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Keywords:	NMR spectra of phenyl benzoates, ^{17}O NMR chemical shifts, substituent effects, ortho effect, correlation equations

Influence of *ortho* substituents on ^{17}O NMR chemical shifts in phenyl esters of substituted benzoic acids

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^{17}O NMR spectra for 29 phenyl esters of *ortho*-, *para*- and *meta*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, at natural abundance in acetonitrile were recorded. The $\delta(^{17}\text{O})$ values of carbonyl and the single-bonded oxygens for *para* derivatives gave good correlation with the σ^+ constants. The $\delta(^{17}\text{O})$ values for *meta* derivatives correlated well with the σ_m constants. The influence of *ortho* substituents on the $\delta(^{17}\text{O})$ values of carbonyl oxygen and the single-bonded oxygens was analyzed using the Charton equation containing the inductive, σ_i , resonance, σ^+_R , and steric, E_s^B , substituent constants. For *ortho* derivatives excellent correlations with the Charton equation were obtained when the data treatment was performed separately for derivatives containing electron-donating $+R$ and electron-attracting $-R$ substituents. The electron-donating substituents in *ortho*-, *meta*- and *para*-substituted esters resulted in shielding of the ^{17}O signal and the electron-withdrawing groups caused deshielding. In phenyl *ortho*-substituted benzoates the substituent-induced positive inductive ($\rho_I > 0$), resonance ($\rho_R > 0$) and steric ($\delta_{\text{ortho}}E_s^B > 0$) effects were found. The steric interaction of *ortho* substituents with ester group was found to produce a deshielding effect on the carbonyl and single-bonded oxygens. For *ortho* derivatives with $-R$ substituents the resonance term was insignificant and the steric term was ca. twice weaker as compared to that for derivatives with $+R$ substituents. The $\delta(^{17}\text{O})$ values for *ortho*-substituted nitrobenzenes, acetophenones and benzoyl chlorides showed a good correlation with the Charton equation as well. In *ortho*-substituted nitrobenzenes the inductive, resonance and steric effect were found to be ca. 1.7 times stronger as compared to that for phenyl *ortho*-substituted benzoates.

Keywords: NMR spectra of phenyl benzoates; ^{17}O NMR chemical shifts; substituent effects; *ortho* effect; correlation equations

INTRODUCTION

In our previous papers the influence of substituent effects, especially *ortho* effect, on the rates of the alkaline hydrolysis in various media (as shown in References^[1-7]), the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} ,^[8] and the carbonyl carbon infrared stretching frequencies, ν_{CO} ,^[9] in substituted phenyl benzoates, ($\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$) were studied. In the present paper we extend our study of the *ortho* substituent effect to the

^{17}O NMR chemical shifts, $\delta(^{17}\text{O})$, in substituted phenyl benzoates, containing substituents in benzoyl moiety ($\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$).

To the best of our knowledge, no study of the *ortho*, *meta*, and *para* substituent effects on the $\delta(^{17}\text{O})$ values for phenyl esters of substituted benzoic acids, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, could be found in the literature. There are also no $\delta(^{17}\text{O})$ data for the phenyl esters of substituted benzoic acids, except unsubstituted phenyl benzoate, $\text{X} = \text{H}$,^[10,11] available in the literature. The values of $\delta(^{17}\text{O})$ in the *ortho*-substituted esters of substituted benzoic acids are available only for methyl benzoates, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$, with $\text{X} = \text{OCH}_3$, Cl , NO_2 , CH_3 and 2,6-disubstituted methyl benzoates, $\text{X}_1\text{X}_2-\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$, with $\text{X}_1 = \text{X}_2 = \text{CH}_3$, $\text{C}(\text{CH}_3)_3$.^[12-14]

Although there are numerous investigations on the $\delta(^{17}\text{O})$ values for esters in literature,^[10-33] the influence of the substituent effects on the $\delta(^{17}\text{O})$ of the carbonyl and methoxy oxygens in esters of substituted benzoic acid, using correlation equations, has been studied only for *meta*- and *para*-substituted methyl benzoates and *para*-substituted methyl 2,6-dimethyl-4-X-benzoates.^[14-16] The $\delta(^{17}\text{O})$ values of carbonyl and methoxy oxygens in *meta*- and *para*-substituted methyl benzoates gave good correlations with σ_m and σ^+ constants, respectively. In the hindered benzoates, 2,6-dimethyl-4-X-benzoates, the through-conjugation was found to be essentially reduced due to the increased torsion angle between the carbonyl group and the ring plane.^[13,14] It was found that in methyl benzoates reaction series an introduction of electron-attracting substituents causes deshielding and electron-donating substituents shielding of the carbonyl and methoxy O atoms.^[14-16] It has been shown^[26-29] that in substituted carbonyl derivatives, $\text{Y}-\text{C}_6\text{H}_4\text{CO}-\text{X}$, $\text{RCO}-\text{X}$, the shielding of the carbonyl oxygen is increased and the sensitivity of the Y substituent is diminished with an increase in the electron-donating power of the X group.

In *ortho*-substituted compounds the $\delta(^{17}\text{O})$ data have been quite extensively studied for nitrobenzenes,^[34,35] acetophenones,^[36-38] benzaldehydes,^[36] and benzoyl chlorides.^[39-40] But to the best of our knowledge, up to now the correlation equations were not applied to describe the influence of *ortho* substituents on the ^{17}O NMR chemical shifts. In *ortho*-substituted derivatives the steric influence of *ortho* substituents on the $\delta(^{17}\text{O})$ values has been explained by steric inhibition of resonance and van der Waals interactions.^[12-14,17,39,41-44] It was suggested that in systems in which the functional group is free to rotate, due to sterical consequences the functional group is rotated out of the plane of the aromatic ring increasing the double bond character of the functional group. In the rigid systems the steric influence of *ortho* substituents was explained by the van der Waals interactions between the ester group and the adjacent bulky substituent.^[41,42]

In the previous papers we found that in substituted phenyl benzoates, ($\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4-\text{X}$) the influence of *ortho* substituents on the $\log k$ values in the alkaline hydrolysis,^[1-7] the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} ,^[8] and the carbonyl carbon infrared stretching frequencies, ν_{CO} ,^[9] was precisely described with the Charton equation^[45] using the inductive, σ_i ,^[8,46] resonance, σ^{R} ,^[8,47] and steric, E_s^{B} ,^[6,48] substituent constants. Nearly the same results were obtained when for *ortho* substituents the Charton steric scale, ν ,^[49] based on van der Waals radii, was used. In the phenyl esters of *ortho*-substituted benzoic acids ($\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$) the contribution of *ortho* inductive and *ortho* steric components were found to be the dominant factors in the alkaline hydrolysis in

water,^[6] the carbonyl carbon infrared stretching frequencies, ν_{CO} ,^[1,9] for *cis* conformers as well as in the ^{13}C NMR chemical shifts, δ_{CO} .^[8]

$$\log k_{\text{ortho}}(\text{H}_2\text{O}, 25^\circ\text{C}) = -0.333 + 2.13\sigma_{\text{I}} + 0.31\sigma_{\text{R}} + 2.67E_{\text{s}}^{\text{B}} \quad (1)$$

$$R = 0.992, s_0 = 0.126, n/n_0 = 11/11$$

$$(\nu_{\text{CO}})_{\text{cis}} = 1742.7 + 16.4\sigma_{\text{I}} - 22.6E_{\text{s}}^{\text{B}} \quad (2)$$

$$R = 0.993, s_0 = 0.117, n/n_0 = 9/9$$

$$(\delta_{\text{CO}})_{\text{ortho}} = 165.32 - 5.08\sigma_{\text{I}} + 1.58\sigma_{\text{R}} - 4.33E_{\text{s}}^{\text{B}} \quad (3)$$

$$R = 0.978, s_0 = 0.257, n/n_0 = 11/11$$

In reaction series considered (Eqns (1)-(2)) the resonance term was negligible. In the ^{13}C NMR chemical shifts, δ_{CO} ,^[8] the value of $(\rho_{\text{R}})_{\text{ortho}}$ has the opposite sign $((\rho_{\text{R}})_{\text{ortho}} = +1.6)$ as compared to that for *para* derivatives $((\rho_{\text{R}})_{\text{para}} = -1.00)$.

Recently we found^[1,8] good correlations between the $\log k$ values of the alkaline hydrolysis of *ortho*-substituted phenyl benzoates and the infrared stretching frequencies of carbonyl group, ν_{CO} , as well as the ^{13}C NMR chemical shifts, δ_{CO} , in case the additional resonance and steric scales were included.

The aim of the present paper was to check the applicability of the Charton equation to describe the influence of *ortho* substituents on the $\delta(^{17}\text{O})$ values in phenyl esters of *ortho*-substituted benzoic acids, $(\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5)$, and to compare the substituent effects in the $\delta(^{17}\text{O})$ values with those in the alkaline hydrolysis,^[6] the infrared stretching frequencies, ν_{CO} ,^[9] and the ^{13}C NMR chemical shifts, δ_{CO} .^[8]

For the comparison, the $\delta(^{17}\text{O})$ values for substituted nitrobenzenes,^[34,35] acetophenones,^[36,38] and benzoyl chlorides,^[39-40] published in literature were correlated with the Charton equation as well.

EXPERIMENTAL

NMR measurements

^{17}O NMR spectra for 29 phenyl esters of *ortho*-, *meta*- and *para*-substituted benzoic acids, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$ ($\text{X} = \text{H}, 4\text{-NO}_2, 4\text{-F}, 4\text{-Cl}, 4\text{-Br}, 4\text{-CH}_3, 4\text{-OCH}_3, 4\text{-NH}_2, 4\text{-C}(\text{CH}_3)_3, 3\text{-NO}_2, 3\text{-CN}, 3\text{-Cl}, 3\text{-F}, 3\text{-CH}_3, 3\text{-OCH}_3, 3\text{-N}(\text{CH}_3)_2, 2\text{-NO}_2, 2\text{-CN}, 2\text{-F}, 2\text{-Cl}, 2\text{-Br}, 2\text{-I}, 2\text{-CF}_3, 2\text{-CH}_3, 2\text{-OCH}_3, 2\text{-N}(\text{CH}_3)_2, 2\text{-NH}_2, 2\text{-SO}_2\text{CH}_3, 2\text{-SCF}_3$), were recorded at natural abundance in acetonitrile (see Table 1). The ^{17}O NMR spectra were recorded on a Bruker Avance II 200 spectrometer equipped with 10 mm BBO probe at the resonance frequency 27.13 MHz. Benzoates were dissolved in the mixture of 1 ml CD_3CN and 2 ml CH_3CN . Acetonitrile- d_3 "Special HOH" 99.8 atom % D, Aldrich and Acetonitrile SPECTRANAL^R, Riedel-de Haën were used. Depending on the type of the benzoate the concentration varied between values from 0.3 molal to 1 molal. Temperature of the measurements was 50 °C. Water at 50 °C was used as an external reference (^{17}O chemical shift was taken 0 ppm). Depending on the sample about 0.5 to 1.8 million scans (measurement time up to 70 hours)

was acquired at the spectral width 23148 Hz and its size 2048 data points. The 10 μ s (at the $\sim 11 \mu$ s 90 degree pulse) excitation pulse with pre-scan delay 64 μ s and with the relaxation delay 50 ms was applied. Acquisition time was 44 ms. The data were processed with Bruker TopSpin 2.0 software package. During the data processing an exponential multiplication of the FID with LB = 40 was applied. For the correction of the baseline rolling caused by acoustic ringing effect a backward linear prediction for the first 10 data points of the FID was applied also during of the data processing. The line width of the ^{17}O spectral lines of the phenyl esters measured was within the range 250-400 Hz and up to 50-60 Hz for the water standard. The error of the chemical shifts measured was estimated on the basis of repetitive measurements and was $\leq \pm 0.4$ ppm.

The standard ^1H and proton-decoupled ^{13}C NMR spectra were recorded in CDCl_3 solution with 1% TMS added for the spectral referencing at a room temperature and at 200.13 and 50.33 MHz correspondingly. 2D HSQC or HETCOR spectra were recorded also for assignment of the ^1H and ^{13}C peaks.

Synthesis of compounds

The preparation procedure and characteristics for the phenyl esters of the *ortho*-, *meta*- and *para*-substituted benzoic acids, ($\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$), has been described in Reference.^[6] The phenyl esters of 2- $\text{N}(\text{CH}_3)_2$ -, 2- SO_2CH_3 - and 2- SCF_3 -substituted benzoic acids were prepared by the addition of thionyl chloride to the mixture of corresponding *ortho*-substituted benzoic acid and phenol in pyridine at 0 $^\circ\text{C}$ with stirring.^[50] Phenyl 2- $\text{N}(\text{CH}_3)_2$ -benzoate was recrystallized from aqueous 80% ethanol: yield 62%, m.p. 63-64 $^\circ\text{C}$, Reference,^[51] m.p. 67-69 $^\circ\text{C}$. Phenyl 2- SO_2CH_3 -benzoate was recrystallized from aqueous 67% ethanol: yield 56%, m.p. 116-117 $^\circ\text{C}$, Reference,^[51] m.p. 108-110 $^\circ\text{C}$. Phenyl 2- SCF_3 -benzoate was extracted from the reaction mixture with diethyl ether. The ether layer was dried with unhydrous magnesium sulfate. Diethyl ether was removed under the reduced pressure. Phenyl 2-(trifluoromethylthio)benzoate: b.p. 145-147 $^\circ\text{C}$ /2.5 mbar, yield 40%. The phenyl esters of 3-CN-, 3-OCH₃- and 3-F-substituted benzoic acids were prepared from corresponding substituted benzoyl chloride and phenol in pyridine solution.^[52] Phenyl 3-CN-benzoate was recrystallized from aqueous ethanol: yield 27%, m.p. 95-96 $^\circ\text{C}$, Reference,^[53] m.p. 92-95. Phenyl 3-OCH₃-benzoate: yield 66%, m.p. 62-63, Reference,^[53] m.p. 64-66 $^\circ\text{C}$. Phenyl 3-F-benzoate: yield 64%, m.p. 55-56, Reference,^[54] m.p. 54-55 $^\circ\text{C}$. Purity of synthesized phenyl esters of 2- $\text{N}(\text{CH}_3)_2$ -, 2- SO_2CH_3 -, 2- SCF_3 -, 3-CN-, 3-OCH₃-, and 3-F-substituted benzoic acids was confirmed by ^1H and ^{13}C NMR spectroscopy in CDCl_3 at 25 $^\circ\text{C}$.

Phenyl 2-(methylsulfonyl)benzoate

^1H NMR: 7.91 m, 1H (H-3); 7.68-7.82 m, 2H (H-4,5); 8.18 m, 1H (H-6); 7.25-7.5 m, 3H (H-9,11,13); 7.45 m, 2H (H-10,12); 3.34 s, 3H (H-14). ^{13}C NMR: 132.67 (C-1); 139.60, (C-x2); 129.82 (C-3); 133.64 (C-4); 131.65 (C-5); 130.05 (C-6); 165.75 (C-7); 150.59 (C-8); 121.56 (C-9,13); 129.69 (C-10,12); 126.50 (C-11); 45.01 (C-14).

Phenyl 2-(trifluoromethylthio)benzoate

^1H NMR: 7.76 d, 1H (H-3), $^3J = 7.8$; 7.35-7.56 m, 4H (H-4,5,10,12); 8.09 dd, 1H (H-6), $^3J = 7.4$, $^4J = 2.0$; 7.19-7.27 m, 3H (H-9,11,13). ^{13}C NMR: 128.46 (C-1); 133.0 (C-2); 133.72 (C-3); 132.81 (C-4); 129.22 (C-5); 131.43 (C-6); 164.74 (C-7); 150.84 (C-8); 121.59 (C-9,13); 129.65 (C-10,12); 126.30 (C-11); 129.77 (C-14), $^1J_{\text{C-F}} = 310.0$.

Phenyl 2-(dimethylamino)benzoate

^1H NMR: 6.99 d, 1H (H-3), $^3J = 8.4$; 7.37-7.45 m, 3H (H-4,10,12); 6.89 m, 1H (H-5), $^3J_{\text{av}} = 7.8$; 7.94 dd, 1H (H-6), $^3J = 7.8$, $^4J = 1.7$; 7.20-7.27 m, 3H (H-9,11,13); 2.92 s, 6H (H-14). ^{13}C NMR: 119.80 (C-1); 153.16 (C-2); 117.05 (C-3); 132.92 (C-4); 118.65 (C-5); 132.19 (C-6); 166.27 (C-7); 151.30 (C-8); 121.72 (C-9,10,13); 129.40 (C-10,12); 125.60 (C-11), 43.78 (C-14).

Phenyl 3-methoxybenzoate

¹H NMR: 7.70 dd, 1H (H-2), ⁴*J* = 2.6 and 1.6; 7.13-7.30 m, 4H (H-4,9,11,13); 7.36-7.47 m, 3H (H-5,10,12); 7.81 ddd, 1H (H-6), ³*J* = 7.6, ⁴*J* = 1.6 and 1.1; 3.86 s, 3H (H-14).
¹³C NMR: 131.14 (C-1); 114.80 (C-2); 159.92 (C-3); 120.14 (C-4); 129.61 (C-5); 122.64 (C-6); 165.00 (C-7); 151.22 (C-8); 121.73 (C-9,13); 129.48 (C-10,12); 125.86 (C-11), 55.54 (C-14).

Phenyl 3-cyanobenzoate

¹H NMR: 8.50 dt, 1H (H-2), ⁴*J*_{aver} = 1.7, ⁵*J* = 0.7; 7.92 ddd, 1H (H-4), ³*J* = 7.8, ⁴*J* = 1.7 and 1.3; 7.67 dt, 1H (H-5), ³*J*_{aver} = 7.9, ⁵*J* = 0.7; 8.43 ddd, 1H (H-6), ³*J* = 7.9, ⁴*J* = 1.3 and 1.7, 7.18-7.35 m, 3H (H-9,11,13); 7.46 m, 2H (H-10,12), ³*J*_{aver} = 7.9.
¹³C NMR: 131.28 (C-1); 133.79 (C-2), 113.53 (C-3), 136.50 (C-4), 129.69 (C-5), 134.11 (C-6), 163.21 (C-7), 150.77 (C-8), 121.47 (C-9,13), 129.67 (C-10,12), 126.35 (C-11), 117.67 (C-14).

Phenyl 3-fluorobenzoate

¹H NMR: 7.87 dddd, 1H (H-2), ³*J*_{F-H} = 9.2, ⁴*J* = 1.6 and 2.7, ⁵*J* = 0.4; 7.16-7.52 m, 7H (H-4,5,9-13); 7.99 ddd, 1H (H-6), ³*J* = 7.7, ⁴*J* = 1.6 and 1.1.
¹³C NMR: 132.06 (C-1), ³*J*_{F-C} = 7.7; 117.07 (C-2), ²*J*_{F-C} = 23.3; 162.79 (C-3), ¹*J*_{F-C} = 247.4; 120.62 (C-4), ²*J*_{F-C} = 21.5; 130.27 (C-5), ³*J*_{F-C} = 7.9; 125.94 (C-6), ⁴*J*_{F-C} = 3.3; 164.00 (C-7), ⁴*J*_{F-C} = 3.1; 151.02 (C-8); 121.62 (C-9,13); 129.56 (C-10,12); 126.07 (C-11).

DATA PROCESSING AND RESULTS

The $\delta(^{17}\text{O})$ values for the carbonyl and single-bonded oxygens in the phenyl esters of *para*- and *meta*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, given in Table 1 were correlated with Eqns (4) and (5). For *meta* substituents σ_{m} , σ_{I} and σ_{R} were used.

$$\delta(^{17}\text{O})_{\text{para(meta)}} = \delta(^{17}\text{O})_{\text{H}} + (\rho^+)_{\text{para(meta)}} \sigma^+(\sigma_{\text{m}}) \quad (4)$$

$$\delta(^{17}\text{O})_{\text{para(meta)}} = \delta(^{17}\text{O})_{\text{H}} + (\rho_{\text{I}})_{\text{para(meta)}} \sigma_{\text{I}} + (\rho^+)_{\text{para(meta)}} \sigma^+(\sigma_{\text{R}}) \quad (5)$$

In the case of *ortho*-substituted derivatives the influence of the inductive, resonance and steric factors on the $\delta(^{17}\text{O})$ values was separated using the following Charton equations^[45]:

$$\delta(^{17}\text{O})_{\text{ortho}} = \delta(^{17}\text{O})_{\text{H}} + (\rho_{\text{I}})_{\text{ortho}} \sigma_{\text{I}} + (\rho^+)_{\text{ortho}} \sigma^+ + \delta_{\text{ortho}} E_{\text{s}}^{\text{B}} \quad (6)$$

$$\delta(^{17}\text{O})_{\text{ortho}} = \delta(^{17}\text{O})_{\text{H}} + (\rho_{\text{I}})_{\text{ortho}} \sigma_{\text{I}} + (\rho^+)_{\text{ortho}} \sigma^+ + \delta_{\text{ortho}} \nu \quad (7)$$

The correlation of the $\delta(^{17}\text{O})$ values with Eqns (6) and (7) was performed separately for *ortho*-substituted derivatives containing the *ortho* electron-donating +*R* substituents ($\text{X} = \text{OCH}_3, \text{CH}_3, \text{N}(\text{CH}_3)_2, \text{F}, \text{Cl}, \text{Br}, \text{H}$) and derivatives with the *ortho* electron-withdrawing -*R* substituents ($\text{X} = \text{NO}_2, \text{CN}, \text{CF}_3, \text{SCF}_3, \text{SO}_2\text{CH}_3, \text{H}$). The Brown and Okamoto constants, σ^+ ,^[55,56] the polar substituent constants, σ_{m} ,^[56] the Taft inductive σ_{I} ,^[8,46] resonance σ^+_{R} constants ($\sigma^+_{\text{R}} = \sigma^+_{\text{p}} - \sigma_{\text{I}}$), and $\sigma^{\circ}_{\text{R}}$ ($\sigma^{\circ}_{\text{R}} = \sigma^{\circ}_{\text{p}} - \sigma_{\text{I}}$)^[8,47] were used in the data processing. As the steric constants for *ortho* substituents two steric scales were employed: the E_{s}^{B} constants and the Charton scale of ν .^[49,60,61] The steric constants, E_{s}^{B} , determined on the basis of the acid hydrolysis of *ortho*-substituted phenyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$,^[6,48] in the case of substituents $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{CH}_3, \text{C}(\text{CH}_3)_3, \text{CF}_3$, were found to be nearly linear function of the ν values, calculated on the bases of van der Waals radii, r_{v} .

The results of correlations of the carbonyl oxygen and the single-bonded oxygen $\delta(^{17}\text{O})$ values, for phenyl esters of *para*-, *meta*- and *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, with Eqns (4)-(7) are listed in Table 2. For comparison, the correlation of the $\delta(^{17}\text{O})$ values published in literature for *ortho*-, *para*- and *meta*-substituted nitrobenzenes,^[17,34,35,57,58] $\text{X-C}_6\text{H}_4\text{NO}_2$, acetophenones,^[36-38,59] $\text{X-C}_6\text{H}_4\text{COCH}_3$, and benzoyl chlorides,^[27,39,40] $\text{X-C}_6\text{H}_4\text{COCl}$, with Eqns (4)-(6) are shown in Table 2 as well.

To compare of the substituent effects on the $\delta(^{17}\text{O})$ values of the carbonyl oxygen and the single-bonded oxygen for phenyl esters of *ortho*-, *para*- and *meta*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, with those in the kinetic data of the alkaline hydrolysis, $\log k$, the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , and the infrared stretching frequencies of the carbonyl group, ν_{CO} , in substituted phenyl benzoates, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, the following relationships were used:

$$\delta(^{17}\text{O})_{\text{ortho}} = \delta(^{17}\text{O})_{\text{H}} + a_{1(\text{ortho})} \Delta \log k_{\text{X}} + a_{2(\text{ortho})} \sigma^+_{\text{R}} + a_{3(\text{ortho})} E_{\text{s}}^{\text{B}} \quad (8)$$

$$\delta(^{17}\text{O})_{\text{ortho}} = \delta(^{17}\text{O})_{\text{H}} + a_{1(\text{ortho})} (\Delta \delta_{\text{CO}})_{\text{X}} + a_{2(\text{ortho})} \sigma^+_{\text{R}} + a_{3(\text{ortho})} E_{\text{s}}^{\text{B}} \quad (9)$$

$$\delta(^{17}\text{O})_{\text{ortho}} = \delta(^{17}\text{O})_{\text{H}} + a_{1(\text{ortho})}(\Delta\nu_{\text{CO}})_{\text{X}} + a_{2(\text{ortho})}\sigma^+_{\text{R}} + a_{3(\text{ortho})}E_{\text{s}}^{\text{B}} \quad (10)$$

$$\delta(^{17}\text{O})_{\text{para(meta)}} = \delta(^{17}\text{O})_{\text{H}} + a_{1(\text{para(meta)})}\Delta\log k_{\text{X}} + a_{2(\text{para(meta)})}\sigma^+_{\text{R}}(\sigma^{\circ}_{\text{R}}) \quad (11)$$

$$\delta(^{17}\text{O})_{\text{para(meta)}} = \delta(^{17}\text{O})_{\text{H}} + a_{1(\text{para(meta)})}(\Delta\delta_{\text{CO}})_{\text{X}} + a_{2(\text{para(meta)})}\sigma^+_{\text{R}}(\sigma^{\circ}_{\text{R}}) \quad (12)$$

$$\delta(^{17}\text{O})_{\text{para(meta)}} = \delta(^{17}\text{O})_{\text{H}} + a_{1(\text{para(meta)})}(\Delta\nu_{\text{CO}})_{\text{X}} + a_{2(\text{para(meta)})}\sigma^+_{\text{R}}(\sigma^{\circ}_{\text{R}}) \quad (13)$$

In Eqns (8)-(13) $\Delta\log k_{\text{X}} = \log k_{\text{X}} - \log k_{\text{H}}$, $(\Delta\delta_{\text{CO}})_{\text{X}} = (\delta_{\text{CO}})_{\text{X}} - (\delta_{\text{CO}})_{\text{H}}$ and $(\Delta\nu_{\text{CO}})_{\text{X}} = (\nu_{\text{CO}})_{\text{X}} - (\nu_{\text{CO}})_{\text{H}}$. The $\log k$ values for the alkaline hydrolysis in water and aqueous 50% DMSO, the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , and the IR stretching frequencies of the carbonyl group, ν_{CO} , for phenyl benzoates, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, used in correlations with Eqns (8)-(13) are given in References.^[6,8,9,51,52] In the case of phenyl esters of *ortho*-substituted benzoic acids, the ν_{CO} values for *cis* conformers estimated by the carbonyl stretching frequencies deconvolution were used. The results of data treatment with Eqns (8)-(13) are listed in Table 3. For the data processing a multiple-parameter linear least-squares (LLSQ) procedure^[62] was used.

DISCUSSION

The $\delta(^{17}\text{O})$ values in phenyl esters of *para*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, (Table 1) gave excellent correlations so with the single parameter treatment using the Brown and Okamoto σ^+ constants^[55,56] (Eqn (4)) as the dual substituent parameter treatment with the Taft $\sigma_{\text{I}}^{\text{[8,46]}}$ and σ^+_{R} ($\sigma^+_{\text{R}} = \sigma^+ - \sigma_{\text{I}}$) constants (Eqn (5), Table 2):

$$\delta(^{17}\text{O})_{\text{para}} = (345.2 \pm 0.3) + (9.07 \pm 0.55)\sigma^+_{\text{R}} \quad (14)$$

$R = 0.986$, $s = 0.918$, $n/n_0 = 9/9$

$$\delta(^{17}\text{O})_{\text{para}} = (345.9 \pm 0.5) + (7.21 \pm 0.99)\sigma_{\text{I}} + (9.71 \pm 0.54)\sigma^+_{\text{R}} \quad (15)$$

$R = 0.990$, $s = 0.752$, $n/n_0 = 9/9$

In *para*-substituted phenyl benzoates the calculated sensitivity of the $\delta(^{17}\text{O})$ values of the carbonyl oxygen towards the inductive effect and through-conjugation shown by Eqns (14) and (15) (Table 2) were approximately the same as earlier were found for methyl benzoates in References^[15,16] ($\rho^+ = 9.76$,^[15] 9.03 ,^[16] 9.66 (Table 2)). The excellent correlation of the $\delta(^{17}\text{O})$ values obtained with σ^+ , σ_{I} and σ^+_{R} constants (Eqns (14) and (15)) suggests that the $\delta(^{17}\text{O})$ values for phenyl esters of *para*-substituted benzoic acids are besides the inductive effect dependent on the through-conjugation between substituent and the carbonyl oxygen similar to that for *para*-substituted methyl benzoates,^[14-16] acetophenones,^[36,37,59] benzoyl chlorides,^[27,39,40] nitrobenzenes.^[35,57-58] The $\delta(^{17}\text{O})$ values of the single-bonded phenoxy oxygen show good correlations with Eqns (4) and (5) as well. The influence of *para*

substituents from the benzoyl part of esters on the $\delta(^{17}\text{O})$ of the single-bonded phenoxy oxygen was ca. one-half the size of substituent effects in the $\delta(^{17}\text{O})$ of carbonyl oxygen (Table 2) which is similar to that in References.^[14-16] The chemical shifts of carbonyl oxygen for *meta* derivatives correlated well with the single parameter treatment using the Taft σ_m constants as the dual substituent parameter treatment with the Taft σ_I and σ_R constants (Table 2).

In *meta*-substituted phenyl benzoates the calculated sensitivity of the $\delta(^{17}\text{O})$ values of carbonyl oxygen towards the σ_m constants was nearly the same as earlier found for methyl benzoates in Reference^[15] ($\rho_m = 6.44$,^[15] 7.17 Table 2). In the case of *meta* derivatives the $\delta(^{17}\text{O})$ values for single-bonded phenoxy oxygen showed very low sensitivity towards the substituent effects in benzoyl moiety ($\rho_m = 1.71$ Table 2). In case the $\delta(^{17}\text{O})$ values of single-bonded phenoxy oxygen for *meta* derivatives were correlated with the Taft σ_I and σ_R constants; the resonance term was excluded as insignificant.

The positive values of ρ^+ , ρ_I and ρ_R^+ calculated using the $\delta(^{17}\text{O})$ values for carbonyl oxygen and single-bonded phenoxy oxygen in phenyl esters of substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, (Table 2) prove that the electron-withdrawing substituents cause high-frequency shift of the ^{17}O signal showing deshielding effect of the O atom. The electron-donating substituents have an opposite effect resulting in low-frequency shift and shielding of the O atom. This is consistent with the increased double bond character of the carbonyl group produced by an electron-withdrawing groups and an increase in single bond character resulting from the electron-donating substituents.^[26,36,63,65] An increase in the negative charge on the carbonyl oxygen indirectly causes the oxygen lone pair to be less tightly bound. Earlier^[8,9] the increased double bond character of the carbonyl group produced by an electron-withdrawing groups in phenyl esters of substituted benzoic acids was proved by the carbonyl carbon ^{13}C NMR chemical upfield shifts, δ_{CO} , and the increased infrared stretching frequencies of the carbonyl group, ν_{CO} .

We determined the $\delta(^{17}\text{O})$ values for thirteen phenyl esters of *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, (Table 1). All measured *ortho*-substituted benzoates, except $\text{X} = 2\text{-NH}_2$, showed the high-frequency shift of the ^{17}O signal. It could be mentioned that the substituent-induced ^{17}O NMR chemical shifts, $\Delta\delta(^{17}\text{O}) = \delta(^{17}\text{O})_{\text{X}} - \delta(^{17}\text{O})_{\text{H}}$, for phenyl esters of substituted benzoic acids for $\text{X} = \text{OCH}_3$, Cl , NO_2 determined in the present work (see Table 1) were essentially larger ($\Delta\delta(^{17}\text{O})_{\text{OCH}_3} = 21.2$, $\Delta\delta(^{17}\text{O})_{\text{Cl}} = 21.2$, $\Delta\delta(^{17}\text{O})_{\text{NO}_2} = 22.7$) as compared with those given earlier in Reference^[12] for *ortho*-substituted methyl benzoates ($\Delta\delta(^{17}\text{O})_{\text{OCH}_3} = -1.2$, $\Delta\delta(^{17}\text{O})_{\text{Cl}} = 2.9$, $\Delta\delta(^{17}\text{O})_{\text{NO}_2} = -1.7$).

The $\delta(^{17}\text{O})$ values for phenyl esters of *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, listed in Table 1 showed excellent correlations with the Charton equation (Eqns (6) and (7)) in case the data treatment was carried out separately for derivatives with $+R$ substituents and with $-R$ substituents. In the case of $+R$ substituents ($\text{X} = \text{H}$, 2-F, 2-Cl, 2-Br, 2-CH₃, 2-OCH₃, 2-N(CH₃)₂) the influence of *ortho* substituents to the carbonyl oxygen chemical shifts could be expressed as follows:

$$(\delta^{17}\text{O})_{\text{ortho}} = (346.2 \pm 1.8) + (17.3 \pm 1.8)\sigma_I + (9.68 \pm 1.13)\sigma_R^+ - (81.2 \pm 5.2)E_s^B \quad (16)$$

$R = 0.993$, $s = 1.06$, $n/n_0 = 7/7$

Equation (16) was obtained in case the more significantly deviating ($\delta^{17}\text{O}$) values for 2-NH₂ and 2-I derivatives were excluded before data treatment. In the case of 2-NH₂ ester the deviation was attributed to the intramolecular hydrogen-bonding shielding effect.^[9,17] Thus, in the *ortho*-substituted esters the carbonyl oxygen is deshielded by $-I$ and steric effects and shielded by $+R$ substituent effects.

For phenyl esters of *ortho*-substituted benzoic acids containing electron-withdrawing $-R$ substituents ($X = \text{H}, \text{NO}_2, \text{CN}, \text{CF}_3, \text{SO}_2\text{CH}_3, \text{SCF}_3$) we found:

$$(\delta^{17}\text{O})_{\text{ortho}} = (346.9 \pm 3.1) + (16.0 \pm 5.1)\sigma_1 - (32.6 \pm 4.0)E_s^B \quad (17)$$

$$R = 0.979, s = 2.40, n/n_0 = 6/6$$

The data treatment with Eqns (6) and (7) using two steric scales for *ortho* substituents, E_s^B and the modified Charton ν constants, gave nearly identical results (Table 2). When the Charton steric ν constants were used, the susceptibility to the steric effect, δ_{ortho} , was positive and approximately twice smaller as compared to the δ_{ortho} value obtained using the E_s^B scale. We found the influence of *ortho* substituents to the $\delta^{17}\text{O}$ values in phenyl benzoates containing substituents in benzoyl moiety, to be influenced by the positive inductive effect approximately by the same extent for both $+R$ substituents ($(\rho_1)_{\text{ortho}} = 17.3$, Eqn (16)) and $-R$ substituents ($(\rho_1)_{\text{ortho}} = 16.0$, Eqn (17)). The influence of the *ortho* inductive effect was found to be approximately one-half the size of the corresponding influence from the *para* position (Eqns (14) and (15)). For phenyl esters of substituted benzoic acids, $X\text{-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, nearly the same ratio $(\rho_1)_{\text{ortho}}/(\rho_1)_{\text{para}} \approx 2$ was observed in the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} ,^[8] and infrared stretching frequencies, ν_{CO} .^[9] For the alkaline hydrolysis of substituted phenyl benzoates in water for both series containing the substituents in benzoyl and in the phenyl part of benzoates $(\rho_1)_{\text{ortho}}/(\rho_1)_{\text{para}}$ was approximately 1.5.^[6]

In the case of *ortho* derivatives with $+R$ substituents the contribution of the through-conjugation between substituent and the carbonyl oxygen was observed by the same extent as that for *para* substituents. The sensitivity of the $\delta^{17}\text{O}$ toward the through-conjugation in the case of *ortho* $+R$ substituents was 9.68 (Eqn (16), Table 3). The same value for *para*-substituted derivatives was 9.71 (Eqn (16)). In the case of esters with $-R$ substituents the resonance factor was excluded as insignificant.

Results of correlations in Eqns (16) and (17), and Table 2 show that due to the steric positive requirements of *ortho* substituents the $\delta^{17}\text{O}$ values increase (high-frequency shift of the ^{17}O signal) showing deshielding effect of the O atom in the case of both the *ortho* $+R$ substituents and *ortho* $-R$ substituents. We found that the steric requirement in the case of *ortho* $+R$ substituents was approximately twice as strong as in the case of $-R$ substituents.

In the case of the single-bonded phenoxy oxygen, similar to the inductive and resonance terms, the influence of the steric term appeared to be one-half the size of the steric term for carbonyl oxygen (Table 2). The influence of *ortho* substituents to the single-bonded $\delta^{17}\text{O}$ values in the case of $+R$ substituents could be expressed as follows:

$$(\delta^{17}\text{O})_{\text{ortho}} = (187.7 \pm 1.1) + (7.12 \pm 1.13)\sigma_1 + (2.48 \pm 0.70)\sigma_R^+ - (33.5 \pm 3.2)E_s^B \quad (18)$$

$R = 0.986, s = 0.648, n/n_0 = 7/7$

Separation of the inductive, resonance and steric components of substituent effects in the $\delta^{17}\text{O}$ values for phenyl esters of *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, with donor $+R$ substituents (Eqn (16)) show that the influence of the through-conjugation between *ortho* $+R$ substituents and the carbonyl oxygen occurs by the same extent as that for *para* substituents. This confirms that in esters considered with $+R$ substituents the carbonyl group is still coplanar with the *ortho*-substituted aryl ring and due to the through-resonance effect of electron-donating substituents the carbonyl oxygen shows a strong shielding effect. Consequently, in the *ortho*-substituted esters with $+R$ substituents only one substituent in the *ortho* position could not distort the planarity between the carbonyl group and the ring plane essentially. Similarly to esters considered, in the case of the $\delta^{17}\text{O}$ values for nitrobenzenes^[34] the resonance effect remains important despite of the steric interactions between the substituent and the nitro group. It was concluded^[43,65,66] that a small steric effect of *ortho* substituent in the case of 2-methylbenzoate doesn't necessarily distort planarity or result in steric inhibition of resonance. In a series of substituted benzoate anions, the ab initio calculations of the carbonyl group rotation barriers indicated^[67] that due to π -resonance effect the planar conformations are preferred.

We suggest that in the case of $+R$ substituents the observed steric effects in the $\delta^{17}\text{O}$ values similar to that for carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} ,^[8] are caused by the repulsive van der Waals deshielding effect. Due to the bulky *ortho* substituents the π -electron density around the CO oxygen in an *ortho*-substituted ester would be reduced due to the electrostatic repulsion between the orbitals of the substituent and those of the CO bond, with the effect increasing as substituent increases the size (the van der Waals deshielding^[17,41,42,44,68]). In the case of the electron-donating substituents due to the repulsive van der Waals steric effect the shielding effect of the O atom is reduced.

We found that in the case of the $-R$ electron-withdrawing substituents ($\text{X} = \text{H}, \text{NO}_2, \text{CN}, \text{CF}_3, \text{SO}_2\text{CH}_3, \text{SCF}_3$) the steric deshielding effect to be twice weaker as compared to that for the electron-donating substituents and the resonance factor was insignificant. We admit that in the case of $-R$ substituents the carbonyl group is rotated out of the *ortho*-substituted aryl plane and similar to that for electron-donating substituents, the steric effect is caused by the repulsive van der Waals deshielding effect.^[17,41,42,44,68] Evidently, in the case of $-R$ substituents the observed repulsive van der Waals deshielding effect was approximately twice weaker as compared to that for planar esters with $+R$ substituents due to the increased torsion angle between the carbonyl group and the *ortho*-substituted aryl plane.^[13] In the case of *ortho* electron-withdrawing substituents the deviation from a coplanar configuration between the ring and the carbonyl group is presumably due to prevention of the positive charge delocalization.^[36]

In phenyl esters of *ortho*-substituted benzoic acids the calculated sensitivities of the $\delta^{17}\text{O}$ values towards the substituent inductive effect, $(\rho_1)_{\text{ortho}}$, was more than three times stronger ($(\rho_1)_{\text{ortho}} \approx 17$, Table 2) as compared to the same sensitivities, $(\rho_1)_{\text{ortho}}$, in the case of the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , ($(\rho_1)_{\text{ortho}} = 5.00$ ^[8]). In the substituent-induced chemical shifts of carbonyl carbon for phenyl esters of *ortho*-substituted benzoic

acids with +*R* substituents the contribution of the steric effect ($\delta_{\text{ortho}} = -81.2$, Table 2) was ca 18 times stronger compared to the steric effect in the case of the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} ($\delta_{\text{ortho}} = -4.40$). Dahn and Carrupt^[26] have reported that the (de)shielding effect of the carbonyl oxygen atom is mainly determined by the energy of the $n-\pi^*$ excitation; donor-acceptor type interactions influence the level of both orbitals. As the n orbital of this transition is nearly exclusively located on the O atom, the extinction acts less on ^{13}C and thus mainly responsible for the difference in the substituent sensitivity between ^{13}C and ^{17}O shifts. Chao^[40] concluded that the ^{17}O shift values in carbonyl compounds are strongly influenced by the $n-\pi^*$ mixing, whereas the ^{13}C values are determined by multiple factors. The $n-\pi^*$ mixing does not affect the ^{13}C chemical shifts because the lone pair is located on the O atom. Studying the ^{17}O chemical shifts in benzamides derivatives De Rosa^[69] suggested that in localized excited state the through-conjugation is possible between the substituent and the carbonyl oxygen and is not affected by the ground state torsion angle.

Correlation of the ^{17}O NMR chemical shifts, $\delta(^{17}\text{O})$, for *ortho*- and *para*-substituted nitrobenzenes, benzoyl chlorides and acetophenones

To compare the substituent effects in the $\delta(^{17}\text{O})$ values for *ortho*- and *para*-substituted nitrobenzenes, $\text{X-C}_6\text{H}_4\text{NO}_2$, benzoyl chlorides, $\text{X-C}_6\text{H}_4\text{COCl}$, and acetophenones, $\text{X-C}_6\text{H}_4\text{COCH}_3$, with those in $\delta(^{17}\text{O})$ values for the phenyl esters of *para*- and *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, the corresponding $\delta(^{17}\text{O})$ values were correlated with Eqns (4)-(6).

Similarly to the phenyl esters of *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, (Eqns (16) and (17)), the $\delta(^{17}\text{O})$ values for *ortho*-substituted nitrobenzenes showed excellent correlation with the Charton equation (6) in case the data treatment was performed separately for nitrobenzenes with +*R* substituents and with -*R* substituents. For $\delta(^{17}\text{O})$ values of *ortho*-substituted nitrobenzenes, $\text{X-C}_6\text{H}_4\text{NO}_2$, with +*R* substituents ($\text{X} = \text{H}$, CH_3 , CH_2CH_3 , $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$, OCH_3 , SCH_3 , $\text{N}(\text{CH}_3)_2$, F , Cl , Br , $2,6-(\text{CH}_3)_2$) we obtained (Table 2):

$$(\delta^{17}\text{O})_{\text{ortho}} = (578.1 \pm 3.5) + (26.8 \pm 5.2)\sigma_1 + (11.7 \pm 2.4)\sigma_R^+ - (108.4 \pm 7.8)E_s^B \quad (19)$$

$R = 0.975$, $s = 3.47$, $n/n_0 = 11/12$

In the case of *ortho*-substituted nitrobenzenes, $\text{X-C}_6\text{H}_4\text{NO}_2$, with -*R* substituents ($\text{X} = \text{H}$, NO_2 , CN , CF_3 , CONH_2 , CO_2CH_3) the substituent effect $(\delta^{17}\text{O})_{\text{ortho}}$ is expressed as follows (Table 2):

$$(\delta^{17}\text{O})_{\text{ortho}} = (573.7 \pm 3.5) + (20.2 \pm 6.3)\sigma_1 - (58.4 \pm 6.0)E_s^B \quad (20)$$

$R = 0.981$, $s = 3.12$, $n/n_0 = 6/6$

The $\delta(^{17}\text{O})$ values of carbonyl oxygen for the phenyl esters of *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, showed excellent correlation with $\delta(^{17}\text{O})$ values for *ortho*-

substituted nitrobenzenes, $X-C_6H_4NO_2$, including simultaneously derivatives with +*R* and –*R* substituents.

$$\delta(^{17}O)_{2-X\text{-nitrobenzenes}} = (572.2 \pm 1.7) + (1.63 \pm 0.08)\Delta\delta(^{17}O)_{2-X\text{-benzoates}} \quad (21)$$

$$R = 0.986, s = 2.90, n/n_0 = 12/12$$

$$\delta(^{17}O)_{4-X\text{-nitrobenzenes}} = (575.1 \pm 1.4) + (1.70 \pm 0.24)\Delta\delta(^{17}O)_{4-X\text{-benzoates}} \quad (22)$$

$$R = 0.935, s = 3.73, n/n_0 = 8/12$$

We can see (Eqns (21) and (22), Table 2) that in substituted nitrobenzenes the inductive, resonance and steric substituent effects appeared to be 1.7 times stronger as compared to that for the phenyl esters substituted benzoic acids, $X-C_6H_4CO_2C_6H_5$.

In the case of *ortho*-substituted benzoyl chlorides, $X-C_6H_4COCl$, and acetophenones, $X-C_6H_4COCH_3$, the correlations with the Charton equation (Eqn (6)) was performed for derivatives with +*R* *ortho* substituents only. Unfortunately in literature there are available only very few values on $\delta(^{17}O)$ for *ortho*-substituted benzoyl chlorides and acetophenones with –*R* substituents, to treat the corresponding $\delta(^{17}O)$ values with Eqn (6).

For *ortho*-substituted benzoyl chlorides, $X-C_6H_4COCl$, containing +*R* substituents we found (Table 2):

$$(\delta(^{17}O))_{ortho} = (486.0 \pm 2.2) + (35.0 \pm 2.9)\sigma_1 + (16.3 \pm 2.5)\sigma^+_R - (93.3 \pm 4.9)E_s^B \quad (23)$$

$$R = 0.994, s = 1.38, n/n_0 = 6/6$$

In the case of *ortho*-substituted acetophenones, $X-C_6H_4COCH_3$, containing +*R* substituents, the substituent effect is described as follows (Table 2):

$$(\delta(^{17}O))_{ortho} = (550.6 \pm 2.3) + (26.2 \pm 2.9)\sigma_1 + (40.8 \pm 2.7)\sigma^+_R - (148.0 \pm 5.4)E_s^B \quad (24)$$

$$R = 0.996, s = 1.68, n/n_0 = 7/7$$

The $\delta(^{17}O)$ values for *para*-substituted nitrobenzenes, benzoyl chlorides and acetophenones showed excellent correlation with Eqn (5) and (6) using the Brown and Okamoto substituent constants σ^+ .^[55,56] The calculated sensitivities towards the through-resonance, ρ^+ , for *para*-substituted benzoyl chlorides and acetophenones were respectively 21.2, and 24.1 (Table 2). The corresponding values of ρ^+ coincide well with the similar ρ^+ values reported earlier (for benzoyl chlorides $\rho^+ = 21.7$,^[39] for acetophenones $\rho^+ = 22.5$ ^[27,59]). For *para*-substituted nitrobenzenes we obtained $\rho^+ = 14.9$ (Table 2, $\rho_1 = 18.6$ ^[34] and $\rho^+_R = 24.0$ ^[34]).

Correlation of the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, for *meta*-substituted methyl benzoates, nitrobenzenes, and acetophenones

For comparison the $\delta(^{17}O)$ values published in literature for *meta*-substituted methyl benzoates, $X-C_6H_4COCH_3$, nitrobenzenes, $X-C_6H_4NO_2$, and acetophenones, $X-$

C₆H₄COCH₃, were correlated with Eqns (4)-(6) as well. The $\delta^{17}\text{O}$ values for *meta*-substituted methyl benzoates showed good correlations so with the single parameter treatment using σ_{m} constants (Eqn (4)) as the dual substituent parameter treatment with the Taft σ_{I} and $\sigma_{\text{R}}^{\circ}$ constants (Table 2). In methyl benzoates for the $\delta^{17}\text{O}$ values of the carbonyl oxygen the calculated ρ_{m} value was 5.53 ($\rho_{\text{I}} = 6.86$, $\rho_{\text{R}}^{\circ} = 1.93$) and for nitrobenzenes $\rho_{\text{m}} = 5.28$ ($\rho_{\text{I}} = 6.78$, $\rho_{\text{R}}^{\circ} = 0$). The calculated values of ρ_{m} for methyl benzoates and nitrobenzenes coincide well with the similar ρ_{m} values reported earlier (for methyl benzoates $\rho_{\text{m}} = 6.44^{[15]}$, for nitrobenzenes $\rho_{\text{I}} = 6.5^{[58]}$, $\rho_{\text{R}}^{\circ} = 0.6^{[58]}$). In *meta*-substituted nitrobenzenes and acetophenones the susceptibility to the inductive effect was ca one-half the size of that for the corresponding *para* derivatives and the resonance term was excluded as insignificant (Table 2).

Correlation of the ^{17}O NMR chemical shifts, $\delta^{17}\text{O}$, with the substituent-induced rates of the alkaline hydrolysis, $\Delta\log k$, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{\text{CO}}$, and IR carbonyl stretching frequencies, $\Delta\nu_{\text{CO}}$

We correlated the $\delta^{17}\text{O}$ values of the carbonyl oxygen and the single-bonded oxygen for phenyl esters of *ortho*-, *para*-, and *meta*-substituted benzoic acids, X-C₆H₄CO₂C₆H₅, with the corresponding rates of the alkaline hydrolysis, $\Delta\log k$, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{\text{CO}}$, and IR carbonyl stretching frequencies, $\Delta\nu_{\text{CO}}$, using Eqns (8)-(13) (Table 3). The $\delta^{17}\text{O}$ values for *ortho* derivatives, show a good correlation with the corresponding $\Delta\log k$ values of the alkaline hydrolysis, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{\text{CO}}$, and IR carbonyl stretching frequencies, $\Delta\nu_{\text{CO}}$, ($0.998 > R > 0.963$, Table 3) in case the additional resonance and steric terms were included (Eqns (8)-(13)) and the data treatment was carried out separately for esters with +*R* substituents and -*R* substituents. The $\delta^{17}\text{O}$ values for *para* derivatives were correlated well with the corresponding values of $\Delta\log k$ for the alkaline hydrolysis, the ^{13}C NMR chemical shifts, $\Delta\delta_{\text{CO}}$, and IR the stretching frequencies, $\Delta\nu_{\text{CO}}$, when the additional resonance term, $a_{2(\text{para})}\sigma_{\text{R}}^+$, (Eqns (11)-(13), Table 3) was included. To correlate the $\delta^{17}\text{O}$ values for *meta* derivatives the additional $a_{2(\text{meta})}\sigma_{\text{R}}^{\circ}$ scale was included. The slope a_1 in Eqn (8)-(13) is the ratio of inductive effects in the ^{17}O NMR chemical shifts and in the corresponding process compared. So the slope a_1 in Eqn (8) represents the ratio of the substituent-dependent inductive effects in the $\delta^{17}\text{O}$ values and in $\Delta\log k$ values of the alkaline hydrolysis and the slope a_1 in Eqn (9) is the ratio of the susceptibility to the inductive effect in the $\delta^{17}\text{O}$ values and in the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{\text{CO}}$. The slope a_1 in Eqn (10) corresponds to the ratio of the inductive effects in $\delta^{17}\text{O}$ values and in the IR stretching frequencies, $\Delta\nu_{\text{CO}}$, for the *ortho*-substituted esters. Correlation equations obtained in Table 3 could be used to estimate the rates of the alkaline hydrolysis, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{\text{CO}}$, and IR carbonyl stretching frequencies, $\Delta\nu_{\text{CO}}$, using the $\delta^{17}\text{O}$ values for esters considered.

We found the carbonyl ^{17}O NMR chemical shifts, $\delta^{17}\text{O}$, for the phenyl esters of *ortho*-substituted benzoic acids with +*R* substituents to be correlated well with the $\Delta\log k$ values

of the alkaline hydrolysis in water at 25 °C, the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{\text{CO}}$, and the IR stretching frequencies, $\Delta\nu_{\text{CO}}$, as follows (Eqns (25)-(27), Table 3):

$$\delta(^{17}\text{O})_{\text{ortho}} = (346.2 \pm 1.7) + (8.90 \pm 0.89)\Delta\log k + (7.93 \pm 1.10)\sigma^+_{\text{R}} - (98.3 \pm 5.0)E_{\text{s}}^{\text{B}} \quad (25)$$

$$R = 0.993, s = 0.990, n/n_0 = 7/7$$

$$\delta(^{17}\text{O})_{\text{ortho}} = (345.4 \pm 2.0) - (3.62 \pm 0.43)\Delta\delta_{\text{CO}} + (10.0 \pm 1.3)\sigma^+_{\text{R}} - (95.2 \pm 5.8)E_{\text{s}}^{\text{B}} \quad (26)$$

$$R = 0.991, s = 1.17, n/n_0 = 7/7$$

$$\delta(^{17}\text{O})_{\text{ortho}} = (346.3 \pm 1.6) + (0.64 \pm 0.08)\Delta\nu_{\text{CO}} + (7.76 \pm 1.56)\sigma^+_{\text{R}} - (75.1 \pm 4.8)E_{\text{s}}^{\text{B}} \quad (27)$$

$$R = 0.990, s = 0.942, n/n_0 = 6/6$$

The same relationships for the phenyl esters of *ortho*-substituted benzoic acids with $-R$ substituents are expressed as follows:

$$\delta(^{17}\text{O})_{\text{ortho}} = (347.0 \pm 2.9) + (6.31 \pm 2.08)\Delta\log k - (50.3 \pm 5.5)E_{\text{s}}^{\text{B}} \quad (28)$$

$$R = 0.978, s = 2.47, n/n_0 = 6/6$$

$$\delta(^{17}\text{O})_{\text{ortho}} = (346.0 \pm 1.1) - (3.97 \pm 1.14)\Delta\delta_{\text{CO}} - (47.4 \pm 5.8)E_{\text{s}}^{\text{B}} \quad (29)$$

$$R = 0.996, s = 1.09, n/n_0 = 6/6$$

$$\delta(^{17}\text{O})_{\text{ortho}} = (345.4 \pm 1.9) + (1.32 \pm 0.13)\Delta\nu_{\text{CO}} \quad (30)$$

$$R = 0.987, s = 2.09, n/n_0 = 4/4$$

In Eqn (8) $a_1 = \rho_{\text{I}}(^{17}\text{O})/\rho_{\text{I}}(\text{AH})$, $a_2 = \rho_{\text{R}}(\delta^{17}\text{O}) - a_1\rho_{\text{R}}(\text{AH})$ and $a_3 = \delta_{\text{S}}(\delta^{17}\text{O}) - a_1\delta_{\text{S}}(\text{AH})$. In Eqn (9) $a_1 = \rho_{\text{I}}(^{17}\text{O})/\rho_{\text{I}}(\delta_{\text{CO}})$, $a_2 = \rho_{\text{R}}(\delta^{17}\text{O}) - a_1\rho_{\text{R}}(\delta_{\text{CO}})$ and $a_3 = \delta_{\text{S}}(\delta^{17}\text{O}) - a_1\delta_{\text{S}}(\delta_{\text{CO}})$. In Eqn (10) $a_1 = \rho_{\text{I}}(\delta(^{17}\text{O}))/\rho_{\text{I}}(\nu_{\text{CO}})$, $a_2 = \rho_{\text{R}}(\delta^{17}\text{O}) - a_1\rho_{\text{R}}(\nu_{\text{CO}})$ and $a_3 = \delta_{\text{S}}(\delta^{17}\text{O}) - a_1\delta_{\text{S}}(\nu_{\text{CO}})$. In relations shown the alkaline hydrolysis is denoted by (AH), the susceptibility to the steric factor by δ_{S} , the carbonyl carbon ^{13}C chemical shifts by (δ_{CO}) , and the IR carbonyl stretching frequencies by (ν_{CO}) .

Using for the alkaline hydrolysis of the phenyl esters of substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\rho_{\text{I}}(\text{AH})_{\text{ortho}} = 2.13$, $\rho_{\text{R}}(\text{AH})_{\text{ortho}} = 0.31$ and $\delta(\text{AH})_{\text{ortho}} = 2.67$ in water at 25 °C^[6] as well as $\rho_{\text{I}}(^{17}\text{O})_{\text{ortho}} = 17.3$, $\rho_{\text{R}}(^{17}\text{O})_{\text{ortho}} = 9.68$ and, $\delta_{\text{S}}(^{17}\text{O})_{\text{ortho}} = -81.2$ for esters with $+R$ substituents (Table 3) we obtained the values of $a_1 = 8.12$, $a_2 = 7.28$ and $a_3 = -102.8$ which are approximately the same as shown by Eqn (25) (Table 3).

The positive values of the parameter a_1 in Table 3 prove that the substituent-induced $\delta(^{17}\text{O})$ values, the $\Delta\log k$ values of the alkaline hydrolysis and the IR carbonyl stretching frequencies, (ν_{CO}) , grow with increase of the inductive effects of substituent included. In correlation of the $\delta(^{17}\text{O})$ values with the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{\text{CO}}$, (Eqn (9)) the negative value of the parameter a_1 shows that in phenyl esters of substituted benzoic acids the influence of the substituent-induced inductive effect on the $\delta(^{17}\text{O})$ values is opposite to that in the ^{13}C NMR chemical shifts, $\Delta\delta_{\text{CO}}$. With increase in σ_{I} values of substituents the $\delta(^{17}\text{O})$ values were found to increase but the carbonyl carbon ^{13}C NMR

chemical shifts, $\Delta\delta_{\text{CO}}$, were found to diminish when the electron-attracting substituents are involved.

When the carbonyl $\delta(^{17}\text{O})$ values for the phenyl esters of *ortho*-substituted benzoic acids with $-R$ substituents were correlated with Eqns (8)-(10) (Table 3) the magnitudes of a_2 do not differ from zero and the corresponding resonance term during the data treatment was excluded as insignificant. In the case of esters with $-R$ substituents the influence of the steric term was approximately twice weaker as compared to that for derivatives with $+R$ substituents (Table 3).

When the single bonded $\delta(^{17}\text{O})$ values were correlated with Eqns (8)-(13) the magnitudes of parameters a_1 , a_2 and a_3 were twice smaller as compared to that for the carbonyl $\delta(^{17}\text{O})$ values (Table 3).

CONCLUSIONS

The ^{17}O NMR spectra for 29 phenyl esters of *ortho*-, *para*-, and *meta*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, were recorded. The electron-donating substituents in *ortho*-, *para*- and *meta*-substituted esters resulted in shielding of the ^{17}O signal (upfield shift) and electron-withdrawing groups caused deshielding (downfield shift). The ^{17}O NMR chemical shifts of the carbonyl oxygen and the single-bonded oxygen for *para* derivatives correlated well with the σ^+ constants. The $\delta(^{17}\text{O})$ values for the *ortho* derivatives showed excellent correlation with the inductive, σ_{I} , resonance, σ_{R}^+ , and steric, E_{s}^{B} , substituent constants in case the data treatment was performed separately for derivatives containing the electron-donating $+R$ substituents and electron-attracting $-R$ substituents. The steric interaction of *ortho* substituents with the ester group was found to produce deshielding effect of the carbonyl and single-bonded oxygens. We suggest that in phenyl esters of *ortho*-substituted benzoic acids the steric effect is caused by the repulsive van der Waals deshielding effect. For *ortho* derivatives with $-R$ substituents the resonance term was insignificant and the steric term was ca. twice weaker as compared to that for derivatives with $+R$ substituents. The $\delta(^{17}\text{O})$ values for *para*- and *ortho*-substituted nitrobenzenes correlated well with the σ^+ , inductive, σ_{I} , resonance, σ_{R}^+ , and steric, E_{s}^{B} , substituent constants, respectively, similar to that for phenyl esters of substituted benzoic acids. Only, in $\delta(^{17}\text{O})$, for nitrobenzenes ($\text{XC}_6\text{H}_4\text{NO}_2$) the susceptibility to the σ^+ , inductive σ_{I} , resonance, σ_{R}^+ , and steric, E_{s}^{B} , substituent constants, was 1.7 times stronger as compared to that for phenyl esters of substituted benzoic acids. The $\delta(^{17}\text{O})$ values for *meta*-derivatives correlated well with the σ_{m} substituent constants.

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Table 1. ^{17}O NMR chemical shifts, $\delta(^{17}\text{O})$, of the carbonyl oxygen and the single-bonded oxygen for phenyl esters of *ortho*-, *para*- and *meta*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, in CH_3CN at 50 °C

Substituent	$\delta(^{17}\text{O})_{\text{C=O}}$	$\delta(^{17}\text{O})_{\text{OPh}}$	Other functions	$\text{C}_{\text{ester}}^{\text{a}}$	$\delta(^{13}\text{CO})$
2-NO ₂	368.4	196.3	600.1		
2-CN	358.3	191.0			
2-F	362.4	195.6			
2-Cl	370.2	197.7			
2-Br	372.4	199.1			
2-I	368.8	197.1			
2-CF ₃	375.1	199.4			
2-SO ₂ CH ₃	375.4	201.5	161.1		165.75
2-SCF ₃	373.9	197.4			164.74
2-OCH ₃	366.9	197.8	54.0		
2-CH ₃	364.6	195.9			
2-N(CH ₃) ₂	364.2	197.8			166.27
2-NH ₂	340.6	188.7			
H	345.7	187.3			165.17 ^b
	345.8	187.5		0.4 m	
4-NO ₂	351.9	188.3	574.6	0.4 m	
4-F	344.4	187.0		0.5 m	
4-Cl	346.7	187.5		0.5 m	
4-Br	345.4	187.1		0.5 m	
4-CH ₃	343.2	186.5			
	342.7	186.8		0.3 m	
4-OCH ₃	336.7	184.9	60.8		
4-NH ₂	333.5	183.8		0.3 m	
4-C(CH ₃) ₃	344.1	187.0		0.5 m	
3-NO ₂	350.8	187.6	576.8	0.5 m	
	349.9	187.7	574.6		
3-CN	350.6	188.2		0.5 m	163.21
3-F	348.1	186.9			164.00
3-Cl	349.0	188.0			
3-CH ₃	346.5	188.2			
3-OCH ₃	346.7	187.8	51.9		165.00
3-N(CH ₃) ₂	344.4	186.9			

^a Approximately 1 molal solutions of *ortho* and *para* derivatives in mixture of CH₃CN and CD₃CN (2 ml + 1 ml) were used, except where shown otherwise. ^b Reference^[2].

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Table 2. Correlation of the ^{17}O NMR chemical shifts, $\delta(^{17}\text{O})$, of the carbonyl oxygen and the single-bonded oxygen (OPh) with Eqns (4)-(7)

Scales	$\delta(^{17}\text{O})_{\text{H}}$	ρ_{I} or $\rho^+(\rho)$	$\rho^+_{\text{R}}(\rho^{\circ}_{\text{R}})$	δ_{ortho}	R^a	$(R_0^2)^b$	s^c	n/n_0^d
Phenyl esters of <i>ortho</i> -substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$								
$\text{C}=\text{}^{17}\text{O}$ + <i>R</i> substituents included, acetonitrile at 50 °C								
$\sigma_{\text{I}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	346.2 ± 1.8	17.3 ± 1.8	9.68 ± 1.13	-81.2 ± 5.2	0.993	0.182	1.06	7/7 ^e
$\sigma_{\text{I}}, \sigma^+_{\text{R}}, \nu$	347.4 ± 3.5	14.3 ± 4.3	4.62 ± 2.08	33.2 ± 5.0	0.961	0.182	2.41	7/7 ^{e,f}
- <i>R</i> substituents included, acetonitrile at 50 °C								
$\sigma_{\text{I}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	346.9 ± 3.1	16.0 ± 5.1	0	-32.6 ± 4.0	0.979	0.304	2.40	6/6 ^g
σ_{I}, ν	346.5 ± 2.0	18.1 ± 1.3	0	15.9 ± 1.3	0.991	0.304	1.61	6/6 ^f
$^{17}\text{OC}_6\text{H}_5$ + <i>R</i> substituents included, acetonitrile at 50 °C								
$\sigma_{\text{I}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	187.7 ± 1.1	7.12 ± 1.13	2.48 ± 0.70	-33.5 ± 3.2	0.986	0.100	0.648	7/7 ^e
$\sigma_{\text{I}}, \sigma^+_{\text{R}}, \nu$	188.2 ± 1.1	6.04 ± 1.85	0	13.0 ± 1.7	0.963	0.100	1.06	7/7 ^{e,f}
- <i>R</i> substituents included, acetonitrile 50 °C								
$\sigma_{\text{I}}, E_{\text{s}}^{\text{B}}$	187.3 ± 1.2	5.52 ± 1.90	—	-15.5 ± 1.5	0.986	0.225	0.895	6/6 ^{g,h}
σ_{I}, ν	187.1 ± 1.7	6.76 ± 2.80	—	7.35 ± 1.10	0.967	0.225	1.35	6/6 ^f
<i>ortho</i> -substituted nitrobenzenes, $\text{X-C}_6\text{H}_4\text{NO}_2$								
$\text{N}(^{17}\text{O})_2$ + <i>R</i> substituents included, acetonitrile at 75 °C								
$\sigma_{\text{I}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	578.1 ± 3.5	26.8 ± 5.2	11.7 ± 2.4	-108.4 ± 7.8	0.975	-0.072	3.47	11/12 ^{e,i,j,k}
- <i>R</i> substituents included, acetonitrile								
$\sigma_{\text{I}}, E_{\text{s}}^{\text{B}}$	573.7 ± 3.5	20.2 ± 6.3	0	-58.4 ± 6.0	0.981	0.072	3.12	6/6 ^l
<i>ortho</i> -substituted benzoyl chlorides, $\text{X-C}_6\text{H}_4\text{COCl}$								
$\text{C}=\text{}^{17}\text{O}$ + <i>R</i> substituents included, acetonitrile at 75 °C								
$\sigma_{\text{I}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	486.0 ± 2.2	35.0 ± 2.9	16.3 ± 2.5	-93.3 ± 4.9	0.994	-0.188	1.38	6/6 ^{k,m,n}
<i>ortho</i> -substituted acetophenones, $\text{X-C}_6\text{H}_4\text{COCH}_3$								
$\text{C}=\text{}^{17}\text{O}$ + <i>R</i> substituents included, dioxane at 30 °C								
$\sigma_{\text{I}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	550.6 ± 2.3	26.2 ± 2.9	40.8 ± 2.7	-148.0 ± 5.4	0.996	-0.187	1.68	7/7 ^{k,o,p}
Phenyl esters of <i>para</i> -substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$								
$\text{C}=\text{}^{17}\text{O}$ Acetonitrile at 50 °C								
σ^+_{P}	345.2 ± 0.3	9.07 ± 0.55	—	—	0.986	—	0.918	9/9
$\sigma_{\text{I}}, \sigma^+_{\text{R}}$	345.9 ± 0.5	7.21 ± 0.99	9.71 ± 0.54	—	0.990	0.106	0.752	9/9
$^{17}\text{OC}_6\text{H}_5$								
σ^+_{P}	187.1 ± 0.2	2.26 ± 0.26	—	—	0.952	—	0.428	9/9
$\sigma_{\text{I}}, \sigma^+_{\text{R}}$	187.5 ± 0.2	1.26 ± 0.41	2.60 ± 0.22	—	0.976	0.004	0.307	9/9
Methyl esters of <i>para</i> -substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{CH}_3$								
$\text{C}=\text{}^{17}\text{O}$ Acetonitrile at 40 °C								
σ^+_{P}	337.8 ± 0.2	9.66 ± 0.29	—	—	0.990	—	0.970	23/23 ^q

$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	337.6 ± 0.5	10.0 ± 1.1	9.56 ± 0.41	—	0.990	0.437	0.991	23/23
	$^{17}\text{OCH}_3$							
σ_{p}^+	127.8 ± 0.2	3.72 ± 0.26	—	—	0.949	—	0.884	23/23
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	127.4 ± 0.5	4.64 ± 0.97	3.47 ± 0.37	—	0.948	0.443	0.884	23/23
	$\text{C}=\text{}^{17}\text{O}$							
								Acetonitrile- d_3 at 40 °C
σ_{p}^+	335.8 ± 0.4	11.5 ± 0.6	—	—	0.990	—	1.12	8/8 ^r
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	336.8 ± 0.6	8.72 ± 1.38	12.2 ± 0.6	—	0.994	0.086	0.885	8/8
	$^{17}\text{OCH}_3$							
σ_{p}^+	125.8 ± 0.3	3.85 ± 0.54	—	—	0.935	—	0.969	8/8
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	126.2 ± 0.7	2.70 ± 1.56	4.14 ± 0.67	—	0.931	0.044	1.00	8/8
	$\text{C}=\text{}^{17}\text{O}$							
								Acetone at 40 °C
σ_{p}^+	341.7 ± 0.2	9.40 ± 0.43	—	—	0.993	—	0.616	8/8 ^s
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	341.5 ± 0.5	9.89 ± 0.97	9.19 ± 0.59	—	0.992	0.317	0.654	8/8
	$^{17}\text{OCH}_3$							
σ_{p}^+	128.4 ± 0.2	3.90 ± 0.34	—	—	0.974	—	0.491	8/8
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	127.9 ± 0.3	5.07 ± 0.53	3.39 ± 0.32	—	0.986	0.464	0.359	8/8
								<i>para</i> -substituted nitrobenzenes, $\text{X}-\text{C}_6\text{H}_4\text{NO}_2$
	$\text{N}(\text{}^{17}\text{O})_2$							
								Acetonitrile at 75 °C
σ_{p}^+	573.3 ± 0.7	14.9 ± 0.8	—	—	0.980	—	2.57	14/14 ^t
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	574.3 ± 1.6	12.1 ± 3.6	15.3 ± 1.0	—	0.979	0.158	2.61	14/14
								<i>para</i> -substituted benzoyl chlorides, $\text{X}-\text{C}_6\text{H}_4\text{COCl}$
	$\text{C}=\text{}^{17}\text{O}$							
								Acetonitrile at 75 °C
σ_{p}^+	485.5 ± 0.1	21.2 ± 0.3	—	—	0.999	—	0.485	11/11 ^m
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	485.6 ± 0.5	20.9 ± 0.6	21.4 ± 0.3	—	0.999	0.239	0.502	11/11
	$\text{C}=\text{}^{17}\text{O}$							
								Tetrachloromethane at 40 °C
σ_{p}^+	490.8 ± 0.3	21.0 ± 0.5	—	—	0.998	—	0.706	8/8 ^u
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	491.3 ± 0.5	20.0 ± 1.1	21.5 ± 0.7	—	0.998	0.365	0.696	8/8
								<i>para</i> -substituted acetophenones, $\text{X}-\text{C}_6\text{H}_4\text{COCH}_3$
	$\text{C}=\text{}^{17}\text{O}$							
								Acetonitrile at 60 °C
σ_{p}^+	548.3 ± 0.9	22.8 ± 1.4	—	—	0.986	—	2.65	9/9 ^v
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	549.1 ± 1.9	20.3 ± 4.0	23.6 ± 1.8	—	0.985	0.230	2.75	9/9
	$\text{C}=\text{}^{17}\text{O}$							
								Dioxane at 30 °C
σ_{p}^+	547.9 ± 1.2	24.1 ± 1.9	—	—	0.976	—	3.52	9/9 ^o
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	550.1 ± 2.7	19.4 ± 5.1	25.8 ± 2.5	—	0.976	0.259	3.53	9/9
	$\text{C}=\text{}^{17}\text{O}$							
								Deuteriochloroform at 25 °C
σ_{p}^+	542.6 ± 0.4	24.9 ± 0.5	—	—	0.998	—	1.25	12/12 ^w
$\sigma_{\text{I}}, \sigma_{\text{R}}^+$	542.3 ± 0.8	25.7 ± 1.8	24.7 ± 0.6	—	0.998	0.336	1.30	12/12
								Phenyl esters of <i>meta</i> -substituted benzoic acids, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$
	$\text{C}=\text{}^{17}\text{O}$							
								Acetonitrile at 50 °C
σ_{m}	346.1 ± 0.3	7.17 ± 0.68	—	—	0.969	—	0.564	8/8
$\sigma_{\text{I}}, \sigma_{\text{R}}^0$	346.5 ± 0.4	6.16 ± 0.86	3.87 ± 0.90	—	0.967	0.735	0.584	8/8
	$^{17}\text{OC}_6\text{H}_5$							

σ_m	187.4 ± 0.1	1.71 ± 0.33	—	—	0.932	—	0.187	5/5 ^x
σ_I, σ_R^0	187.2 ± 0.2	1.82 ± 0.63	0	—	0.783	—	0.309	5/5 ^y
Methyl esters of <i>meta</i> -substituted benzoic acids, X-C ₆ H ₄ CO ₂ CH ₃								
C=O ¹⁷ Acetonitrile at 40 °C								
σ_m	337.5 ± 0.2	5.53 ± 0.41	—	—	0.945	—	0.603	23/23 ^q
σ_I, σ_R^0	337.1 ± 0.2	6.86 ± 0.52	1.93 ± 0.46	—	0.966	0.880	0.481	23/23
¹⁷ OCH ₃								
σ_m	127.3 ± 0.1	3.20 ± 0.29	—	—	0.923	—	0.430	22/23 ^{q,z}
σ_I, σ_R^0	127.0 ± 0.1	3.79 ± 0.28	0	—	0.955	—	0.245	19/23 ^{aa}
<i>meta</i> -substituted nitrobenzenes, X-C ₆ H ₄ NO ₂								
N(O ¹⁷) ₂ Acetonitrile at 75°C								
σ_m	575.7 ± 0.4	5.28 ± 0.82	—	—	0.904	—	0.778	10/10 ^t
σ_I, σ_R^0	575.0 ± 0.3	6.78 ± 0.66	0	—	0.960	—	0.512	10/10
<i>meta</i> -substituted acetophenones, X-C ₆ H ₄ COCH ₃								
C=O ¹⁷ Dioxane at 30 °C								
σ_m	549.8 ± 0.6	10.6 ± 1.8	—	—	0.931	—	1.34	6/6 ^o
σ_I, σ_R^0	548.6 ± 0.9	12.8 ± 2.5	0	—	0.910	—	1.52	6/6

^a R – correlation coefficient.

^b R_0 – zeroth correlation coefficient.

^c s – standard deviation.

^d n_0 reflects the total number of data involved in the correlation; n – the number of points remaining after exclusion of significantly deviating points.

^eThe $\delta^{17}\text{O}$ values for 2-NH₂ and 2-I derivatives were omitted.

^fCharton's modified steric constants, ν ,^[6,8,49] were used.

^gFor 2-SCF₃ substituent the isosteric constant $E_s^B = -0.582$ was calculated with relation: $\nu = (0.026 \pm 0.049) - (2.05 \pm 0.15)E_s^B$, ($R = 0.976$, $n = 10$) using steric constant, $\nu = 1.22$ ^[60] for OC(CH₃)₃ substituent.

^hFor 2-SO₂CH₃ substituent the steric constant $E_s^B = -0.667$ was calculated from relation^[6] $\Delta \log k = 0.021 + 2.284\sigma_1 + 0.862\sigma_R + 2.477E_s^B$, using $\Delta \log k = -0.309$ for alkaline hydrolysis of phenyl ester of 2-(methylsulfonyl)benzoic acid in aqueous 50% DMSO.^[51]

ⁱData from References^[34,35] were used.

^jThe 2-SCH₃ derivative ($E_s^B = -0.366$ was calculated using $\Delta \log k = -0.522$ (Note h)), was excluded at confidence level $t = 0.99$.

^kFor 2,6-(CH₃)₂ derivative the duple values of inductive, resonance and the steric constants were used.

^lFor 2-CO₂CH₃ substituent the isosteric constant $E_s^B = -0.485$ was calculated using $\nu = 1.02$ ^[61] for CH(CH₃)CH₂CH₃ substituent (Note g) and for 2-CONH₂ substituent the steric constants for 2-CH(CH₃)₂ substituent $E_s^B = -0.341$ was used.

^mData from Reference^[39] were used.

ⁿData from Reference.^[40]

^oData from Reference.^[36]

^pThe $\delta^{17}\text{O} = 604$ for 2,6-(CH₃)₂-acetophenone was calculated using $\Delta\delta^x$ value ($\Delta\delta^x = \delta^x - \delta^H = 54$).^[38]

^qData from Reference.^[15]

^rData from Reference.^[14]

^sData from Reference.^[16]

^tData from References.^[17,57,58]

^uData from Reference.^[27]

^vData from Reference.^[59]

^wData from Reference.^[37]

^xThe $\delta^{17}\text{O}$ values for 3-NO₂, 3-CH₃ and 3-F derivatives were omitted. When these values were included no correlation was found ($R^2 = -0.064$).

^yThe $\delta^{17}\text{O}$ values for 3-NO₂, 3-CH₃ and 3-F derivatives were omitted. When these values were included no correlation was found ($R^2 = 0.054$).

^zThe 3-SO₂NH₂ derivative was excluded.

^{aa}The 3-SO₂NH₂, 3-SO₂CH₃, 3-SO₂Cl, and 3-CH₂Cl derivatives were excluded.

Table 3. Correlation of the ^{17}O NMR chemical shifts, $\delta(^{17}\text{O})$, for the carbonyl oxygen and the single-bonded oxygen with the $\Delta\log k$ values of the alkaline hydrolysis, the carbonyl carbon chemical shifts, $\Delta\delta_{\text{CO}}$, and IR stretching frequencies of carbonyl carbon, $\Delta\nu_{\text{CO}}$, with Eqns (8)-(13)

Scales	$(\delta^{17}\text{O})_{\text{H}}$	a_1	a_2	a_3	R^a	$(R^2)^b$	s^c	n/n_0^d
Phenyl esters of <i>ortho</i> -substituted benzoic acids ^{e,f,g,h,i}								
	$\text{C}=\text{}^{17}\text{O}$	+R substituents						
$\Delta\log k_1, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	346.2 ± 1.7	8.90 ± 0.89	7.93 ± 1.10	-98.3 ± 5.0	0.993	-0.193	0.990	7/7 ^j
$\Delta\log k_2, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	345.6 ± 0.9	6.91 ± 0.34	4.61 ± 0.62	-98.9 ± 2.5	0.997	-0.199	0.495	7/7
$\Delta\delta_{\text{CO}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	345.4 ± 2.0	-3.62 ± 0.43	10.0 ± 1.3	-95.2 ± 5.8	0.991	-0.136	1.17	7/7 ^k
$\Delta\nu_{\text{CO}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	346.3 ± 1.6	0.64 ± 0.08	7.76 ± 1.56	-75.1 ± 4.8	0.990	0.364	0.942	6/6 ^l
		-R substituents						
$\Delta\log k_1, E_{\text{s}}^{\text{B}}$	347.0 ± 2.9	6.31 ± 2.08	—	-50.3 ± 5.5	0.978	0.065	2.47	6/6 ^m
$\Delta\log k_2, E_{\text{s}}^{\text{B}}$	347.4 ± 3.1	5.66 ± 2.14	—	-48.5 ± 5.7	0.973	0.011	2.72	6/6 ⁿ
$\Delta\delta_{\text{CO}}, E_{\text{s}}^{\text{B}}$	346.0 ± 1.1	-3.97 ± 1.14	—	-47.4 ± 2.1	0.996	-0.135	1.09	6/6 ^o
$\Delta\nu_{\text{CO}}, E_{\text{s}}^{\text{B}}$	345.4 ± 1.9	1.32 ± 0.13	—	0	0.987	0.974	2.09	4/4 ^p
	$^{17}\text{OC}_6\text{H}_5$	+R substituents						
$\Delta\log k_1, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	187.7 ± 1.2	3.64 ± 0.61	1.77 ± 0.76	-40.6 ± 3.4	0.985	-0.194	0.679	7/7 ^j
$\Delta\log k_2, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	187.4 ± 0.4	2.99 ± 0.18	0	-40.1 ± 1.3	0.997	-0.152	0.313	7/7
$\Delta\delta_{\text{CO}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	187.3 ± 0.4	-1.54 ± 0.10	2.61 ± 0.28	-39.4 ± 1.3	0.998	-0.175	0.266	7/7 ^k
$\Delta\nu_{\text{CO}}, \sigma^+_{\text{R}}, E_{\text{s}}^{\text{B}}$	187.7 ± 1.0	0.24 ± 0.06	0	-28.8 ± 3.3	0.984	0.373	0.761	6/6 ^l
		-R substituents						
$\Delta\log k_1, E_{\text{s}}^{\text{B}}$	187.3 ± 1.1	2.15 ± 0.80	—	-21.6 ± 2.1	0.984	0.146	0.948	6/6 ^m
$\Delta\log k_2, E_{\text{s}}^{\text{B}}$	187.4 ± 1.0	2.03 ± 0.72	—	-21.2 ± 1.9	0.985	0.076	0.918	6/6 ⁿ
$\Delta\delta_{\text{CO}}, E_{\text{s}}^{\text{B}}$	187.8 ± 1.5	-0.82 ± 0.68	—	-19.4 ± 2.7	0.963	0.005	1.43	6/6 ^o
$\Delta\nu_{\text{CO}}, E_{\text{s}}^{\text{B}}$	187.5 ± 1.1	0.30 ± 0.06	—	-9.2 ± 1.9	0.997	0.927	0.412	4/4 ^p
	$\text{C}=\text{}^{17}\text{O}$	Phenyl esters of <i>para</i> -substituted benzoic acids ^{e,f,g,h}						
$\Delta\log k_1, \sigma^+_{\text{R}}$	346.0 ± 0.9	4.19 ± 0.84	5.58 ± 1.19	—	0.982	0.854	1.04	9/9 ^q
$\Delta\log k_2, \sigma^+_{\text{R}}$	346.0 ± 0.9	3.15 ± 0.60	5.67 ± 1.12	—	0.983	0.849	0.994	9/9 ^r
$\Delta\delta_{\text{CO}}, \sigma^+_{\text{R}}$	345.6 ± 0.6	-3.10 ± 0.54	8.66 ± 0.71	—	0.986	0.367	0.921	9/9
$\Delta\nu_{\text{CO}}, \sigma^+_{\text{R}}$	346.6 ± 1.2	0.78 ± 0.16	4.22 ± 1.42	—	0.981	0.922	1.05	9/9
	$^{17}\text{OC}_6\text{H}_5$							
$\Delta\log k_1, \sigma^+_{\text{R}}$	187.5 ± 0.3	0.66 ± 0.30	1.97 ± 0.42	—	0.964	0.724	0.371	9/9 ^q
$\Delta\log k_2, \sigma^+_{\text{R}}$	187.5 ± 0.3	0.52 ± 0.21	1.94 ± 0.39	—	0.968	0.730	0.350	9/9 ^r
$\Delta\delta_{\text{CO}}, \sigma^+_{\text{R}}$	187.5 ± 0.3	-0.48 ± 0.21	2.45 ± 0.28	—	0.966	0.206	0.363	9/9
$\Delta\nu_{\text{CO}}, \sigma^+_{\text{R}}$	187.5 ± 0.3	0.16 ± 0.04	1.46 ± 0.34	—	0.984	0.889	0.248	9/9
	$\text{C}=\text{}^{17}\text{O}$	Phenyl esters of <i>meta</i> -substituted benzoic acids ^{e,g,h}						

$\Delta \log k_1, \sigma_R$	346.0 ± 0.2	4.22 ± 0.37	–	–	0.974	–	0.521	8/8 ^s
$\Delta \delta_{CO}, \sigma_R$	346.1 ± 0.2	-2.20 ± 0.16	–	–	0.981	–	0.447	8/8 ^t
$\Delta \nu_{CO}, \sigma_R$	346.0 ± 0.9	0.61 ± 0.08	–	–	0.970	–	0.624	5/5 ^u

^a R – correlation coefficient.

^b R_0 – zeroth correlation coefficient.

^c s – standard deviation.

^d n_0 reflects the total number of data involved in the correlation; n – the number of points remaining after exclusion of significantly deviating points.

^eThe values of $\Delta \log k_1 = \log k^X - \log k^H$ for the alkaline hydrolysis in water at 25 °C.^[6]

^fThe $\Delta \log k_2$ values for alkaline hydrolysis in aqueous 50% DMSO at 25 °C.^[51,52]

^gThe $\Delta \delta_{CO}$ values from Reference.^[8]

^hThe ν_{CO} values from Reference.^[9]

ⁱThe 2-I and 2-NH₂ derivatives were omitted.

^jThe $\log k = -1.422$ for 2-N(CH₃)₂ derivative was calculated from relation:^[6] $\log k = -0.333 + 2.128\sigma_I + 0.312\sigma_R + 2.699E_s^B$.

^kThe $\Delta \delta_{CO} = 1.1$ for 2-N(CH₃)₂ derivative was calculated using δ_{CO} from Table 1.

^lThe value of ν_{CO} for 2-N(CH₃)₂ derivative is not available.

^mThe $\log k = -0.98$ for 2-SCF₃ derivative and the $\log k = -0.82$ for 2-SO₂CH₃ derivative for alkaline hydrolysis in water were calculated (see Note j).

ⁿThe $\Delta \log k = -0.566$ for 2-SCF₃ derivative and the $\Delta \log k = 1.344$ for 2-CN derivative for alkaline hydrolysis in aqueous 50% DMSO were calculated from relation:^[6] $\Delta \log k = 0.021 + 2.31\sigma_I + 0.777\sigma_R + 2.693E_s^B$.

^oThe $\Delta \delta_{CO} = -0.43$ for 2-SCF₃ derivative and $\Delta \delta_{CO} = 0.58$ for 2-SO₂CH₃ were calculated using δ_{CO} (Table 1).

^pThe ν_{CO} values for 2-SCF₃ and 2-SO₂CH₃ derivatives are not available.

^qThe $\log k = -0.055$ for 4-Br derivative and the $\log k = -0.795$ for 4-C(CH₃)₃ derivative were calculated from relation:^[6] $\log k = -0.451 + 1.72\sigma$.

^rThe $\Delta \log k = -0.464$ for 4-C(CH₃)₃ derivative for alkaline hydrolysis in aqueous 50 % DMSO was calculated from relation:^[6] $\Delta \log k = -0.018 + 2.322\sigma$.

^sThe $\log k = 0.134$ for 3-F derivative, $\log k = 0.615$ for 3-CN derivative, $\log k = -0.313$ for 3-OCH₃ derivative, $\log k = -0.657$ for 3-N(NH₃)₂ derivative in water were calculated (see Note q).

^tThe δ_{CO} values from Table 1 and Reference.^[8]

^uThe ν_{CO} values for 3-F, 3-CN and 3-OCH₃ derivatives are not available.