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# Effects of neutral and charged substituents on the infrared carbonyl stretching frequencies in phenyl and alkyl benzoates in DMSO

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The carbonyl infrared stretching frequencies for 57 *meta-*, *para-* and *ortho-*substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4$ -X and alkylbenzoates,  $C_6H_5CO_2R$ , containing besides neutral substituents the charged substituents in phenoxy and alkoxy part in dimethyl sulfoxide (DMSO) have been recorded. The carbonyl stretching frequencies,  $v_{CO}$ , for *meta-* and *para-*substituted phenyl esters of benzoic acids in the case of neutral substituents were found to correlate well with the substituent constants,  $\sigma^{\circ}$ . The  $v_{CO}$  values for *ortho* derivatives correlated with the inductive substituent constants,  $\sigma_{1r}$  only. The values of constants for charged substituents,  $\sigma^{\circ}_{\pm}$ , calculated on the basis of the  $v_{CO}$  and the <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , in DMSO agree well with the  $\sigma^{\circ}_{\pm}$  values for the corresponding ion pairs reported by Hoefnagel and Wepster and those determined from the log *k* values of the alkaline hydrolysis in 4.4 M NaCl solution at 50 °C. Thus, the values of substituent constants for ion pairs of charged substituents estimated on the basis of aqueous data could be successfully used in non-aqueous solution (DMSO) simultaneously with neutral substituents in case the charged substituents were not completely ionized and are in ion pair form. Copyright © 2016 John Wiley & Sons, Ltd.

**Keywords:** carbonyl carbon <sup>13</sup>C NMR chemical shifts; charged substituents; infrared spectra; *ortho* effect; phenyl and alkyl benzoates; SUP

## INTRODUCTION

Infrared stretching frequency of the carbonyl group,  $v_{CO}$ , has been perhaps the most widely used infrared spectral feature for elucidating interactions within and between molecules. Numerous electronic, steric and solvation effects in a myriad of compounds – ketones,<sup>[1–5]</sup> carboxylic acids,<sup>[6,7]</sup> esters,<sup>[8–10]</sup> metal carbonyl complexes<sup>[11–13]</sup>, etc. – have been studied *via* the carbonyl group stretching frequency.

We have previously recorded the infrared (IR) spectra of 33 substituted phenyl and alkyl esters of benzoic acid,  $C_6H_5CO_2C_6H_4$ -X,  $C_6H_5CO_2R$ , and 22 phenyl esters of substituted benzoic acids, X- $C_6H_4CO_2C_6H_5$ , in tetrachloromethane.<sup>[10]</sup> In substituted phenyl benzoates, X- $C_6H_4CO_2C_6H_5$ , in the case of *or*-*tho* substituents (X = Cl, Br, I, F, OCH<sub>3</sub>, CF<sub>3</sub>) in the benzoyl part, doublet IR carbonyl stretching bands were observed. In phenyl esters of *ortho*-substituted benzoic acids, the existence of *cis* and *trans* isomeric conformations was supported by frequency calculations with density functional theory (DFT) method at B3LYP/6-311+ G\*\* level.<sup>[10]</sup>

Previously,<sup>[10]</sup> we studied the influence of substituent effects on the carbonyl stretching frequencies,  $v_{CO}$ , in substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4$ -X,  $X-C_6H_4CO_2C_6H_5$ , and alkyl benzoates,  $C_6H_5CO_2R$ , in tetrachloromethane containing neutral (uncharged) substituents in benzoyl and phenyl part in benzene ring and alkyl chain. In the present paper, we extended the study of the carbonyl stretching frequencies,  $v_{CO}$ , dependent on the substituent effects to cationic and anionic charged substituents. To study the influence of charged (cationic and anionic) and neutral substituent effects on the carbonyl stretching frequencies,  $v_{CO}$ , in substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, containing substituents in phenyl part and alkyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R, in the present work, the IR spectra for 42 *meta-*, *para-* and *ortho-*substituted phenyl benzoates and 15 alkyl benzoates with neutral substituents and charged substituents (X = 3-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>, 4-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>, 2-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>, 4-SO<sub>3</sub><sup>-</sup>Na<sup>+</sup>, 3-COO<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub>, 4-COO<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub>, 3-O<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub>, 4-O<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub>, R = CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>CI<sup>-</sup>, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>) were recorded in dimethyl sulfoxide (their solubility in tetrachloromethane is too low).

In our previous works in *ortho-*, *meta-* and *para-*substituted phenyl and alkyl esters of benzoic acids (C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, X-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R), the influence of the substituent inductive, resonance and steric effects, especially *ortho* effect, on the carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , in CDCl<sub>3</sub>,<sup>[14] 17</sup>O NMR chemical shifts,  $\delta^{(17O)}$  for carbonyl oxygen and singlebonded oxygen in CH<sub>3</sub>CN<sup>[15,16]</sup> and on the rates of the alkaline hydrolysis in various media dependent of solvent electrophilicity parameter were studied.<sup>[17-21]</sup> It was shown that the <sup>13</sup>C NMR chemical shifts,  $\delta^{(17O)}$ , and the log *k* values of the alkaline hydrolysis could be successfully correlated with the carbonyl stretching frequencies  $v_{CO}$  values for the substituted phenyl and alkyl benzoates.<sup>[14-16,19-21]</sup> The

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obtained correlation equations enable to predict the NMR chemical shifts,  $\delta_{\rm CO}$  and  $\delta(^{17}{\rm O})$ , the IR  $v_{\rm CO}$  and log *k* values of the alkaline hydrolysis for esters of benzoic acid.

For substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, and alkyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R, in DMSO, no study of the ortho, meta, para and alkyl substituent effects on the carbonyl stretching frequencies  $v_{CO}$  values in the case of neutral and charged (anionic and cationic) substituents can be found in the literature. There are also no studies addressing the carbonyl stretching frequencies, v<sub>CO</sub>, in DMSO for the substituted phenyl esters of benzoic acid, except unsubstituted phenyl benzoate (in DMSO  $v_{CO} = 1733$ ,<sup>[22]</sup>) available in the literature. Similarly, we could find only limited data on the IR carbonyl stretching frequencies,  $v_{CO}$ , for alkyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R, with electronegative substituents measured in DMSO (R = CH<sub>2</sub>CN, CH<sub>2</sub>CF<sub>3</sub>, CH<sub>2</sub>CCl<sub>3</sub>, CH<sub>2</sub>CHCl<sub>2</sub><sup>[16]</sup>). There are more data in the literature on the carbonyl stretching frequencies,  $v_{CO}$ , in DMSO for esters containing substituents in the acyl component.<sup>[22-</sup> <sup>32]</sup> It was found<sup>[25-32]</sup> that the IR frequencies,  $v_{CO}$ , in DMSO in the case of anionic substituents in acyl part of esters could be correlated with the Hammett equation using the  $\sigma^+$  substituent constants similarly to neutral meta and para substituents.

The substituent effects of charged substituents in aprotic solvents are considerably less studied as compared with that for neutral substituents. While the substituent effects of charged substituents were found to be dependent on solvent effects and processes considered, it was interesting to establish the substituent constants  $\sigma^{\circ}$  for charged substituents on the basis of the  $v_{CO}$  values for phenyl and alkyl benzoates in DMSO and to compare them with those obtained for other processes in DMSO and aqueous solvents.

For aqueous solution, it was shown<sup>[33–37]</sup> that in the case of charged substituents in processes involving changes in the ionic charge at some structural units in course of reaction, activation or excitation, the electrostatic correction should be taken into account. To describe the effects not only for the neutral (dipole) substituents but also those of charged substituents, Hoefnagel and Wepster<sup>[33]</sup> proposed an extended Hammett equation (Eqn 1):

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

where  $\Delta = \log K^X - \log k^H$ , or  $\log k^X - \log k^H$ ,  $\rho = \rho_m$  is the reaction constant obtained with a set of standard *meta*  $\sigma$  values,  $\sigma^L$  is a "normal"  $\sigma$  value for neutral substituents, for charged substituents,  $\sigma^L$  is  $\sigma$  value without electrostatic term, that is, the  $\sigma$  value for dipoles equal to that for ion pairs, and  $\delta^B$  is the electrostatic Coulombic term.<sup>[38]</sup> In alkaline hydrolysis of substituted phenyl benzoates and phenyl tosylates with charged substituents in concentrated NaCl aqueous solutions (4.4 M), the log k values attained a limiting  $k_{\infty}$  value, characteristic for ion pairs<sup>[34,39,40]</sup>: log  $k_{\infty} - \log k_0 \cong \pm \delta^B$ , where  $k_0$  is the rate constant at infinite dilution.

The aim of this work was to establish on the basis of carbonyl stretching frequencies,  $v_{CO}$ , of substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4$ -X, and alkyl benzoates,  $C_6H_5CO_2R$ , in DMSO the  $\sigma$  substituent constants for charged substituents that could be applicable to correlate the influence of substituent effects on the carbonyl stretching frequencies,  $v_{CO}$ , of substituted phenyl and alkyl benzoates in DMSO simultaneously with those of electroneutral substituents. For comparison, the  $\sigma$  substituent constants for charged substituents were estimated from the corresponding carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , in DMSO, measured in this work.

For more accurate comparison of substituent effects of electroneutral substituents on the carbonyl stretching frequencies,

 $v_{CO}$ , in DMSO with those in CCl<sub>4</sub>, additionally, the carbonyl stretching frequencies,  $v_{CO}$ , for seven *ortho*-substituted phenyl benzoates and four alkyl benzoates were measured in CCl<sub>4</sub>. The present data set of carbonyl stretching frequencies,  $v_{CO}$ , is the most comprehensive data set of this type available in DMSO.

## **EXPERIMENTAL**

## Infrared measurements

The IR spectra for 42 *meta-*, *para-* and *ortho-*substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4$ -X, containing neutral and charged substituents in phenoxy part (Table 1) and 15 alkylbenzoates,

**Table 1.** Infrared carbonyl stretching frequencies,  $v_{CO}$ , for or-<br/>tho-, meta- and para-substituted phenyl benzoates,<br/> $C_6H_5CO_2C_6H_4$ -X, in DMSO and in CCl<sub>4</sub> (in brackets)

Substituent X	$v_{\rm CO}~({\rm cm}^{-1})$	Substituent X	$v_{\rm CO}~({\rm cm}^{-1})$
4-NO <sub>2</sub>	1741.1	2-NO <sub>2</sub>	1745.3
3-NO <sub>2</sub>	1740.5	2,6-(NO <sub>2</sub> ) <sub>2</sub>	1755.1 (1767)
$4-SO_2CH_3$	1740.5	$2-SO_2CH_3$	1748.5 (1759,
			1745)
4-CF <sub>3</sub>	1739.0	2-CN	1746.2 (1755)
3-CF <sub>3</sub>	1738.0	2-CF <sub>3</sub>	1745.3
3-Br	1739.3		1746.2
3-Cl	1737.5	2-F	1744.7
4-Cl	1738.5	2-Cl	1741.4
3-COOH	1737.6	2-Br	1742.3 (1750)
4-COOH	1734.5	2-I	1740.3
4-SO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	1736.5	2-COOH	1737.6
3-OH	1732.8	$2-COCH_3$	1739.4, 1735.6
	1733.2		(1759, 1745.0)
Н	1734.7	2-OH	1734.0
	1733.7	$2-OCH_3$	1734.4
	1733.8		1735.6
3-NH <sub>2</sub>	1731.8	$2-CH_3$	1732.8
3-N(CH <sub>3</sub> ) <sub>2</sub>	1732.3	2,6-(CH <sub>3</sub> ) <sub>2</sub>	1731.6 (1742)
4-OCH <sub>3</sub>	1732.3	2-C(CH <sub>3</sub> ) <sub>3</sub>	1735.6, 1730.8
4-OH	1731.1	2-N(CH <sub>3</sub> ) <sub>2</sub>	1733.3
4-NH <sub>2</sub>	1729.4	$2-N^{+}(CH_{3})_{3}I^{-}$	1748.3
3-N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> I <sup>-</sup>	1738.5		
4-N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> I <sup>-</sup>	1741.4		
3-COO <sup></sup> N <sup>+</sup> Bu <sub>4</sub>	1734.4		
	1734.5 <sup>a</sup>		
$4-COO^-N^+Bu_4$	1734.5		
3-O <sup>-</sup> N <sup>+</sup> Bu <sub>4</sub>	1729.2 <sup>b</sup>		
$4-O^-N^+Bu_4$	1729.2 <sup>b</sup>		

<sup>a</sup>Phenyl benzoate prepared from the corresponding COOH derivative, so by addition of equimolar (1:1) and twice lower (1:0.5) amounts of dry sodium methoxide in methanol and tetrabutylammonium hydroxide (*tert*-( $C_4H_9$ )<sub>4</sub>OH in methanol), their spectra were recorded immediately (refer to Supporting Information, Table S1).

<sup>b</sup>Phenyl benzoate prepared from the corresponding OH derivative, so by addition of equimolar (1:1) and twice lower (1:0.5) amounts of dry sodium methoxide in methanol and tetrabutylammonium hydroxide (tert-(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>OH in methanol), their spectra were recorded immediately (refer to Supporting Information, Table S1).

 $C_6H_5CO_2R$ , with neutral and charged substituents in alkoxy part (Table 2) in DMSO (Aldrich for IR spectroscopy) as well as 7 *ortho*-substitued phenyl benzoates and 4 alkyl benzoates in  $CCl_4$  were recorded on Nicolet 6700 FT-IR spectrometer in the region 225–4000 cm<sup>-1</sup> (resolution 2 cm<sup>-1</sup>) in approximately 0.013 M solution. A KRS-5 cell with path length 1.02 mm was used. The wavelength scale of the spectrometer was calibrated using polystyrene film (0.013 mm thick). The day-to-day reproducibility of the maxima was  $\pm 0.3$  cm<sup>-1</sup>. Thermo Electron's OMNIC9 for FT-IR spectrometer software was used to collect and process the IR spectra.

#### Synthesis of compounds

The preparation procedure and characteristics of *ortho-*, *meta*and *para*-substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4X$ , and R-substituted alkyl benzoates,  $C_6H_5CO_2R$ , are given in Supporting Information. Purity of the synthesized phenyl benzoates,  $C_6H_5CO_2C_6H_4X$  (X = 3-COOH, 4-COOH, 2-COOH,3-COO<sup>-</sup>N<sup>+</sup>(C\_4H\_9) 4, 4-COO<sup>-</sup>N<sup>+</sup>(C\_4H\_9)\_4, 4-SO<sub>3</sub><sup>-</sup>Na<sup>+</sup>, 2-N<sup>+</sup>(CH\_3)\_3I<sup>-</sup>, 4-OH, 2-OH), was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy in deuterated DMSO at 25 °C (refer to Supporting Information). In the case of tetrabutylammonium 4- and 3-benzoyloxybenzoate ( $C_6H_5CO_2C_6H_4COO^{-}N^+(C_4H_9)_4$ ) in <sup>1</sup>H NMR spectra, the band for H in COOH group ( $\delta$  = 13.06 and  $\delta$  = 13.22) was not detected.

#### NMR measurements

The carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$  (in ppm), for 21 substituted phenyl esters of benzoic acid and 4 alkyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R, in DMSO were determined (Table 3).

For compound characterization, the <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 700.1 or 400.1 MHz (<sup>1</sup>H) and 176.0 or 100.6 MHz (<sup>13</sup>C). All NMR measurements with the 700 MHz NMR spectrometer were carried out at 20 °C, and NMR measurements with the 400 MHz NMR spectrometer were carried out at 25 °C. Chemical shifts (<sup>1</sup>H and <sup>13</sup>C) were indirectly referenced to TMS

**Table 2.** Infrared carbonyl stretching frequencies, v<sub>CO</sub>, for al-

kyl benzoates, C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> R		
Substituent	$v_{\rm CO}~({\rm cm}^{-1})$	
R	DMSO	CCl <sub>4</sub>
CH₃	1718.8	
CH <sub>3</sub> CH <sub>2</sub>	1713.4	
CICH <sub>2</sub>	1739.0, 1704.9	
NCCH <sub>2</sub>	1731.8	
F <sub>3</sub> CCH <sub>2</sub>	1734.8 <sup>a</sup>	1743.4
Cl <sub>3</sub> CCH <sub>2</sub>	1732.3 <sup>a</sup>	1741.2
Cl <sub>2</sub> CHCH <sub>2</sub>	1726.5 <sup>a</sup>	1733.2
$HC \equiv CCH_2$	1723.4	
CICH <sub>2</sub> CH <sub>2</sub>	1718.9	
BrCH <sub>2</sub> CH <sub>2</sub>	1718.4 <sup>a</sup>	1729.3
$C_6H_5CH_2$	1716.4	
$CH_3OCH_2CH_2$	1716.8	
$CI^-$ ( $CH_3$ ) <sub>3</sub> N <sup>+</sup> CH <sub>2</sub>	1742.5	
$I^-$ (CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup> CH <sub>2</sub> CH <sub>2</sub>	1722.1	
$I^-$ (CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	1717.3	
<sup>a</sup> Ref <sup>[16]</sup> .		

*via* the residual solvent signal (DMSO- $d_6$ , 2.50 and 49.52 ppm, respectively). NMR signals were assigned using information from gs-HSQC, gs-HMBC, gs-NOESY and TOCSY spectra. The reported <sup>13</sup>C NMR data corresponds to the <sup>1</sup>H-decoupled <sup>13</sup>C NMR data.

#### **Kinetic measurements**

The rate constant for the alkaline hydrolysis of  $2-N^+(CH_3)_3I^-$ -phenyl benzoate in aqueous 4.4 M NaCl at 50 °C was determined: log k = 1.353 (refer to Supporting Information).

## **DATA ANALYSIS**

The values of the carbonyl stretching frequencies,  $v_{CO}$ , for *meta-*, *para-* and *ortho*-substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4$ -X, in DMSO (Table 1) in the case of neutral substituents were treated according to the Taft<sup>[46]</sup> and the Charton<sup>[47]</sup> equations (Eqns 2–4):

$$(v_{\rm CO})_{\rm m,p} = (v_{\rm CO})_0 + \rho_{\rm m,p}\sigma^{\circ}$$
 (2)

$$(v_{\rm CO})_{\rm ortho} = (v_{\rm CO})_0 + (\rho_I)_{\rm ortho} \sigma_I + (\rho^{\circ}_{\rm R})_{\rm ortho} \sigma^{\circ}_{\rm R} + \delta_{\rm ortho} E_{\rm s}^{\rm B}$$
(3)

$$(\mathbf{v}_{CO})_{ortho} = (\mathbf{v}_{CO})_{0} + (\rho_{l})_{ortho}\sigma_{l} + (\rho_{R})_{ortho}\sigma^{\circ}_{R} + \delta_{ortho}v$$
 (4)

The values of the carbonyl stretching frequencies,  $\nu_{CO^{\prime}}$  for substituted alkyl benzoates,  $C_6H_5CO_2R$ , in DMSO were analyzed with Eqn 5:

$$(\mathbf{v}_{CO})_{Alk} = (\mathbf{v}_{CO})_{CH3} + (\rho_I)_{Alk}\sigma_I + \delta_{Alk}E_s^{B}$$
 (5)

The Taft polar  $\sigma^{\circ}_{[46,48,49]}$  inductive  $\sigma^{[49,50]}_{I}$  and resonance  $\sigma^{\circ}_{R} = \sigma^{\circ}_{P} - \sigma_{I})^{[49,51]}$  scales were used for data analysis. In the case of ortho substituents, two steric scales were employed: the  $E_{s}^{B}$  constants<sup>[14,52-54]</sup> ( $E_{s}^{B} = \log k_{H+}^{X} - \log k_{H+}^{H}$ , where  $k_{H+}^{X}$  and  $k_{H+}^{H}$  are the rate constants for the acidic hydrolysis of ortho-substituted and unsubstitued phenyl benzoates in water at 50 °C,  $E_{s}^{B} < 0$ ) and the Charton scale of v.<sup>[55-57]</sup> The steric constants,  $E_{s}^{B}$  ( $E_{s}^{B} < 0$ ) determined on the basis of the acid hydrolysis of ortho-substitued phenyl benzoates,  $C_{e}H_{5}CO_{2}C_{6}H_{4}$ -X,<sup>[52]</sup> in the case of substituents X = H, F, Cl, Br, I, CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>3</sub>, CF<sub>3</sub>, were found to be nearly linearly related to the v values, calculated on the bases of van der Waals radii,  $r_{v}$ . The steric substituent constants,  $E_{s}^{B}$  ( $\log k_{H+}^{R} - \log k_{H+}^{CH}$ ), where  $k_{H+}^{R}$  and  $k_{H+}^{CH3}$  are the rate constants,  $E_{s}^{B} = (\log k_{H+}^{R} - \log k_{H+}^{CH3})$ , where  $k_{H+}^{R}$  and  $k_{H+}^{CH3}$  are the rate constants for acid hydrolysis of R-substituted alkyl benzoates,  $C_{6}H_{5}CO_{2}R$ , in water.<sup>[59]</sup>

The results of the statistical data treatment are listed in Table S3. The values of substituent constants  $\sigma^{\circ}$ ,  $\sigma_{\nu}$ ,  $\sigma^{\circ}_{R}$  and  $E_{s}^{\beta}$  are given in Table S4. For the data processing, a multiple-parameter linear least-squares procedure<sup>[60]</sup> was used.

## DISCUSSION

## Influence of substituents in *meta* and *para* position of $C_6H_5CO_2C_6H_4$ -X

As can expected<sup>[22]</sup> on the basis of the high polarity of DMSO compared with tetrachloromethane, all the  $v_{CO}$  values for *ortho-, meta-* and *para-*substituted phenyl benzoates as well as

benzoates, C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub>	R, in DMSO			
Х	$\delta_{CO}$	X or R	$\delta_{CO}$	
Н	164.6	4-N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> I <sup>-</sup>	164.30	
4-NO <sub>2</sub>	163.96	3-N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> I <sup>-</sup>	164.31	
4-OCH <sub>3</sub>	164.92, 164.91	2-N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> I <sup>-</sup>	163.70	
4-COOH	164.2, 166.6 (COOH)	4-SO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	164.63	
3-COOH	164.5, 166.5 (COOH)	4-COO <sup>-</sup> N <sup>+</sup> (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub>	164.6 (167.5)	
2-COOH	164.7, 165.6 (COOH)	3-COO <sup>-</sup> N <sup>+</sup> (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub>	164.76 (167.0)	
4-OH	165.0	$CH_2N^+(CH_3)_3CI^-$	163.64	
3-OH	164.55	$CH_2CH_2CH_2N^+(CH_3)_3I^-$	165.58	
2-OH	164.1	$CH_2CH_2N^+(CH_3)_3I^-$	165.16, 165.1ª	
4-NH <sub>2</sub>	165.21	CH <sub>3</sub>	166.22, 166.18 <sup>b</sup>	
4-Cl	164.43			
		C <sub>6</sub> H₅COOH	167.3 <sup>c</sup> , 167.18 <sup>d</sup>	
			167.48 <sup>e</sup>	
		4-CI-C <sub>6</sub> H₅COOH	166.74 <sup>e</sup>	
<sup>a</sup> Pof <sup>[41]</sup>				
<sup>b</sup> Pof <sup>[42]</sup>				
CRof <sup>[43]</sup>				
d <sub>Dof</sub> [44]				
epof <sup>[45]</sup>				
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**Table 3.** The carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$  (in ppm), for substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4$ -X, and alkyl benzoates,  $C_6H_5CO_2R_6$  in DMSO

for alkylbenzoates in DMSO (Tables 1 and 2) in the case of neutral substituents were ca 7–11 cm<sup>-1</sup> lower as compared with the corresponding  $v_{CO}$  values measured earlier in tetrachloromethane.<sup>[10]</sup> In the case of electroneutral *ortho, meta, para* and alkyl substituents, the  $v_{CO}$  values of phenyl benzoates in DMSO (Tables 1 and 2) were found to be linearly correlated with the corresponding  $v_{CO}$  values in CCl<sub>4</sub> as follows:

$$(v_{CO})_{DMSO} = (82.8 \pm 37.6) + (0.947 \pm 0.022)(v_{CO})_{CCl4}$$
 (6)  
 $R^2 = 0.984, s = 0.132, n/n_0 = 35/35$ 

The value  $v_{CO} = 1733.7 \text{ cm}^{-1}$  for phenyl benzoate in DMSO (Table 1) agrees well with  $v_{CO} = 1733 \text{ cm}^{-1}$  reported by Nyquist.<sup>[22]</sup> Similarly to previous works,<sup>[10,61-64]</sup> we found that the carbonyl stretching frequencies,  $v_{CO}$ , for benzoates in DMSO increasing in the case of electron-withdrawing substituents and decreasing when the electron-donating substituents are included. The electron-donating substituents are considered to increase the bond length and ionic character of the carbonyl bond. The <sup>13</sup>C NMR and <sup>17</sup>O NMR data for the carbonyl group in substituted phenyl benzoates<sup>[14,16,65]</sup> support this point of view. It was found that the electron-withdrawing substituents shield the carbonyl carbon and deshield the carbonyl oxygen as compared with unsubstituted derivative.<sup>[14,16,65]</sup> The electron-donating substituents act in the opposite direction.

To establish which  $\sigma$  substituent constants for charged substituents (for ion pairs, they also contains an additional electrostatic component) could be applicable to correlate the influence of charged substituent effects on the carbonyl stretching frequencies,  $v_{CO}$ , of substituted phenyl benzoates in DMSO simultaneously with those of electroneutral substituents, the substituent constants,  $\sigma^{\circ}_{X\pm r}$  for *meta*- and *para*-charged substituents in DMSO were calculated with Eqn 7 (Table 4):

$$\sigma^{\circ}_{X\pm} = \left[ (v_{CO})_{X\pm} - (v_{CO})_{0} \right] / \rho_{m,p}$$
(7)

The  $\rho_{m,p}$  constant in Eqn 7 was estimated from the dependence of the  $v_{CO}$  values on the Taft polar substituent constants,  $\sigma^{\circ}$ , for *meta* and *para* electroneutral substituents (Eqn 2) in substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, in DMSO (Eqn 8, Table S3):

$$(v_{CO})_{m,p} = (1733.5\pm0.4) + (10.3\pm0.6)\sigma^{\circ}$$
  
 $R^2 = 0.935, s = 0.255, n/n_0 = 19/20$ 
(8)

The  $v_{CO}$  value for 4-COOH derivative was excluded first during the data processing as the most deviating point. In literature,<sup>[76]</sup> there was for 4-COOH-phenyl benzoate  $v_{CO} = 1734$  in DMSO detected that was approximately the same as found in the present work ( $v_{CO} = 1734.5$ , Table 1). The lower  $v_{CO}$  value for 4-benzoyloxybenzoic acid could be explained by formation of the dimer form through hydrogen bond association of carboxyl groups.<sup>[77]</sup>

The polar influence of *meta* and *para* substituents on the carbonyl stretching frequencies,  $v_{CO}$ , in DMSO ( $\rho = 10.3$ , Eqn 8, Table S3) was found to be about two units of  $\rho$  stronger than in tetrachlorometane ( $\rho = 8.19$ ,<sup>101</sup> Table S3). A good correlation of the  $v_{CO}$  values with the  $\sigma^{\circ}$  constants for *para*-substituted phenyl benzoates, once more, shows the absence of the through resonance between the electron-donating substituents and the carbonyl group and that in phenyl esters, the carbonyl group was found to be nearly perpendicular to the aroxy plane.<sup>[10,62,78,79]</sup>

The substituent constants,  $\sigma^{\circ}_{X\pm}$ , for charged substituents estimated with Eqn 7 using the corresponding carbonyl stretching frequencies,  $v_{CO}$ , in DMSO (Table 1) and the value of  $\rho_{m,p}$  from

**Table 4.** The values of substituent constants,  $(\sigma^{\circ})_{X\pm}$ , for charged substituents estimated from the infrared stretching frequencies,  $v_{CO}$ , <sup>13</sup>C NMR carbonyl chemical shifts,  $\delta_{CO}$ , in DMSO, and rates of alkaline hydrolysis of phenyl and alkyl benzoates,  $C_6H_5CO_2C_6H_4$ -X,  $C_6H_5CO_2R$ , in aqueous 4.4 M NaCl solution at 50 °C

X or R	$\sigma^{\circ}(v_{CO})^{a}$	$\sigma^{\circ} \left( \boldsymbol{\delta}_{CO}  ight)^{b}$	$\sigma^{\circ}$ (4.4 M NaCl) <sup>c</sup>	Recommended $(\sigma^{\circ}_{\pm})_{av}{}^{d}$	$\sigma^{\circ}$ for ion pairs <sup>e</sup>	$\sigma^{\circ}$ with electrostatic component (in aqueous solution) <sup>f</sup>
4-N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> I <sup>-</sup>	0.65	0.44	0.53 <sup>g</sup>	0.54	0.53	1.025, <sup>g</sup> 0.88, <sup>i</sup> 0.96 <sup>h</sup>
3-N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> I <sup>-</sup>	0.46	0.44	0.46 <sup>g</sup>	0.45	0.59	1.094, <sup>g</sup> 1.04, <sup>i</sup> 0.99 <sup>h</sup>
$2-N^{+}(CH_{3})_{3}I^{-}$	0.78	0.69 <sup>i</sup>	0.83 <sup>j</sup>	0.76	_	1.15 <sup>k</sup>
$4-COO^{-}N^{+}(C_{4}H_{9})_{4}$	0.08	0.14	0.06 <sup>g</sup>	0.09	0.26	-0.078, <sup>g</sup> -0.122 <sup>g</sup>
3-COO <sup>-</sup> N <sup>+</sup> (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub>	0.07	-0.02	0.04 <sup>g</sup>	0.03	0.24	-0.194, <sup>g</sup> -0.195 <sup>g</sup>
$4-SO_3$ $^-Na^+$	0.28	0.11	0.37 <sup>m</sup>	0.25	0.51	-0.037 <sup>1</sup>
$4-O^{-}N^{+}(C_{4}H_{9})_{4}$	-0.44		-0.37,-0.58 <sup>g</sup>	-0.41	-0.45	-0.833, <sup>g</sup> -0.815 <sup>g</sup>
3-O <sup>-</sup> N <sup>+</sup> (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub>	-0.44		-0.34,-0.57 <sup>g</sup>	-0.39	-0.28	-0.886, <sup>g</sup> -0.874 <sup>g</sup>
		Values	of σ <sub>l</sub> <sup>n</sup>			
$CH_2N^+(CH_3)_3CI^-$	0.51°				0.56	0.84 <sup>p</sup>
$(CH_2)_2 N^+ (CH_3)_3 I^-$	0.17 <sup>o</sup>				0.31	0.42 <sup>p</sup>
$(CH_2)_3N^+(CH_3)_3I^-$	0.09 <sup>o</sup>				0.03	0. 24 <sup>p</sup>

<sup>a</sup>The  $\sigma^{\circ}$  substituent constant values calculated using infrared carbonyl stretching frequencies,  $v_{CO}$ , in DMSO for substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, (Table 1) with Eqns 7 and 8. In the calculation of  $\sigma^{\circ}$  constant for 4-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup> substituent,  $v_{CO}$  = 1734.7 for phenyl benzoate was used.

<sup>b</sup>The  $\sigma^{\circ}$  values calculated from the carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , for substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, in DMSO (Table 3) according to Eqns 7 and 9.

<sup>c</sup>The  $\sigma^{\circ}$  values were calculated from the rate constants for the alkaline hydrolysis of substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, in aqueous 4.4 M NaCl solution at 50 °C with Eqn log  $k = \log k_0 + \rho_{m,p}\sigma^{\circ}$  using the corresponding rate constants  $k_{\alpha}^{[66]}$  and for unsubstituted derivative log  $k_{\rm H} = 0.070$  and  $\rho = 0.90$  in aqueous 4.4 M NaCl.<sup>[67,68]</sup>

<sup>d</sup>The averaged values of the substituent constants,  $(\sigma_{X\pm}^{\circ})_{av}$ , for ion pairs of charged substituents calculated on the bases of the experimental data for substituted phenyl benzoates: the carbonyl stretching frequencies,  $v_{CO}$ , and the carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , in DMSO and log k values for the alkaline hydrolysis in aqueous 4.4 M NaCl solution.

<sup>e</sup>The  $\sigma^{\circ}$  values for ion pairs calculated by Wepster as free from the electrostatic interaction term.<sup>[33]</sup>

<sup>f</sup>The  $\sigma^{\circ}$  constants containing the electrostatic component for reactions between substrate containing charged substituent and the ionic reagent. To calculate the  $\sigma^{\circ}$  values, the rate constants or *pK* values were extrapolated to pure water were used. <sup>g</sup>Ref<sup>[66]</sup>.

<sup>h</sup>Ref<sup>[49]</sup>.

 $^{i}\rho_{\text{ortho}} = 1.47 \text{ was used.}^{[14]}$ 

<sup>j</sup>log k = 1.353 for the alkaline hydrolysis of 2-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>-phenyl benzoate in aqueous 4.4 M NaCl solution at 50 °C was used (refer to Supporting Information). log  $k_{\rm H} = 0.070$  and  $\rho_{\rm ortho} = 1.50^{1691}$  were used; influence of the steric term was considered minimal. <sup>k</sup>The  $\sigma^{\circ}$  values calculated from the rate constants for the alkaline hydrolysis of substituted phenyl tosylates, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>-X,

for pure water. log  $k_0 = -2.940^{[70]}$  and  $\rho_{\text{ortho}} = 2.99^{[71]}$  were used.

<sup>1</sup>The  $\sigma^{\circ}$  values calculated from the rate constants for the alkaline hydrolysis of substituted phenyl tosylates, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>-X, for pure water.<sup>[66]</sup>

<sup>m</sup>Ref<sup>[72]</sup>.

The steric constants,  $E_s^B$ , for charged alkyl substituents were calculated with the following equation: log  $k = \log k_{CH3} + 3.39\sigma_1 + 1.2E_s^B$ , log k = 0.684 for  $R = CH_2N(CH_3)_3^+Cl^-$ , log k = -0.535 for  $R = CH_2CH_2N(CH_3)_3^+l^-$ , log k = -1.034 for  $R = CH_2CH_2N(CH_3)_3^+l^-$ , from Ref<sup>[73]</sup> and log k = -1.034 for  $R = CH_3$  in aqueous 5.3 M NaClO<sub>4</sub> solution at 50 °C were used.<sup>[74,75]</sup>

<sup>p</sup>Calculated with the following equation: log  $k = -0.640 + 3.38\sigma_1 + 1.05 E_s^{B[73-75]}$  for the alkaline hydrolysis of alkylbenzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R, in water at 50 °C using for ester with charged substituents the values of rate constants extrapolated to pure water.

Eqn 8 for neutral meta- and para-substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4\mbox{-}X$ , in DMSO are listed in Table 4.

For comparison, the magnitudes of substituent constants,  $\sigma^{\circ}_{X\pm}$ , for *meta*- and *para*-charged substituents were calculated on the basis of the carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , for substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, in DMSO (Tables 3 and 4) using Eqn 9:

$$(\delta_{\rm CO})_{\rm m,p} = (164.72 \pm 0.04) - (1.020 \pm 0.11)\sigma^{\circ} R^2 = 0.945, s = 0.10, n/n_0 = 6/6$$
 (9)

The magnitudes of the carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , of substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4$ -X, measured in the present work in DMSO (Table 3), appeared to be approximately the same as compared with the corresponding

carbonyl carbon <sup>13</sup>C NMR chemical shifts, recorded earlier in deuterated cloroform (CDCl<sub>3</sub>).<sup>[14]</sup> The  $\sigma^{\circ}$  constants for charged substituents,  $\sigma^{\circ}_{X\pm}$ , estimated with Eqn 9 using the carbonyl carbon chemical shifts,  $\delta_{CO}$ , in DMSO (Table 3) are shown in Table 4.

The substituent constants,  $\sigma^{\circ}_{X\pm r}$  for charged substituents estimated using the corresponding carbonyl stretching frequencies,  $v_{CO}$  (Table 1), and the carbonyl carbon chemical shifts,  $\delta_{CO}$  (Table 3), in DMSO are in good agreement with constants,  $\sigma^{\circ}_{X\pm r}$  for ion pairs proposed by Hoefnagel and Wepster<sup>[33]</sup> and those calculated from the kinetic data of the alkaline hydrolysis of substituted phenyl benzoates in concentrated aqueous NaCl solution (4.4 M NaCl,<sup>[66]</sup> Table 4).

The averaged values of the substituent constants,  $(\sigma^{\circ}_{X\pm})_{av}$ , for charged substituents calculated on the basis of the experimental data for substituted phenyl benzoates (the carbonyl stretching frequencies,  $v_{CO}$ , and the carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , in DMSO and log *k* values for the alkaline hydrolysis in aqueous 4.4 M NaCl solution (Table 4)) were proposed as "recommended"  $\sigma^{\circ}$  substituent constants for ion pairs of charged substituents (Table 4).

The magnitudes of the averaged  $(\sigma_{X\pm})_{av}$  values for ion pairs of charged substituents are quite close to the Hoefnagel and Wepster  $\sigma_{\pm}^{\circ}$  values<sup>[33]</sup> in the case of 3-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>, 4-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>, 3-O<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub> and 4-O<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub> substituents (Table 4). The  $\sigma_{\pm}^{\circ}$  values of 0.62 and 0.47 for 3-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup> and 4-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup> substituents estimated from the pK<sub>a</sub> values of benzoic acids in DMSO (9.36<sup>[80]</sup> and 9.79,<sup>[80]</sup>  $\rho = 2.6<sup>[81]</sup>$ ),  $\sigma_{\pm}^{\circ} = 0.62$  for 4-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup> calculated from pK<sub>a</sub> value of 4-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup> substitued phenol in DMSO (14.7,<sup>[82]</sup>  $\rho = 5.3<sup>[81]</sup>$ ) and of  $\sigma^{\circ} = 0.01$  for the 4-COO<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub> group, estimated from the pK<sub>2</sub> value of 4-phthalic acid in aqueous 7.75 m Bu<sub>4</sub>NBr solution (pK<sub>2</sub> = 6.28<sup>[83]</sup>  $\rho = 2.09<sup>[84]</sup>$ ), coincide as well with the corresponding ( $\sigma_{\pm}^{\circ}_{av}$  values found from our experimental data (for 3-COO<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub> group ( $\sigma_{\pm}^{\circ}_{av} = 0.03$ , Table 4).

In the case of substituents  $3\text{-}COO^-\text{N}^+\text{Bu}_4$ ,  $4\text{-}COO^-\text{N}^+\text{Bu}_4$  and  $4\text{-}SO_3^-\text{Na}^+$ , the constants  $(\sigma_{\pm}^{\circ})_{av}$  were found to be less about 0.2 units of  $\sigma$  as compared with those estimated by Hoefnagel and Wepster with Eqn 1 using  $pK_a$  or log k values for aqueous solutions. Probably, this difference is caused by the strong hydration of the ionic carboxylate and sulfonate groups by water molecules<sup>[85]</sup> that makes the negative charge on the carboxylate and sulfonate anion less negative as assumed in calculation of the electrostatic term with Eqn 1.

The  $v_{CO}$  values for *meta-* and *para-*substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, in DMSO (Table 1) showed a good correlation with the corresponding carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , in DMSO (Table 3) in case both benzoates with the charged substituents and electroneutral substituents were included (Table S5,  $R^2 = 0.925$ ,  $s_0 = 0$ , 271,  $n/n_0 = 11/12$ ).

Similarly, the  $v_{CO}$  values for *meta*- and *para*-substituted phenyl benzoates in DMSO (Table 1) correlated well with the corresponding log *k* values for the alkaline hydrolysis of substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, in aqueous 4.4 M NaCl solution at 50 °C including both derivatives with the charged substituents and electroneutral substituents (Table S5,  $R^2 = 0.921$ ,  $s_0 = 0.282$ ,  $n/n_0 = 10/10$ ). When the log *k* values for pure water were correlated with the  $v_{CO}$  values, the data for charged substituents deviated essentially because of additional electrostatic interaction in the alkaline hydrolysis of phenyl benzoates (Table S5,  $R^2 = 0.817$ ,  $s_0 = 0.426$ ).

The good agreement of the  $(\sigma^{\circ}_{\pm})_{av}$  values for charged substituents estimated using carbonyl stretching frequencies,  $v_{CO}$ , and

the carbonyl carbon chemical shifts,  $\delta_{CO}$ , in DMSO with the Hoefnagel and Wepster  $\sigma$  constants for ion pairs and those obtained from the kinetic data of the alkaline hydrolysis of phenyl benzoates in 4.4 M NaCl solution (Table 4) shows that in substituted phenyl benzoates,  $C_6H_5CO_2C_6H_4$ -X, the charged substituents X = 3-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>l<sup>-</sup>, 4-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>l<sup>-</sup>, 3-COO<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub>, 4-COO<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub>, 3-O<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub>, 4-O<sup>-</sup>N<sup>+</sup>Bu<sub>4</sub> and 4-SO<sub>3</sub><sup>-</sup>Na<sup>+</sup> in DMSO are not completely ionized and are in ion pair form. The corresponding estimated  $\sigma^{\circ}_{\pm}$  values for charged substituents do not include the component of the electrostatic interaction between charged substituent and reaction center as shown in Eqn 1. Similarly, Kosugi and Takeuchi<sup>[43]</sup> concluded that in DMSO, benzoate anions form tight ion pairs with sodium or tetraalkylammonium cations.

Correlation of data using the substituent constants ( $\sigma_{\pm}^{\circ}$ )<sub>av</sub> for charged substituents enables to evaluate the state of charged substituents (compounds) in solution whether they are dissociated into ions, ion pairs or are they in non-dissociated form.

#### Influence of ortho substituents in C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X

In the IR spectra of phenyl benzoates with *ortho* substituents in the aroxy part,  $C_6H_5CO_2C_6H_4$ -X, in the present work in DMSO, only one carbonyl stretching band was detected and splitting of the carbonyl stretching bands was not observed similarly to previous findings in  $CCI_4$ .<sup>[1]</sup> In phenyl benzoates, the aromatic plane in the phenoxy part is rotated out of the carbonyl plane by nearly 90°,<sup>[10,62,78,79]</sup> and for *ortho* derivatives, there is only one conformation possible.

When the carbonyl stretching frequencies,  $v_{CO}$ , for orthosubstituted phenyl esters of benzoic acid in DMSO in the case of electroneutral substituents were correlated with the Charton Eqns 3 and 4, the resonance and steric terms were excluded as insignificant and a good correlation obtained with the inductive constant,  $\sigma_{lr}$  only (Eqn 10), Table S3):

$$(v_{CO})_{ortho} = (1732.9\pm0.8) + (19.7\pm1.6)\sigma_l$$
  
 $R^2 = 0.906, s = 0.306, n/n_0 = 16/16$  (10)

Almost the same correlation of the  $v_{CO}$  values with  $\sigma_{I}$  constants was obtained when 2-OH- and 2-COOH-substituted derivatives were included in the data set as well (Table S3). The influence of the *ortho* inductive term on the  $v_{CO}$  values in DMSO (Eqn 10) was found to be the same as in CCl<sub>4</sub> (Eqn 11) in the case the same substituents were included (in the present work, the additional  $v_{CO}$  values for five *ortho*-substituted phenyl benzoates in CCl<sub>4</sub> were determined (Table 1 and Table S3):

In the case of *ortho* substituents, the resonance and steric factors appeared to be insignificant both in DMSO and  $CCl_4$  (Eqns 10 and 11), Table S3).

Approximately the same  $\sigma_1$  values for *ortho* N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup> substituent (Table 4) were found: with Eqn 10 using the  $v_{CO}$  value in DMSO in Table 1 ( $\sigma_1$ =0.78), from the carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , for 2-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>-substituted phenyl benzoate in DMSO in Table 3 ( $\sigma_1$ =0.69), from the rate constants for the alkaline hydrolysis of 2-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I-substituted phenyl benzoate ( $\sigma_1$ =0.83) and 2-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup>-phenyl tosylate (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>-X) in aqueous 4.4 M NaCl solution at 50 °C ( $\sigma_1$ =0.89, log k=-0.079,<sup>[86]</sup>  $\rho_1$ =3.02,<sup>[68]</sup> log  $k_{\rm H}$ =2.78<sup>[87]</sup> were used).

For charged *ortho* substituent  $X = 2-N^+(CH_3)_3I_1^-$  the estimated  $\sigma_1$  values (Table 4) were essentially lower than the  $\sigma_1$  value for  $X = 2-N^+(CH_3)_3I^-$  found for pure water (at zero ionic strenth  $\sigma_1 = 1.15$ , Table 4) and approximately twice larger as compared with the corresponding  $(\sigma_{\pm}^{\circ})_{av}$  constants for *meta* and *para* substituents (Table 4).

This shows that in the case of *ortho* N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup> substituent in processes considered, the plus charge on nitrogen atom is less efficiently neutralized by the I<sup>-</sup> ion as compared with that in the case of corresponding *meta* and *para* substituents. In the case of *ortho* N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I<sup>-</sup> substituent because of the steric consequencies, the distance of the iodide anion from the reaction center could be essentially greater as compared with the same distance of the *ortho* N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub> substituent, and the plus charge on the nitrogen atom is not completely neutralized (solvent separated ion pairs).<sup>[34]</sup> Similarly, the *ortho* polar substituent effects were found to be about twice less dependent on the solvent electrophilicity parameters than that in the case of *meta* and *para* substituents.<sup>[18,88]</sup>

#### Influence of substituents in alkyl groups of C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R

Similar to phenyl benzoates, all the  $v_{\rm CO}$  values of substituted alkyl benzoates in DMSO (Tables 2) in the case of neutral substituents were ca 8–9 cm<sup>-1</sup> lower as compared with the corresponding  $v_{\rm CO}$  values measured earlier in CCl<sub>4</sub>.<sup>[10]</sup> The carbonyl stretching frequencies,  $v_{\rm CO}$ , of substituted alkyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R, in DMSO (Table 2) in the case of neutral substituents showed excellent correlation with the inductive constants  $\sigma_1$  (for substituent X in  $R = CH_2X$ ) and the steric  $E_s^{\rm B}$  constants ( $R^2 = 0.986$ , s = 0.120,  $n/n_0 = 12/12$ , Table S3). The influence of the inductive and steric term of alkyl substituents on the carbonyl stretching frequencies,  $v_{\rm CO}$ , in DMSO ( $\rho_1 = 59.8$  and  $\delta = 36.4$ , Table S3) was found to be approximately the same as that in CCl<sub>4</sub> ( $\rho_1 = 60.8$  and  $\delta = 35.8$  Table S3).

When data set included both the charged substituents  $(R = CH_2N^+(CH_3)_3Cl^-, CH_2CH_2N^+(CH_3)_3l^-, CH_2CH_2CH_2N^+(CH_3)_3l^-, Table 2)$  and the neutral substituents, we obtained excellent correlation with Eqns 5 and 12, in case for the charged substituents, the Hoefnagel and Wepster inductive substituent constants,  $\sigma_{I}$ , for dipoles<sup>[33]</sup> (i.e. for ion pairs, free from the electrostatic Coulombic term) were used (Table S3, Table 4):

$$(v_{CO})_{Alk} = (1717.4\pm1.1) + (55.7.\pm2.3)\sigma_l + (31.6\pm3.5)E_s^B$$
(12)  
$$R^2 = 0.980, s = 0.141, n/n_0 = 15/15$$

Similarly to *meta* and *para* derivatives, the carbonyl stretching frequencies,  $v_{CO}$ , for alkyl benzoates,  $C_6H_5CO_2R$ , in DMSO (Table 2) correlated well with the corresponding log k values for the alkaline hydrolysis of substituted alkyl benzoates in aqueous 4.4 M NaCl solution at 50 °C including both derivatives with the charged substituents and electroneutral substituents (Table S5,  $R^2 = 0.943$ , s = 0.238,  $n/n_0 = 10/10$ ). This correlation indicates that charged alkyl substituents similarly to *meta* and *para* derivatives of phenyl benzoates are not completely ionized in DMSO and are in ion pair form.

## CONCLUSIONS

The IR carbonyl frequencies,  $v_{CO}$ , for 57 *meta-*, *para-* and *ortho*-substituted phenyl benzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-X, and substituted alkylbenzoates, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>R, as well as the carbonyl carbon <sup>13</sup>C

NMR chemical shifts,  $\delta_{CO}$ , for 21 substituted phenyl benzoates and alkyl benzoates with neutral and charged substituents in DMSO have been recorded. Using carbonyl stretching frequencies,  $v_{CO}$ , and the carbonyl carbon <sup>13</sup>C NMR chemical shifts,  $\delta_{CO}$ , in DMSO for charged substituents, the polar substituent constants  $\sigma^{\circ}_{\pm}$  were calculated. These substituent constants  $\sigma^{\circ}_{\pm}$  for charged substituents in DMSO showed a good agreement with ones obtained from the kinetic data of the alkaline hydrolysis of phenyl benzoates in 4.4 M aqueous NaCl solution and the Wepster and Hoefnagel  $\sigma$  values for ion pairs of the charged substituents estimated for aqueous solutions (Table 4). The estimated polar substituent constants  $\sigma^{\circ}_{\pm}$  for the charged substituents characterize the reactivity of ion pairs in DMSO and constitute a single scale with  $\sigma^{\circ}$  and  $\sigma_{1}$  constants for the uncharged electronegative substituents.

The carbonyl stretching frequencies,  $v_{CO}$ , for *meta*- and *para*substituted phenyl esters of benzoic acid in DMSO in the case of neutral substituents were found to correlate well with the substituent constants,  $\sigma^{\circ}$ , the  $v_{CO}$  values for *ortho* derivatives with the inductive substituent constants,  $\sigma_{I}$ , only. The  $v_{CO}$  values for substituted alkyl benzoates in DMSO in the case of neutral substituents showed excellent correlation with the inductive constants  $\sigma_{I}$  (for substituent X in R=CH<sub>2</sub>X) and the steric  $E_{s}^{B}$ constants.

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## REFERENCES

- [1] R. A. Nyquist, Appl Spectrosc. 1990, 44, 433-438.
- [2] J. V. Coelho, M. P. Freitas, T. C. Ramalho, C. R. Martins, M. Bitencourt, R. A. Cormanich, C. F. Tormena, R. Rittner, *Chem Phys Lett.* **2010**, *494*, 26–30.
- [3] S. I. Vdovenko, I. I. Gerus, V. P. Kukhar, Spectrochim Acta A. 2008, 71, 779–785.
- [4] S. M. Kashid, S. Bagchi, J Phys Chem Lett. 2014, 5, 3211–3215.
- [5] R. Rajalakshmi, R. Arulmani, A. N. Palanappan, S. Srinivasan, Der Pharma Chemica. 2013, 5, 153–160.
- [6] M. Banno, K. Ohta, K. Tominaga, *J Phys Chem.* **2008**, *112*, 4170–4175.
   [7] T. M. Nickels, A. L. Ingram, D. K. Maraoulaite, R. L. White, *Appl*
- Spectrosc. 2015, 69, 850–856. [8] B. Fang, T. Wang, X. Chen, T. Jin, R. Zhang, W. Zhuang, J Phys Chem B.
- **2015**, *119*, 12390–12396. [9] L. Chuntonov, I. M. Pazos, J. Ma, F. Gai, J Phys Chem. **2015**, *119*,
- [9] L. Chuntonov, I. M. Pazos, J. Ma, F. Gal, J Phys Chem. 2015, 119, 4512–4520.
- [10] V. Nummert, O. Travnikova, S. Vahur, I. Leito, M. Piirsalu, V. Mäemets, I. Koppel, I. A. Koppel, J Phys Org Chem. 2006, 19, 654–663.
- [11] R. Świslocka, Spetrosc. **2010**, *24*, 439–443.
- [12] E. Ö. Üstün, C. Kaya, J Mol Struct (Theochem). **2004**, 710, 133–137.
- [13] O. Okpareke, E. Okafor, P. Ukoha, S. Okereke, *Chem and Material Res.* 2014, 6, 104–111.
- [14] V. Nummert, M. Piirsalu, V. Mäemets, S. Vahur, I. A. Koppel, J Phys Org Chem. 2009, 22, 1155–1165.
- [15] V. Nummert, V. Maemets, M. Piirsalu, I. A. Koppel, J Phys Org Chem. 2011, 24, 539–552.
- [16] V. Nummert, V. Mäemets, M. Piirsalu, S. Vahur, I. A. Koppel, Collect Czech Chem Commun. 2011, 76, 1737–1763.
- [17] V. Nummert, M. Piirsalu, I. A. Koppel, J Phys Org Chem. 2010, 23, 497–504.
- [18] V. Nummert, M. Piirsalu, V. Mäemets, I. A. Koppel, J Phys Org Chem. 2005, 18, 1138–1144.
- [19] V. Nummert, M. Piirsalu, I.A. Koppel, J Phys Org Chem. 2013, 26, 352–359.

- [20] V. Nummert, M. Piirsalu, I. Koppel, Cent Eur J Chem. 2013, 11, 1964–1975.
- [21] V. Nummert, M. Piirsalu, S. Vahur, O. Travnikova, I. A. Koppel, *Collect Czech Chem Commun.* **2009**, *74*, 29–42.
- [22] R. A. Nyquist, V. Chrzan, T. Kirchner, L. Yurga, C. L. Putzig, *Appl Spectrosc.* **1990**, *44*, 243–263.
- [23] R. A. Nyquist, C. L. Putzig, T. L. Clark, A. T. McDonald, Vib Spectrosc. 1996, 12, 93–102.
- [24] R. A. Nyquist, S. Fiedler, R. Streck, Vib Spectrosc. 1994, 6, 285-291.
- [25] P. J. Vassiljeva, I. G. Binev, I. N. Juchnovski, Spectrochim Acta A. 1983, 39, 709–712.
- [26] I. G. Binev, A. Fattah Nazir, P. J. Vassiljeva, I. N. Juchnovski, Commun Dept Chem Bulg Acad Sci. 1985, 18, 22–29.
- [27] I. G. Binev, P. J. Vassiljeva, T. M. Kolev, I. N. Juchnovski, J Mol Struct. 1984, 114, 371–374.
- [28] I. G. Binev, T. M. Kolev, I. N. Juchnovski, Can J Chem. 1985, 63, 3149–3154.
- [29] E. A. Velcheva, I. N. Juchnovski, I. G. Binev, Spectrochim Acta. 2003, 59, 1745–1749.
- [30] I. G. Binev, R. B. Kuzmanova, J. Kaneti, I. N. Juchnovski, J Chem Soc Perkin Trans. 2. 1982, 1533–1536.
- [31] I. G. Binev, E. A. Velcheva, I. N. Juchnovski, Spectrochim Acta. 1995, 51, 1871–1878.
- [32] I. G. Binev, E. A. Velcheva, Spectrosc Letters. 1999, 32, 793-802.
- [33] A. J. Hoefnagel, M. A. Hoefnagel, B. M. Wepster, J Org Chem. 1978, 43, 4720–4745.
- [34] V. A. Palm, V. M. Nummert, T. O. Püssa, M. M. Karelson, I. A. Koppel, Reakts Sposobnost Org Soedin (Tartu). 1973, 10, 223–242.
- [35] B. van de Graaf, A. J. Hoefnagel, B. M. Wepster, J Org Chem. 1981, 46, 653–657.
- [36] B. M. Wepster, J Org Chem. 1982, 47, 2318-2323.
- [37] A. J. Hoefnagel, W. Oosterbeek, B. M. Wepster, J Org Chem. 1984, 49, 1993–1997.
- [38] N. Bjerrum, Z Phys Chem. 1923, 106, 219-242.
- [39] V. M. Nummert, V. A. Palm, Org Reactiv (Tartu). 1976, 13, 75-83.
- [40] V. M. Nummert, Org Reactiv (Tartu). **1976**, 13, 151–162.
- [41] M. Karakaya, F. Ucun, A. Tokatli, J Spectroscopy. 2013, 2013, 1–10.
- [42] C. Dell'Erba, A. Mele, M. Novi, G. Petrillo, F. Sancassan, D. Spinelli, J Chem Soc, Perkin Trans 2. 1990, 2055–2058.
- [43] Y. Kosugi, T. Takeuchi, Bull Chem Soc Japan. 1978, 51, 2008–2011.
- [44] J. Niwa, M. Yamazaki, Chem. Lett. 1974, 3, 765–768.
- [45] J. Kulhanek, O. Pytela, A. Lyčka, Collect Czech Chem Commun. 2000, 65, 106–116.
- [46] R. W. Taft Jr. , J Phys Chem. 1960, 64, 1805–1815.
- [47] M. Charton, J Am Chem Soc. **1969**, 91, 624–628.
- [48] V. A. Palm (Ed), Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions 5 Publishing House of VINITI, Moscow, 1979, 5(2), 164–165.
- [49] O. Exner, in: Correlation Analysis in Chemistry (Edss: N. B. Chapman, J. Shorter), Plenum Press, New York, London, **1978**, 439–540.
- [50] R. W. Taft Jr., I. C. Lewis, J Am Chem Soc. 1958, 80, 2436–2443.
- [51] R. W. Taft Jr., S. Ehrenson, I. C. Lewis, R. E. Glick, J Am Chem Soc. 1959, 81, 5352–5361.
- [52] V. M. Nummert, M. V. Piirsalu, Org Reactiv (Tartu). 1975, 11, 921–932.
- [53] V. Nummert, M. Piirsalu, V. Mäemets, I. Koppel, Collect Czech Chem Commun. 2006, 71, 107–128.
- [54] V. Nummert, K. Ojassalu, A. Bogdanov, Org Reactiv (Tartu). 1989, 26, 92–97.

- [55] M. H. Aslam, A. G. Burden, N. B. Chapman, J. Shorter, M. Charton, J Chem Soc Perkin Trans 2. 1981, 500–508.
- [56] M. Charton, in: Steric Effects in Drug Design (Edss: M. Charton, I. Motoc), Academie-Verlag, Berlin, 1983, 107–118.
- [57] M. Charton, J Am Chem Soc. 1975, 97, 1552–1556
- [58] V. Nummert, M. Piirsalu, J Phys Org Chem. 2002, 15, 353-361.
- [59] T. O. Püssa, V. A. Palm, Reakts Sposobnost Org Soedin (Tartu). 1972, 9, 1209–1224.
- [60] V. Palm, J Chem Inf Comput Sci. **1990**, 30, 409–412.
- [61] H. H. Freedman, J Am Chem Soc. 1960, 82, 2454–2459.
- [62] L. A. Cohen, S. Takahashi, J Am Chem Soc. 1973, 95, 443-448.
- [63] L. J. Bellamy, Advances in Infrared Group Frequencies. Methuen & Co. LTD, Bungay, Soffolk, **1968**.
- [64] L. J. Bellamy, The Infrared Spectra of Complex Molecules. Chapman and Hall, London, 1980.
- [65] H. Neuvonen, K. Neuvonen, P. Pasanen, J Org Chem. 2004, 69, 3794–3800.
- [66] V. Nummert, Org Reactiv (Tartu). **1975**, *11*, 621–636.
- [67] V. Nummert, I. Alakivi, Org Reactiv (Tartu). 1976, 13, 536–554.
- [68] V. Nummert, M. Piirsalu, I. A. Koppel, J Phys Org Chem. 2007, 20, 778–790.
- [69] V. Nummert, M. Piirsalu, J Chem Soc, Perkin Trans. 2. 2000, 583–594.
- [70] V. Maremäe, V. A. Palm, V. Nummert, Reakts Sposobnost Org Soedin (Tartu). 1964, 1, 85–102.
- [71] V. Nummert, Org Reactiv (Tartu). 1989, 26, 89-121.
- [72] V. Nummert, I. Alakivi, Org Reactiv (Tartu). 1976, 13, 105–114.
- [73] V. Nummert, M. Piirsalu, Org Reactiv (Tartu). 1979, 16, 251–260.
- [74] V. Nummert, M. Piirsalu, Org Reactiv (Tartu). 1978, 15, 240-257.
- [75] V. Nummert, M. Piirsalu, I. A. Koppel, Czech Chem Commun. 2006, 71, 1557–1570.
- [76] J. Yuan, D.-Y. Huang, C.-H. Jiang, G.-L. Zhang, H.-Z. Zhang, Chem J Chinese Univ. 1997, 18, 2070–2072.
- [77] J. Yuan, G.-L. Zhang, D.-Y. Huang, H.-Z. Zhang, *Liq Cryst.* **1997**, *22*, 693–696.
- [78] O. Exner, Z. Fidlerova, V. Jehlička, Collect Czech Chem Commun. 1968, 33, 2019–2028.
- [79] R. Wrzalik, K. Merkel, A. Kocot, J Mol Model. 2003, 9, 248–258.
- [80] J. Picha, R. Cibulka, F. Liška, P. Pařik, O. Pytela, Collect Czech Chem Commun. 2004, 69, 2239–2252.
- [81] F. G. Bordwell, Acc Chem Res. 1988, 21, 456–463.
- [82] http://www.chem.wisc.edu/areas/reich/pktable/
- [83] J. Steigman, R. De Iasi, H. Lilenfeld, D. Sussman, J Phys Chem. 1968, 72, 1132–1137.
- [84] V. Nummert, V. Palm, Org Reactiv (Tartu). **1980**, *17*, 292–312.
- [85] T. B. McMahon, P. Kebarle, J Am Chem Soc. 1977, 99, 2222-2230.
- [86] V. M. Maremäe, T. O. Püssa, V. A. Palm, Reakts. Sposobnost Organ Soedin (Tartu). 1971, 8, 127–151.
- [87] V. Nummert, M. Piirsalu, Org Reactiv (Tartu). 1982, 19, 67–81.
- [88] V. Nummert, M. Piirsalu, M. Lepp, V. Mäemets, I. Koppel, Collect Czech Chem Commun. 2005, 70, 198–222.

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