{ortho}\upsilon \tag{5}$$

Two steric scales were used for *ortho* substituents: the E^B_s constants[37–39] and the Charton scale of υ.[40,41] For the data processing, a multiple-parameter linear least-squares procedure[42]was used.

The results of the statistical data treatment of the sulfonyl SO_2 oxygen and the single-bonded bridging oxygen $\delta(^{17}O)$ values for substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, in DMSO (in Table 1) with the Taft and Charton Equations 2 to 5 are shown in Table 2. The substituent constants used in correlations are shown in Table 3.

4 | DISCUSSION

4.1 | Influence of *para* and *meta* substituents in 4-CH_3-$C_6H_4SO_2OC_6H_4$-X

The total NMR chemical shift σ_{tot} is considered to be dependent upon a local diamagnetic, σ_d, and a paramagnetic, σ_p, components.[8,9,43] The paramagnetic term σ_p as mainly responsible for the structure variability of ^{17}O NMR chemical shifts is usually described by Karplus-Pople Equation 6[8,43]:

$$\sigma_p = -\text{const.}\left(\Delta E^{-1}\right)\left(r^{-3}\right)\left(\sum Q\right) \tag{6}$$

In Equation 6, ΔE is the mean electronic excitation energy, r^{-3} is the average inverse cube of the radius for the 2p orbitals, and $\sum Q$ describes the charge density on oxygen and the extent of multiple bond order.

In the present work, the NMR $\delta(^{17}O)$ shift values for the sulfonyl S=O oxygen in substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, in DMSO (from 163.2 to 172 ppm, Table 1) were detected at much lower chemical shift values than the ^{17}O signals of the carbonyl C=O group in substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, in CH_3CN (from 344 to 350 ppm).[7] As it follows from the Karplus-Pople Equation 6,[8,43] the $\delta(^{17}O)$ values at lower ppm values demonstrate the higher charge density

TABLE 2 Correlation of the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, of the sulfonyl oxygen and single-bonded phenoxy oxygen for *ortho*-substituted, *para*-substituted, and *meta*-substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_3C_6H_4$-X, in DMSO (Table 1) with Equations (2) to (5)

Scales	$\delta(^{17}O)_H$	ρ_I or ρ°	ρ°_R	δ	R[a]	s[b]	n/n_0[c]
		***ortho*-Substituted Phenyl Tosylates**					
	$S{=}^{17}O$	$+R$ substituents					
σ_I, σ^o_R, E^B_s	165.8 ± 0.2	4.94 ± 0.34	8.59 ± 0.63	−4.43 ± 0.60	0.987	0.153	7/7[d]
σ_I, σ^o_R, υ	165.8 ± 0.2	4.56 ± 0.28	7.53 ± 0.50	1.85 ± 0.21	0.991	0.132	7/7[d]
		$-R$ substituents					
σ_I, σ^o_R, E^B_s	165.9 ± 0.4	10.8 ± 0.4	−38.2 ± 1.7	−5.80 ± 0.3	0.997	0.109	6/7[e]
	165.9 ± 0.8	11.0 ± 2.5	−37.6 ± 11.2	−5.09 ± 1.7	0.857	0.717	7/7[f]
σ_I, σ^o_R, υ	165.9 ± 0.4	11.0 ± 0.5	−38.0 ± 2.4	2.69 ± 0.18	0.994	0.154	6/7[e]
	165.9 ± 2.0	11.1 ± 2.5	−37.5 ± 11.1	2.61 ± 0.29	0.858	0.717	7/7[f]
	$^{17}OC_6H_4X$	$+R$ substituents					
σ_I, σ^o_R, E^B_s	190.6 ± 6.8	18.2 ± 9.4	57.7 ± 17.5	−9.33 ± 16.6	0.777	4.24	7/7[d]
	192.3 ± 4.3	16.7 ± 8.2	53.6 ± 14.4	–	0.820	3.86	7/7[d]
σ_I, σ^o_R, υ	190.5 ± 6.0	17.5 ± 9.0	55.7 ± 16.0	4.14 ± 6.8	0.781	4.20	7/7[d]
		$-R$ substituents					
σ_I, σ^o_R, E^B_s	191.6 ± 0.8	−12.4 ± 1.8	–	–	0.970	0.804	4/4[g]
	$S = {}^{17}O$	*para*-substituted phenyl tosylates					
σ°_{para}	165.2 ± 0.2	3.56 ± 0.47	–	–	0.943	0.456	8/8[h]
σ_I, σ^o_R	165.8 ± 0.2	2.05 ± 0.40	4.87 ± 0.34	–	0.988	0.219	8/8[h]
	$^{17}OC_6H_4X$						
σ°_{para}	189.4 ± 1.1	10.34 ± 30	–	–	0.890	1.98	6/6[i]
σ_I, σ^o_R	193.2 ± 1.1	2.52 ± 2.12	16.4 ± 2.6	–	0.948	1.47	6/6[i]
	$S{=}^{17}O$	*meta*-substituted phenyl tosylates					
σ°_{meta}	165.9 ± 0.1	1.37 ± 0.23	–	–	0.933	0.158	6/6[j]
σ_I, σ^o_R	165.8 ± 0.1	1.60 ± 0.29	0.34 ± 0.26	–	0.937	0.154	6/6[j]
σ_I	165.6 ± 0.1	2.29 ± 0.09	–	–	0.998	0.033	4/6[k]
	$^{17}OC_6H_4X$						
σ°_{meta}	191.5 ± 0.2	3.46 ± 0.52		–	0.956	0.353	5/5[l]
σ_I, σ^o_R	191.7 ± 0.5	3.05 ± 0.88	2.20 ± 0.90	–	0.924	0.460	5/5[l]

[a] R—correlation coefficient.

[b] s—standard deviation.

[c] n_0 reflects the total number of data involved in the correlation; n—the number of points remaining after exclusion of significantly deviating points.

[d] The $\delta(^{17}O)$ values for 2-F, 2-Cl, 2-Br, 2-OCH_3, 2-CH_3, 2-CH $(CH_3)_2$, and unsubstituted derivative were included.

[e] The $\delta(^{17}O)$ values for 2-NO_2, 2-CN, 2-CF_3, 2-$COCH_3$, 2-COPh, 2-COOH, and unsubstituted derivative were included. 2-COOH derivative was excluded during the data processing.

[f] The $\delta(^{17}O)$ values for 2-NO_2, 2-CN, 2-CF_3, 2-$COCH_3$, 2-COPh, 2-COOH, and unsubstituted derivative were included.

[g] The $\delta(^{17}O)$ values for 2-NO_2, 2-CF_3, 2-$COCH_3$, and unsubstituted derivative were included.

[h] The $\delta(^{17}O)$ values for 4-NO_2, 4-CN, 4-COOH, 4-F, 4-Br, 4-OCH_3, 4-OH, and unsubstituted derivative were included.

[i] The $\delta(^{17}O)$ values for 4-NO_2, 4-CN, 4-F, 4-Br, 4-OCH_3, and unsubstituted derivative were included.

[j] The $\delta(^{17}O)$ values for 3-NO_2, 3-Br, 3-COOH, 3-F, 3-NH_2, and unsubstituted derivative were included.

[k] The $\delta(^{17}O)$ values for 3-NO_2, 3-Br, 3-COOH, and 3-NH_2 derivatives were included. 3-F and unsubstituted derivatives were excluded.

[l] The $\delta(^{17}O)$ values for 3-NO_2, 3-Br, 3-F, 3-NH_2, and unsubstituted derivative were included.

TABLE 3 Substituent constants used in the correlations

X	σ_I[a]	σ°_R[b]	E_s^B[c]	υ[d]	σ°[e]
H	0	0	0	0	0
4-NO_2	0.63	0.19	–	–	0.81
4-CN	0.58	0.11	–	–	0.72
4-Br	0.45	−0.19	–	–	0.30
4-F	0.52	−0.35	–		0.21
4-COOH	0.30	0.14	–		0.46
4-OCH_3	0.25	−0.41	–		−0.15
4-OH	0.25	−0.41	–		−0.16
3-NO_2	0.63	0.19	–		0.71
3-F	0.52	−0.35	–	–	0.34
3-Br	0.45	−0.19	–	–	0.39
3-NH_2	0.10	−0.48	–	–	−0.14
3-COOH	0.30	0.14	–	–	0.36
2-NO_2	0.63	0.19	−0.374	0.76	
2-CN	0.58	0.11	−0.03	0	–
2-F	0.52	−0.35	−0.155	0.27	–
2-Cl	0.47	−0.20	−0.243	0.55	–
2-Br	0.45	−0.19	−0.27	0.65	–
2-CF_3	0.41	0.10	−0.593	1.24	–
2-$COCH_3$	0.28	0.16	−0.665	1.39	–
2-COC_6H_5	0.28	0.15	−0.665	1.39	–
2-COOH	0.30	0.14	−0.665	1.39	–
2-OCH_3	0.25	−0.41	−0.308	0.56	–
2-CH_3	−0.05	−0.10	−0.264	0.52	–
2-CH $(CH_3)_2$	−0.05	−0.08	−0.341	0.76	–

[a] The σ_I values from Exner[32] and Taft and Lewis[33] were used.

[b] The σ°_R values from Exner[32] and Taft et al[34] were used.

[c] The steric constant E_s^B values from Nummert et al,[5] Nummert and Piirsalu,[37] Nummert et al,[38] and Nummert et al[39] were used.

[d] The Charton steric constant υ from Nummert et al,[5] Nummert et al,[38] Aslam et al,[40] and Charton[41] was used.

[e] The σ° values in Exner[32] and Palm[35] were used.

at the sulfonyl SO_2 oxygens and the increased ionic bond character of the sulfonyl SO_2 group ($S^+—O^-$) as compared to that of the carbonyl C═O oxygen in phenyl benzoates.[44]

The values of the chemical shifts, $\delta(^{17}O)$, of the sulfonyl oxygen for *para*-substituted and *meta*-substituted phenyl tosylates in DMSO (Table 1) in the case of neutral substituents were ca. 0.5 to 1.5 ppm higher as compared to the corresponding $\delta(^{17}O)$ values measured earlier in CH_3CN.[5] In the case of electroneutral *para* substituents (H, NO_2, CN, F, OCH_3, OH), the $\delta(^{17}O)$ values of the sulfonyl S═O oxygen for substituted phenyl tosylates in DMSO were found to be linearly correlated with the corresponding $\delta(^{17}O)$ values in CH_3CN[5] as follows (Equation 7):

$$\delta\left(^{17}O_{S=O}\right)^X_{DMSO} = (2.5\pm5.7) + (0.993\pm0.033)\delta\left(^{17}O_{S=O}\right)^X_{CH_3CN} \quad (7)$$
$$R = 0.997, s = 0.126, n/n_0 = 6/6$$

When in Equation 7, the intercept was considered as insignificant (=0), then the slope of the dependence (7) was 1.007 ± 0.003, $s = 0.116$, $n/n_0 = 6/6$.

We found in substituted phenyl tosylates the *para* and *meta* electron-withdrawing substituents to cause high-frequency shift for the ^{17}O signal of the sulfonyl S═O oxygen showing deshielding effect of the O atom (Table 1). The electron-donating substituents have an opposite effect resulting in low-frequency shift and shielding of the sulfonyl S═O oxygen atom. The similar influence of the substituents on the $\delta(^{17}O)$ values of the carbonyl oxygen was found in substituted phenyl benzoates.[6,7] The increased double bond character of the carbonyl group produced by an electron-withdrawing groups in substituted phenyl esters of benzoic acid was proved by the carbonyl carbon ^{13}C NMR chemical low-frequency, δ_{CO}, shifts and the increased infrared frequencies of the carbonyl group, ν_{CO}.[4,15,44]

In the case of electroneutral substituents, the sulfonyl oxygen chemical shifts, $\delta(^{17}O)$, for the *para*-substituted phenyl tosylates (Table 1) correlated well with the dual substituent parameter method using the Taft σ_I and σ°_R (Equation 8, Table 2)

$$\left(\delta^{17}O_{S=O}\right)_{para} = (165.8\pm0.2) + (2.05\pm0.40)\sigma_I + (4.87\pm0.34)\sigma^\circ_R \quad (8)$$
$$R = 0.988, s = 0.219, n/n_0 = 8/8$$

and the single parameter treatment using the Taft σ° substituent constants ($R = 0.943$, Table 2). In the case of *para* derivatives, the influence of the resonance term appeared to be stronger in comparison with that of the inductive term (Equation 8). In the case of *meta* derivatives, the effect of resonance term was found to be insignificant (Equation 9, Table 2):

$$\left(\delta^{17}O_{S=O}\right)_{meta} = (165.8\pm0.1) + (1.60\pm0.29)\sigma_I + (0.34\pm0.26)\sigma^\circ_R \quad (9)$$
$$R = 0.937, s = 0.154, n/n_0 = 6/6$$

In phenyl tosylates, the susceptibility of the SO_2 chemical shifts, $\delta(^{17}O)$, in DMSO toward the *para* polar substituent effect from the phenyl side (ρ_I = 2.05,

$\rho_R = 4.87$, Equation 8, Table 2) was approximately the same as was found earlier for the SO_2 chemical shifts, $\delta(^{17}O)$, in phenyl tosylates ($\rho_I = 1.56$, $\rho_R = 4.77$[5]) and for the carbonyl CO oxygen chemical shifts, $\delta(^{17}O)$ in substituted phenyl benzoates, $C_6H_5CO_2C_6H_4\text{-}X$, ($\rho_I = 3.25$, $\rho_R = 4.34$[7]) in CH_3CN.

Using the chemical shifts, $\delta(^{17}O)$, of the sulfonyl oxygen for *para*-substituted and *meta*-substituted phenyl tosylates, $4\text{-}CH_3\text{-}C_6H_4SO_2OC_6H_4\text{-}X$, in DMSO (Table 1) and the results of the statistical data treatment in Table 2 for the charged substituents, the substituent constants, $\sigma_{X\pm}$, which could be applicable to correlate the influence of the charged substituent effects simultaneously with those of electroneutral substituents, were calculated. To compare the values of the substituent constants of charged substituents established in the present work with those $\sigma^\circ_{X\pm}$ values obtained previously by different measurements given in Table 4, for *para* charged substituents, $\sigma^\circ_{X\pm}$ were calculated with Equation 10:

$$(\sigma^\circ_{X\pm})_p = \left[\delta\left(^{17}O_{S=O}\right)_{X\pm} - \delta\left(^{17}O_{S=O}\right)_H\right]/\rho_p \qquad (10)$$

For *meta* charged substituents with Equation 10, the inductive substituent constants $(\sigma_I)_{X\pm}$ were calculated using the corresponding values of $\delta(^{17}O_{S=O})_{X\pm}$ in Table 1 and $(\rho_I)_m$ in Table 2. It could be mentioned that $\sigma_I = \sigma^\circ$ in case $\sigma^\circ_R = 0$.

The substituent constants $(\sigma^\circ_{X\pm})_p$ and $(\sigma_I)_{X\pm}$ for *para* and *meta* charged substituents estimated with Equation 10 using the corresponding sulfonyl oxygen (SO_2) chemical shifts, $\delta(^{17}O_{S=O})$, in DMSO (Table 1) and the values of ρ_p and $(\rho_I)_m$ for neutral *para*-substituted and *meta*-substituted phenyl tosylates in DMSO (Table 2) are listed in Table 4.

TABLE 4 The values of substituent constants, $\sigma^\circ_{X\pm}$, for charged substituents estimated from ^{17}O NMR chemical shifts, $\delta(^{17}O)$, in DMSO for substituted phenyl tosylates, $4\text{-}CH_3\text{-}C_6H_4SO_2OC_6H_4\text{-}X$, the infrared stretching frequencies, ν_{CO}, ^{13}C NMR carbonyl chemical shifts, δ_{CO}, in DMSO, and rates of alkaline hydrolysis for phenyl benzoates, $C_6H_5CO_2C_6H_4\text{-}X$, in 4.4 M aqueous NaCl solution at 50°C

Substituent X	σ°_p, (σ_I) $\delta(^{17}O)$[a]	σ° ν_{CO}[b]	σ° δ_{CO}[c]	σ° 4.4 M NaCl[d]	Recommended $(\sigma^\circ_{X\pm})_{av}$[e]	σ° for Ion Pairs[f]	σ° with Electrostatic Component (in Aq. Solutions)[g]
$4\text{-}N^+(CH_3)_3I^-$	0.70 (0.56)	0.65	0.44	0.53	0.58	0.53	1.025, 0.88, 0.96
$3\text{-}N^+(CH_3)_3I^-$	0.65 (0.56)	0.46	0.44	0.46	0.50	0.59	1.094, 1.04, 0.99
$2\text{-}N^+(CH_3)_3I^-$	0.77	0.78	0.69	0.83	0.77	–	1.15
$4\text{-}CO_2^-N^+Bu_4$	−0.01 (0.18)	0.08	0.14	0.06	0.09	0.26	−0.078, −0.122
$3\text{-}CO_2^-N^+Bu_4$	−0.04 (0.03)	0.07	−0.02	0.04	−0.01	0.24	−0.194, −0.195
$2\text{-}CO_2^-N^+Bu_4$				0.07[h]			
$4\text{-}O^-N^+Bu_4$	–	−0.44[i]		−0.48[i]			
$3\text{-}O^-N^+Bu_4$	–	−0.44[i]		−0.46[i]			

[a] The values of the σ° substituent constants for charged substituent X in DMSO were calculated with Equation (10) using the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, for substituted phenyl tosylates, $4\text{-}CH_3\text{-}C_6H_4SO_2OC_6H_4\text{-}X$, in Table 1. For *para* derivatives $\rho_p = 3.56$, $\delta(^{17}O)_H = 165.2$, for *meta* derivatives $\rho_m = 2.29$, $\delta(^{17}O)_H = 165.6$, and for *ortho* derivatives $\rho_{ortho} = 10.8$, $\delta(^{17}O)_H = 165.9$ (Table 2, for $2\text{-}N^+(CH_3)_3I^-$ substituent the resonance and steric factors appeared to be insignificant[4]). In brackets are shown the $\sigma^\circ_{X\pm}$ values calculated with the chemical shifts, $\delta(^{17}O)$, in Table S1 and using $\delta(^{17}O)_H = 165.4$, and $\rho_{p,m} = 3.79$ (Table S2).

[b] The σ° substituent constants calculated using infrared carbonyl stretching frequencies, ν_{CO}, in DMSO for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4\text{-}X$.[4]

[c] The σ° values calculated from the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4\text{-}X$, in DMSO.[4]

[d] The σ° values calculated from the rate constants for the alkaline hydrolysis of substituted phenyl benzoates, $C_6H_5CO_2C_6H_4\text{-}X$, in aqueous 4.4 M NaCl solution at 50°C.[4]

[e] The averaged values of substituent constants, $(\sigma^\circ_{X\pm})_{av}$, for ion pairs of charged substituents calculated on the bases of the following experimental data: the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, for substituted phenyl tosylates in DMSO (Table 1), the carbonyl stretching frequencies, ν_{CO}, in DMSO, the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, in DMSO and log k values for the alkaline hydrolysis in aqueous 4.4 M NaCl solution for substituted phenyl benzoates.[4]

[f] The σ° values for ion pairs calculated by Wepster as free from the electrostatic interaction term.[1]

[g] The σ° constants containing the electrostatic component for reactions between substrate containing charged substituent and the ionic reagent. To calculate the σ° values, the rate constants or *pK* values extrapolated to pure water were used.[32,48]

[h] Using the $\delta(^{17}O)_{S=O} = 170.4$ ppm for *ortho* $COO^-N^+Bu_4$-phenyl tosylate in DMSO (Table 1) and $\sigma_I = 0.1$ and $\sigma^\circ_R = 0$ with Equation (12), the steric constant $E^B_s = -0.60$ for *ortho* $COO^-N^+Bu_4$ substituent was estimated. The value of $\sigma^\circ = 0.07$ for *ortho* COO^-Na^+ substituent could be calculated from the kinetic data of the alkaline hydrolysis of $2\text{-}COO^-Na^+$-phenyl benzoate in 4.4 M aqueous NaCl at 50°C (log $k = -0.55$,[48] log $k_0 = 0.070$,[49,50] $\delta_{ortho} = 1.2$[50]) using the steric constant $E^B_s = -0.60$ for *ortho* COO^-Na^+ substituent.

[i] Data from Nummert et al.[4]

The $\sigma^{o}_{X\pm}$ values for charged substituents estimated with Equation 10 in Table 4 ($\sigma^{o}_{X\pm}$ = 0.70 for 4-N^{+}(CH$_3$)$_3$I^{-}, −0.01 for 4-COO^{-}N^{+}Bu$_4$ and $(\sigma_I)_{X\pm}$ = 0.65 for 3-N^{+}(CH$_3$)$_3$I^{-}, −0.04 for 3-COO^{-}N^{+}Bu$_4$) are in good agreement with the constants, $\sigma^{o}_{X\pm}$, obtained recently from the IR carbonyl stretching frequencies, ν_{CO}, and the carbonyl carbon chemical shifts, δ_{CO}, for substituted phenyl benzoates series, $C_6H_5CO_2C_6H_4$-X, in DMSO,[4] as well as with the constants, $\sigma^{o}_{X\pm}$, for ion pairs proposed by Hoefnagel and Wepster[1] and those calculated from the kinetic data of the alkaline hydrolysis of substituted phenyl benzoates in concentrated aqueous NaCl solution (Table 4).[4] On the basis of the constants, $\sigma^{o}_{X\pm}$, for charged substituents estimated from the $\delta(^{17}O)$, values of phenyl tosylates in DMSO (Table 3), we can conclude that in substituted phenyl tosylates, the charged substituent X = 3-N^{+}(CH$_3$)$_3$I^{-}, 4-N^{+}(CH$_3$)$_3$I^{-}, 3-COO^{-}N^{+}Bu$_4$, and 4-COO^{-}N^{+}Bu$_4$, in DMSO are not completely ionized and are in ion pair form. Consequently, when correlating data set containing simultaneously derivatives with charged substituents and electroneutral substituents, for charged substituents in DMSO, the substituent constants for ion pairs could be used. The substituent constants for ion pairs do not include the electrostatic component which was proved essential in the case of pure aqueous solutions (Equation 1).[1] A good relationship between $\sigma^{o}_{X\pm}$ values for charged substituents estimated from the $\delta(^{17}O)$ values of phenyl tosylates in DMSO, the IR carbonyl stretching frequencies, ν_{CO}, and the carbonyl carbon chemical shifts, δ_{CO}, for substituted phenyl benzoates in DMSO, and the $\sigma^{o}_{X\pm}$ values for charged substituents calculated from the kinetic data of the alkaline hydrolysis of substituted phenyl benzoates in concentrated 4.4 M aqueous NaCl solution shows that for ion pairs of charged substituents in DMSO and aqueous concentrated salt solution, the same substituent constants, $\sigma^{o}_{X\pm}$, could be used (Figure 1).

In substituted phenyl tosylates, *para* and *meta* substituents in phenyl moiety exert on the electron density at the phenyl *ipso* carbon ($C_{O\text{-}1}$, Table 1) nearly in the same way as in substituted phenyl benzoates. For derivatives with *para* and *meta* electroneutral substituents and charged substituents (3-N^{+}(CH$_3$)$_3$I^{-}, 4-N^{+}(CH$_3$)$_3$I^{-}, 3-COO^{-}N^{+}Bu$_4$, 4-COO^{-}N^{+}Bu$_4$) in DMSO, we obtained Equation 11:

$$\delta\left(^{13}C_{O-1}\right)_{Tos} = (6.66\pm3.92) + (0.944\pm0.026)\delta\left(^{13}C_{O-1}\right)_{Benz} \qquad (11)$$
$$R = 0.996, s = 0.310, n/n_0 = 11/11$$

The chemical shift $\delta(^{13}C_{O\text{-}1})_{Tos}$ values for the phenyl *ipso* carbon were found to be dependent mainly on the resonance effect of substituents. For *para*-substituted phenyl tosylates, 4-CH$_3$-C$_6$H$_4$SO$_2$OC$_6$H$_4$-X (X = H, 4-NO$_2$, 4-CN, 4-COOH, 4-F, 4-Br, 4-OH, 4-OCH$_3$), in DMSO, we found (Equation 12):

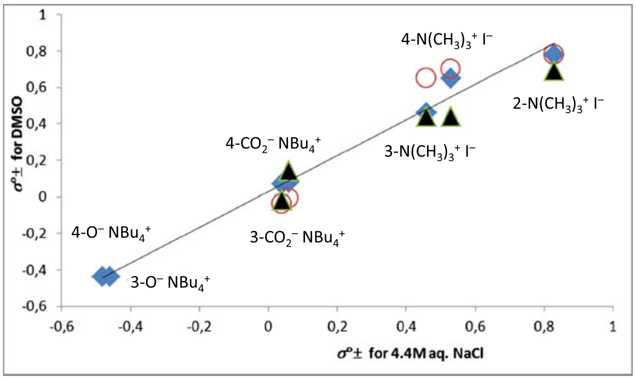


FIGURE 1 Relationship between the $\sigma^{o}_{X\pm}$ values for ion pairs of the charged substituents estimated from the various processes in DMSO and the $\sigma^{o}_{X\pm}$ values of ion pairs of the charged substituents calculated on the basis of the alkaline hydrolysis of substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, in 4.4 M aqueous NaCl solution[4]

$$\sigma^{o}_{X\pm} = (0.102\pm0.292) + (0.973\pm0.061)\sigma^{o}_{X\pm}(4.4\text{ M aq.NaCl})$$
$$R = 0.971, s = 0.097, n/n_0 = 17/17.$$

○ The $\sigma^{o}_{X\pm}$ and $(\sigma_I)_{X\pm}$ values calculated from the ^{17}O NMR chemical shifts of substituted phenyl tosylates, 4-CH$_3$-C$_6$H$_4$SO$_2$OC$_6$H$_4$-X, in DMSO.

◆ The $\sigma^{o}_{X\pm}$ values calculated from the infrared stretching frequencies, ν_{CO}, for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, in DMSO.

▲ The $\sigma^{o}_{X\pm}$ values calculated from the carbonyl carbon ^{13}C NMR chemical shifts for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, in DMSO.

$$\delta\left(^{13}C_{O-1}\right)_{Tos} = (148.7\pm0.8) + (3.01\pm1.73)\sigma_I + (16.7\pm1.4)\sigma^{o}_R \qquad (12)$$
$$R = 0.979, s = 0.939, n/n_0 = 8/8$$

During the data treatment, the inductive component in Equation 12 was excluded as insignificant, and we obtained $\delta(^{13}C_{O\text{-}1})_{Tos} = (149.9 \pm 0.4) + (17.4 \pm 1.6)\sigma^{o}_R$, R = 0.971, s = 1.09, n/n_0 = 8/8. In substituted phenyl tosylates and phenyl benzoates, the $\delta(^{13}C_{O\text{-}1})$ value for 4-N^{+}(CH$_3$)$_3$I^{-} derivative (149.1, 151.2) and 4-COO^{-}N^{+}Bu$_4$ derivative (149.0, 150.6) was found to be practically equal to that for unsubstituted derivative (149.1, 150.7) (Table 1). Therefore, for N^{+}(CH$_3$)$_3$I^{-} and COO^{-}N^{+}Bu$_4$ substituents, $\sigma^{o}_R = 0$ was used.

The sulfonyl oxygen chemical shifts, $\delta(^{17}O)_{S=O}$, in *para*-substituted and *meta*-substituted phenyl tosylates

(Table 1) were found to be correlated well with the corresponding infrared stretching frequencies of the carbonyl group, ν_{CO}, in substituted phenyl benzoates,[4] including data for derivatives with both the charged and electroneutral substituents in DMSO (Equation 13):

$$\begin{aligned}\delta\left(^{17}O_{S=O}\right)_{Tos} &= (-294.0\pm72.7)\\ &\quad+(0.265\pm0.042)(\nu_{CO})_{Benz}\\ &\quad+(1.45\pm0.76)\sigma^{o}{}_{R}\\ R = 0.970, s &= 0.335, n/n_0 = 13/13\end{aligned} \qquad (13)$$

When the data treatment with Equation 13 $\delta(^{17}O_{S=O})_{Tos} = a + b(\nu_{CO})_{Benz} + c\sigma^{o}{}_{R}$ was carried out only for *para* derivatives (X = H, 4-NO_2, 4-OH, 4-OCH_3, 4-Br, 4-NH_2, 4-$N^+(CH_3)_3I^-$, 4-$COO^-N^+Bu_4$), the excellent correlation was obtained: $a = -255.0 \pm 49.4$, $b = 0.243 \pm 0.029$, $c = 2.23 \pm 0.51$, $s = 0.155$, $R = 0.996$, $n/n_0 = 7/8$ (the 4-$COO^-N^+Bu_4$ derivative was excluded). In Equation 13, the parameter *b* shows the relation of the inductive effects in 2 processes compared: $b = \rho_I(\delta(^{17}O_{S=O}))_{Tos}/\rho_I(\nu_{CO})_{Benz}$ and $c = \rho_R(\delta(^{17}O_{S=O}))_{Tos} - b\ \rho_R(\nu_{CO})_{Benz}$.[15]

In substituted phenyl tosylates, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, the oxygen chemical shifts, $\delta(^{17}O)$, in substituents 3-$CO_2^-N^+Bu_4$, 4-$CO_2^-N^+Bu_4$, and 2-$CO_2^-N^+Bu_4$ were observed by ca. 20 to 30 ppm at the higher frequencies (the $\delta(^{17}O)$ values at 283.1, 282.8, and 305.4 ppm, respectively, Table 1) as compared to that in the corresponding carboxylic acid groups (for X = 3-COOH $\delta(^{17}O)$ = 265.8 ppm, 4-COOH $\delta(^{17}O)$ = 254.0, X = 2-COOH $\delta(^{17}O)$ = 267.7 ppm, Table 1). Similarly, the ^{13}C NMR chemical shifts, $\delta(^{13}C)_{COO}$, of the carboxylate group in tetrabutylammonium carboxylate substituents were higher as compared to that in the carboxylic acid substituent: for X = 3-$CO_2^-N^+Bu_4$ $\delta(^{13}C)_{COO}$ = 166.4, 4-$CO_2^-N^+Bu_4$ $\delta(^{13}C)_{COO}$ = 166.9, 2-$CO_2^-N^+Bu_4$ $\delta(^{13}C)_{COO}$ = 166.4. For COOH substituents, the corresponding $\delta(^{13}C)_{COOH}$ values were 166.1 for 3-COOH, 166.4 for 4-COOH, and 165.5 for 2-COOH (Supporting Information). Earlier[4] in substituted phenyl benzoates, the COO^-carbon chemical shifts $\delta(^{13}C)_{COO}$ in tetrabutylammonium carboxylate substituents were found also higher as compared to that in the COOH substituent (for X = 3-$CO_2^-N^+Bu_4$ $\delta(^{13}C)_{COO}$ = 167.0, and for 3-COOH $\delta(^{13}C)_{COOH}$ = 166.5, for 4-$CO_2^-N^+Bu_4$ $\delta(^{13}C)_{COO}$ = 167.5, and for 4-COOH $\delta(^{13}C)_{COOH}$ = 166.6).

The deshielding effect of carbonyl oxygens and the carbonyl carbons in tetrabutylammonium carboxylate substituents compared to that in the case of COOH substituents give evidence that in the tetrabutylammonium carboxylate substituents in ion pair form, the electrons are more delocalized (high-frequency shift) as compared to that in the case of COOH substituents.

4.1.1 | Influence of para and meta substituents on the $\delta(^{17}O)$ values of single-bonded phenoxy oxygen

The influence of the inductive and resonance effects of *para* and *meta* substituents from the phenyl side on the single-bonded phenoxy oxygen $\delta(^{17}O)$ values in substituted phenyl tosylates in DMSO similar to that in CH_3CN was ca. 3.0 times stronger than on the $\delta(^{17}O)$ values of the sulfonyl oxygen (Table 2):

$$\begin{aligned}\delta\left(^{17}O_{OPh}\right)_{m,p} &= -(304.0\pm32.9)\\ &\quad+(2.99\pm0.20)\delta\left(^{17}O_{S=O}\right)_{m,p}\\ R = 0.981, s &= 0.65, n/n_0 = 10/10.\end{aligned} \qquad (14)$$

4.2 | Influence of *ortho* substituents

For *ortho*-substituted phenyl tosylates in the case of neutral substituents, a good correlation between the sulfonyl oxygen chemical shifts, $\delta(^{17}O)$, in DMSO (Table 1) and in CH_3CN[5] was found (Equation 15):

$$\begin{aligned}\delta\left(^{17}O_{S=O}\right)^{X}{}_{DMSO} &= (28.3\pm8.9)\\ &\quad+(0.833\pm0.048)\delta\left(^{17}O_{S=O}\right)^{X}{}_{CH_3CN}\\ R = 0.978, s &= 0.277, n/n_0 = 12/12\end{aligned} \qquad (15)$$

In *ortho*-substituted phenyl tosylates, the sulfonyl oxygen chemical shifts, $\delta(^{17}O)$, in DMSO (Table 1) in the case of neutral substituents showed a good correlation with the Charton equation (Equations 4 and 5, Table 2) when the data treatment was performed separately for derivatives with electron-donating (+*R*) substituents and electron-withdrawing (−*R*) substituents. In the case of *ortho* +*R* substituents (X = H, 2-F, 2-Cl, 2-Br, 2-OCH_3, 2-CH_3, 2-$CH(CH_3)_2$), we obtained (Equation 16, Table 2):

$$\begin{aligned}\delta\left(^{17}O_{S=O}\right)_{ortho} &= (165.8\pm0.2)+(4.94\pm0.34)\sigma_I\\ &\quad+(8.59\pm0.63)\sigma^{o}{}_{R}-(4.43\pm0.60)E^{B}{}_{s}\\ R = 0.987, s &= 0.153, n/n_0 = 7/7\end{aligned} \qquad (16)$$

In *ortho*-substituted phenyl tosylates in the case of +*R* substituents in DMSO, the influence of the inductive, resonance, and steric terms (Equation 16) was approximately the same as was previously found for the sulfonyl oxygen chemical shifts, $\delta(^{17}O)$, for *ortho*-substituted phenyl tosylates in CH_3CN[5] ($\rho_I = 5.23$, $\rho_R = 9.20$, $\delta = -6.74$).

The chemical shifts, $\delta(^{17}O)$, for phenyl tosylates containing electron-withdrawing (−*R*) substituents (X = H, 2-NO_2, 2-CN, 2-CF_3, 2-$COCH_3$, 2-COPh, 2-COOH) showed the following correlation (Equation 17, Table 2):

$$\delta\left({}^{17}\mathrm{O}_{\mathrm{S=O}}\right)_{\mathrm{ortho}} = (165.9\pm0.4) + (10.8\pm0.4)\sigma_{\mathrm{I}} - (38.2\pm1.7)\sigma^{\circ}{}_{\mathrm{R}} - (5.80\pm0.30)E^{\mathrm{B}}{}_{\mathrm{s}} \quad (17)$$
$$R = 0.997, s = 0.109, n/n_0 = 6/7$$

In substituted phenyl tosylates, containing *ortho* $-R$ substituents in the phenyl moiety, the sulfonyl oxygen appeared to be deshielded by an inductive effect but shielded by a resonance effect similar to that in the case of $+R$ substituents. The oxygens in *ortho* COOH group revealed a deshielding effect (for 2-COOH $\delta(^{17}\mathrm{O}) = 267.7$ ppm, see Table 1) as compared to oxygens in *para* COOH group (for 4-COOH $\delta(^{17}\mathrm{O}) = 254.0$ ppm, Table 1). The similar deshielding effect of oxygens in *ortho* NO_2 substituent was detected earlier in substituted phenyl tosylates and phenyl benzoates in CH_3CN.[5,7]

From Equation 17 for *ortho* charged substituent 2-$N^+(CH_3)_3I^-$, the substituent constant $(\sigma_\mathrm{I})_{\mathrm{X}\pm} = 0.77$ was estimated (Table 4). The estimated $(\sigma_\mathrm{I})_{\mathrm{X}\pm}$ substituent constant value for 2-$N^+(CH_3)_3I^-$ is in good agreement with the $(\sigma_\mathrm{I})_{\mathrm{X}\pm}$, constants for 2-$N^+(CH_3)_3I^-$) obtained from the IR carbonyl stretching frequencies, ν_{CO} ($(\sigma_\mathrm{I})_{\mathrm{X}\pm} = 0.78$[4]), the carbonyl carbon chemical shifts, δ_{CO} ($(\sigma_\mathrm{I})_{\mathrm{X}\pm} = 0.69$[4]) for substituted phenyl benzoate series, $C_6H_5CO_2C_6H_4$-X, in DMSO (Table 4).

The correlation using the modified Charton steric constants, υ, gave nearly the same results as with the steric constants, $E^{\mathrm{B}}{}_{\mathrm{s}}$ (Table 2). In the case of the Charton steric constants, υ, the susceptibility to the steric effect was positive and the magnitude of δ_{ortho} was ca. twice smaller as compared to the δ_{ortho} value obtained with the $E^{\mathrm{B}}{}_{\mathrm{s}}$ steric constants ($E^{\mathrm{B}}{}_{\mathrm{s}} < 0$, Table 2). Because of the steric effect of substituents in the phenyl moiety (a van der Waals deshielding effect[45–47]), the sulfonyl oxygens are deshielded more than the unsubstituted derivative.

4.2.1 | Influence of ortho substituents on the $\delta(^{17}\mathrm{O})$ values of single-bonded phenoxy oxygen

The $\delta(^{17}\mathrm{O})$ values for single-bonded phenoxy oxygens in *ortho*-substituted phenyl tosylates in DMSO similar to the $\delta(^{17}\mathrm{O})$ values for sulfonyl oxygen (Equations 16 and 17, Table 2) showed a good correlation with the Charton equation (Equations 4 and 5) when the data treatment was performed separately for derivatives with $+R$ and $-R$ substituents. Similar to *para* substituents in the case of *ortho* $+R$ substituents in the phenyl moiety, the single-bonded phenoxy oxygen is deshielded by $-I$ inductive effect and shielded by the inductive $+I$ and $+R$ resonance effect of *ortho* substituents more than 3 times greater ($\rho_I = 18.2$, $\rho_R = 57.7$, Table 2) than that on the double-bonded sulfonyl oxygen ($\rho_I = 4.94$, $\rho_R = 8.59$, Table 2). The electron-withdrawing ($-R$) substituents in phenyl moiety in *ortho*-substituted phenyl tosylates increase the shielding effect of the single-bonded oxygen by the substituent inductive effect similarly to that in substituted phenyl benzoates.[7]

In the case of phenyl tosylates, approximately the same correlation as shown in Table 2 was obtained when the $\delta(^{17}\mathrm{O})$ values of the sulfonyl oxygen of tosylates in DMSO were determined on a Bruker Avance II 200 spectrometer (Tables S1 and S2).

5 | CONCLUSIONS

The ^{17}O NMR spectra for 31 *ortho*-substituted, *para*-substituted, and *meta*-substituted phenyl esters of *p*-toluenesulfonic acid, 4-CH_3-$C_6H_4SO_2OC_6H_4$-X, (phenyl tosylates) with electroneutral and charged substituents (X = 4-$N^+(CH_3)_3I^-$, 3-$N^+(CH_3)_3I^-$, 2-$N^+(CH_3)_3I^-$, 4-$COO^-N^+Bu_4$, 3-$COO^-N^+Bu_4$, and 2-$COO^-N^+Bu_4$) in DMSO were recorded. The chemical shifts, $\delta(^{17}\mathrm{O})$, for sulfonyl oxygen (SO_2) in DMSO were found at much lower frequencies than the ^{17}O signals of the carbonyl (C=O) group in substituted phenyl benzoates. This shows that in substituted phenyl tosylates in DMSO, similar to that in CH_3CN, the oxygen nuclei in SO_2 group are more shielded as compared to oxygen nucleus in carbonyl (C=O) group in phenyl benzoates, and the extent of the double bond contribution in SO_2 group in benzenesulfonates is reduced as compared to that in the carbonyl C=O bond in phenyl benzoates, $C_6H_5CO_2C_6H_4$-X. The substituent constants $\sigma^{\circ}{}_{\mathrm{X}\pm}$ and $(\sigma_\mathrm{I})_{\mathrm{X}\pm}$ for charged substituents (4-$N^+(CH_3)_3I^-$, 3-$N^+(CH_3)_3I^-$, 2-$N^+(CH_3)_3I^-$, 4-$COO^-N^+Bu_4$, 3-$COO^-N^+Bu_4$) estimated in the present work using ^{17}O NMR chemical shifts, $\delta(^{17}\mathrm{O})$, of the sulfonyl group for phenyl tosylates in DMSO showed a good agreement with the $\sigma^{\circ}{}_{\mathrm{X}\pm}$ substituent constants for charged substituent constants obtained earlier[4] using infrared carbonyl stretching frequencies, ν_{CO}, the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, in DMSO and with constants, $\sigma^{\circ}{}_{\mathrm{X}\pm}$, for ion pairs proposed by Hoefnagel and Wepster[1] and those calculated from the kinetic data of the alkaline hydrolysis of substituted phenyl benzoates in concentrated aqueous NaCl solution (Table 4).[2] The substituent constants, $\sigma^{\circ}{}_{\mathrm{X}\pm}$, for charged substituents obtained from the chemical shifts, $\delta(^{17}\mathrm{O})$, for substituted phenyl tosylates in DMSO similarly to those obtained previously using the infrared carbonyl stretching frequencies, ν_{CO}, and the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, for substituted phenyl benzoates in DMSO[4] prove that in DMSO, the charged substituents are predominantly in ion pair form and are not dissociated into free ions. It was shown that for ion pairs of the charged substituents in DMSO and concentrated aqueous salt solution, the same substituent constants, $\sigma°_{X\pm}$, could be used.

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ORCID

Mare Piirsalu http://orcid.org/0000-0001-5836-2790

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