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Effect of *ortho* substituents on carbonyl carbon ^{13}C NMR chemical shifts in substituted phenyl benzoates

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^{13}C NMR spectra of 37 *ortho*-, *meta*- and *para*-substituted phenyl benzoates, containing substituents in benzoyl and phenyl moiety, 4 *ortho*-substituted methyl and 5 ethyl benzoates, as well as 9 R-substituted alkyl benzoates have been recorded. The influence of the *ortho* substituents on the carbonyl carbon ^{13}C NMR chemical shift, δ_{CO} , was found to be described by a linear multiple regression equation containing the inductive, σ_{I} , resonance, σ_{R} , and steric, E_{s}^{B} , or ν substituent constants. For all the *ortho*-substituted esters containing substituents in acyl part as well as phenyl part the substituent-induced reverse inductive effect ($\rho_{\text{I}} < 0$), the normal resonance effect ($\rho_{\text{R}} > 0$), and the negative steric effect ($\delta_{\text{ortho}} < 0$) with the E_{s}^{B} were observed. In the case of *ortho* substituents in phenyl part the resonance effect was negligible. Due to inductive effect the *ortho* electron-withdrawing substituents showed upfield shift or shielding of the carbonyl carbon, while the electron-donating substituents had an opposite effect. Because of the sterical consequences *ortho* substituents revealed deshielding effect on the ^{13}C NMR chemical shift of the carbonyl carbon. For all the *meta*- and *para*-substituted esters the reverse substituent-induced inductive and resonance effects ($\rho_{\text{I}} < 0$, $\rho_{\text{R}} < 0$) were found to be significant. In alkyl benzoates the alkyl substituents showed the reverse inductive and steric effects. The $\log k$ values for the alkaline hydrolysis in water, aqueous 0.5 M Bu_4NBr and 2.25 M Bu_4NBr and the IR frequencies, ν_{CO} , for *ortho*-, *meta*- and *para*-substituted phenyl benzoates and alkyl benzoates were correlated nicely with the corresponding ^{13}C NMR substituent chemical shifts, $\Delta\delta_{\text{CO}}$.

Keywords: NMR spectra of benzoates; carbonyl carbon NMR chemical shifts; phenyl benzoates; substituent effects; *ortho* effect.

INTRODUCTION

Earlier the influence of substituent effects, especially *ortho* effect, on the rates of the alkaline hydrolysis (see Refs [1-6] and references cited therein) and on the infrared stretching frequencies of carbonyl group, ν_{CO} ,^[7,8] for esters of benzoic acid containing substituents in the benzoyl and phenyl (alkyl) moiety was studied.

It was interesting to study the influence of substituent effects, mainly *ortho* effect, on the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , in substituted phenyl benzoates and to compare with those in the rates of the alkaline hydrolysis as well as in the infrared stretching frequencies of carbonyl group, ν_{CO} , in the case of the corresponding substituted phenyl benzoates.

The main purpose of the present work was to check how in the case of *ortho* substituents the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , of substituted phenyl benzoates containing substituents in benzoyl and phenyl moiety ($\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$) are influenced by the inductive, resonance and the steric effects. To

compare the influence of *meta* and *para* substituents as well as alkyl substituents on the ^{13}C NMR chemical shift of the carbonyl carbon in substituted phenyl and alkyl benzoates were analyzed as well.

To our knowledge, the influence of *ortho* substituents on the ^{13}C NMR chemical shift of the carbonyl carbon in substituted phenyl benzoates using correlation equations, has not been studied in the literature. More thoroughly the influence of the substituent effects on the carbonyl carbon ^{13}C NMR chemical shifts in substituted phenyl, methyl and ethyl benzoates and phenyl acetates was investigated for *meta* and *para* derivatives.^[9-22] In the case of *meta*- and *para*-substituted esters mainly the substituent-induced reverse inductive and resonance effects were observed ($\rho_I < 0$, $\rho_R < 0$).^[9,11,16,18,19,37] The electron-withdrawing substituents showed shielding leading to a smaller positive charge on the carbonyl carbon. The electron-donating substituents had an opposite effect. In carbonyl compounds the influence of the substituent-induced resonance effect on the carbonyl carbon ^{13}C NMR chemical shift ($\rho_R < 0$, $\rho_R > 0$) was found to be dependent on the polarization of the π -electron system in the carbonyl $\text{C}=\text{O}$ bond.^[9,11,19]

The influence of the *ortho* effect on the ^{13}C NMR chemical shift of the side-chain functional group was studied for substituted methyl benzoates,^[17,20,21] ethyl benzoates,^[26] benzoic acids,^[21,23-25] thiocyanatobenzenes,^[27] arylacetamides,^[28-30] acetonitriles,^[31] acetophenones and benzaldehydes,^[32-36]. Guy^[27] obtained the excellent correlations for the ^{13}C NMR chemical shift in *ortho*-substituted thiocyanatobenzenes with the inductive, resonance and the steric substituent parameters. The influence of substituents in alkyl chain on the carbonyl carbon ^{13}C NMR chemical shift was studied mainly the in case of esters containing substituents in the acyl part.^[37-39]

Earlier (see Refs [1-6]) we found the $\log k$ values for the alkaline hydrolysis of phenyl esters of *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, and substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, to be correlated with the Charton equation using the Taft inductive (σ_I) and resonance (σ_R°) constants and the steric scale for *ortho* substituents, E_s^B . In the alkaline hydrolysis of substituted benzoates in pure water, the *ortho* inductive effect and the *meta* and *para* polar effect in acyl part were 1.5-fold and steric influence 2.7-fold higher than the corresponding influences in the aryl part of phenyl benzoates. In the alkaline hydrolysis of phenyl esters of *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, in water the resonance term was negligible ($(\rho_R^\circ)_{\text{ortho}}$ ca 0.3). In the case of phenyl esters of *ortho*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, the infrared stretching frequencies of the carbonyl group, ν_{CO} , for the *cis* and *trans* conformers of *ortho* derivatives appeared to be correlated with dual parameter equations: $(\nu_{\text{CO}})_{\text{cis}} = (\nu_{\text{CO}})_o + 16.4\sigma_I - 22.6E_s^B$ and $(\nu_{\text{CO}})_{\text{trans}} = (\nu_{\text{CO}})_o + 12.6\sigma_p^+ - 11.9E_s^B$.^[7] Recently we found^[8] a 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} , when the additional resonance and steric scales were included.

To study the influence of substituent effects on the carbonyl carbon ^{13}C NMR chemical shifts the values of the chemical shifts, δ_{CO} , for *ortho*-, *meta*- and *para*-substituted phenyl benzoates, $(\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5)$, methyl and ethyl benzoates $(\text{X-C}_6\text{H}_4\text{CO}_2\text{CH}_3, \text{X-C}_6\text{H}_4\text{CO}_2\text{C}_2\text{H}_5)$, phenyl acetates $(\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{-X})$ and alkyl benzoates $(\text{C}_6\text{H}_5\text{CO}_2\text{R})$ were submitted to correlation analysis involving the scales for the corresponding inductive, resonance, and steric factors.

The second purpose of the present work was to compare the substituent effects on the carbonyl carbon ^{13}C NMR chemical shift, δ_{CO} , in substituted phenyl benzoates with those in the rates of the alkaline hydrolysis and the infrared stretching frequencies of carbonyl group, ν_{CO} . For that purpose the $\log k$ values for the alkaline hydrolysis of *ortho*-, *meta*- and *para*-substituted phenyl benzoates and alkyl benzoates in water, aqueous 0.5 M Bu_4NBr and 2.25 M Bu_4NBr as well as the IR frequencies, ν_{CO} , were correlated with the corresponding carbonyl carbon ^{13}C NMR chemical shift, δ_{CO} .

In the present work the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , values for 55 *ortho*-, *meta*- and *para*-substituted phenyl benzoates, ($\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$), methyl and ethyl benzoates ($\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_2\text{H}_5$) and alkyl benzoates ($\text{C}_6\text{H}_5\text{CO}_2\text{R}$) were recorded.

EXPERIMENTAL

NMR measurements

The standard ^1H and proton-decoupled ^{13}C NMR spectra were recorded using a Bruker Avance II 200 spectrometer at 4.7T magnetic field at the corresponding resonance frequencies for ^1H 200.13 MHz and for ^{13}C 50.33 MHz. For the samples a Sigma-Aldrich 99.8 atom % deuterated NMR solvent CDCl_3 containing 1 % of TMS as internal reference was used. Samples were prepared at a concentration of 0.1 M solute. Both chemical shifts (^1H and ^{13}C) were referenced to internal TMS. The spin-spin coupling constants (J values) are given in Hz. ^{13}C NMR spectra of 55 *ortho*-, *meta*- and *para*-substituted phenyl benzoates, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$ ($\text{X} = \text{H}$, 2- NO_2 , 2-CN, 2-F, 2-OCH $_3$, 2-NH $_2$, 4- NO_2 , 4-F, 4-Cl, 4-Br, 4-CH $_3$, 4-OCH $_3$, 4-NH $_2$, 3- NO_2 , 3-Cl, 3-CH $_3$), $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$ ($\text{X} = 2\text{-NO}_2$, 2-CN, 2-F, 2-Cl, 2-I, 2-CF $_3$, 2-CH $_3$, 2-C(CH $_3$) $_3$, 2-OCH $_3$, 2-N(CH $_3$) $_2$, 2-CO $_2$ CH $_3$, 4- NO_2 , 4-CN, 4-F, 4-Cl, 4-CH $_3$, 4-OCH $_3$, 3- NO_2 , 3-Cl, 3-CH $_3$, 3-NH $_2$), alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$ ($\text{R} = \text{CH}_3$, $\text{CH}_2\text{C}_6\text{H}_5$, $\text{CH}_2\text{CH}_2\text{OCH}_3$, $\text{CH}_2\text{CH}_2\text{Cl}$, $\text{CH}_2\text{C}\equiv\text{CH}$, CH_2CF_3 , CH_2CHCl_2 , CH_2CCl_3 , CH_2Cl , CH_2CN), methyl benzoates, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$ ($\text{X} = \text{H}$, 2-Cl, 2-Br, 2-I), and ethyl benzoates, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_2\text{H}_5$, ($\text{X} = \text{H}$, 2- NO_2 , 2-CN, 2-Cl, 2-CF $_3$) were recorded (see Table S1). Carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , for phenyl esters of *ortho*-, *meta*- and *para*-substituted benzoic acids, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, *ortho*-, *meta*- and *para*-substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, substituted alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, methyl and ethyl esters of substituted benzoic acids ($\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_2\text{H}_5$) are given in Tables 1-3.

Synthesis of compounds

The preparation procedure and characteristics of *ortho*-, *meta*- and *para*-substituted phenyl benzoates ($\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$) and alkyl benzoates ($\text{C}_6\text{H}_5\text{CO}_2\text{R}$) have been described.^[4, 40-42] Methyl 2-chlorobenzoate, methyl 2-bromobenzoate and methyl 2-iodobenzoate were obtained commercially (Aldrich). Benzyl benzoate used is the Sigma product and ethyl 2-(trifluoromethyl)benzoate is ABCR GmbH & Co reagent. Cyanomethyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CN}$, was prepared from benzoic acid and chloroacetonitrile in the presence of triethylamine.^[43, 44] The yield was 28.8 %, b.p. 163-165 °C/15 mm Hg (lit.^[43] 152-154 °C/11 mm Hg). IR $\nu_{\text{CO}} = 1731.8$ in DMSO. The 2,2,2-trifluoroethyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CF}_3$, was obtained by

treatment of 2,2,2-trifluoroethanol with benzoyl chloride in pyridine. The yield was 38.4 %, b.p. 107-109 °C/27 mm Hg (lit.^[45] 84-86 °C/19 mm Hg, lit.^[46] 50-52 °C/4 mm Hg). IR ν_{CO} = 1734.8 in DMSO. The 2,2,2-trichloroethyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CCl}_3$, and 2,2-dichloroethyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CHCl}_2$, were synthesized by treatment of 2,2,2-trichloroethanol or 2,2-dichloroethanol with benzoyl chloride in pyridine as described in synthesis of 2,2,2-trifluoroethyl benzoate. 2,2,2-trichloroethyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CCl}_3$; yield 84.0 %. IR ν_{CO} = 1732.3 in DMSO. 2,2-dichloroethyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CHCl}_2$; yield 36.5 %, b.p. 185 °C/27 mm Hg. IR ν_{CO} = 1726.5 in DMSO. The 2- CO_2CH_3 -phenyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$, was prepared from methyl salicylate and benzoyl chloride in pyridine at 0 °C with stirring. A white solid was obtained by recrystallisation from ethanol. M.p. 92 °C (lit.^[47] 92 °C). Ethyl 2-nitrobenzoate, 2- $\text{NO}_2\text{-C}_6\text{H}_4\text{CO}_2\text{CH}_2\text{CH}_3$, was synthesized as previously described.^[48] Yield 47.4 %, b.p. 179-180 °C/25 mm Hg (lit.^[48] 178-179 °C/23 mm Hg). Ethyl 2-chlorobenzoate, 2- $\text{Cl-C}_6\text{H}_4\text{CO}_2\text{CH}_2\text{CH}_3$, was prepared as previously described,^[48] b.p. 143-148 °C/25 mm Hg (lit.^[49] 122-125 °C/15 mm Hg). Ethyl 2-cyanobenzoate, 2- $\text{CN-C}_6\text{H}_4\text{CO}_2\text{CH}_2\text{CH}_3$, was synthesized from phthalic acid monoamide and ethanol in pyridine in the presence of *p*-toluenesulfonyl chloride.^[50] A white crystalline solid was purified by recrystallisation from benzene-pentane: m.p. 62-65 °C (lit.^[50] 64.5-66 °C, lit.^[51] 62-65 °C).

DATA PROCESSING AND RESULTS

For the study of the influence of substituent effects on the carbonyl carbon ^{13}C NMR chemical shift, δ_{CO} , in phenyl esters of substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, and for alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, the corresponding δ_{CO} values measured in the present work (Tables 1-3) were correlated with the following Eqns (1)-(3):

$$(\delta_{\text{CO}})_{\text{m,p}} = (\delta_{\text{CO}})_{\text{H}} + (\rho_{\text{I}})_{\text{m,p}}\sigma_{\text{I}} + (\rho_{\text{R}})_{\text{m,p}}\sigma_{\text{R}} \quad (1)$$

$$(\delta_{\text{CO}})_{\text{ortho}} = (\delta_{\text{CO}})_{\text{H}} + (\rho_{\text{I}})_{\text{ortho}}\sigma_{\text{I}} + (\rho_{\text{R}})_{\text{ortho}}\sigma_{\text{R}} + \delta_{\text{ortho}}E_{\text{s}}^{\text{B}} \quad (2)$$

$$(\delta_{\text{CO}})_{\text{Alk}} = (\delta_{\text{CO}})_{\text{H}} + (\rho_{\text{I}})_{\text{Alk}}\sigma_{\text{I}} + \delta_{\text{Alk}}E_{\text{s}}^{\text{B}} \quad (3)$$

The data treatment of the δ_{CO} values with Eqn (1) was performed separately for *meta* and *para* derivatives. In the data processing the Taft inductive σ_{I} ^[52], resonance σ_{R} constants^[53] [$\sigma_{\text{R}} = (\sigma^{\circ})_{\text{p}} - \sigma_{\text{I}}$] and the steric constants, E_{s}^{B} , for *ortho* substituents determined using the kinetic data for the acid hydrolysis of *ortho*-substituted phenyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$,^[54] were employed. For comparison, the Charton steric scale of ν ,^[55] calculated on the basis of van der Waals radii, r_{v} , was used as well (see Table S2). The steric constants, E_{s}^{B} , were found to be nearly linear function of the ν values in the case of monoatomic substituents $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$ and $\text{X} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3, \text{CF}_3$.^[4] The polyatomic substituents ($\text{NO}_2, \text{NH}_2, \text{N}(\text{CH}_3)_2, \text{CN}, \text{OCH}_3$) deviated from this linearity. Therefore in correlations for polyatomic *ortho* substituents the value of ν for the isosteric substituents were used.^[4] For the variable alkyl substituent in the alcohol component of esters, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, (Eqn (3)) the steric

substituent constants, E_s^B , and the Charton steric scale of ν for alkyl substituents R were used (Table S4). The steric substituent constants, E_s^B , were calculated as follows: $E_s^B = (\log k_{H^+}^R - \log k_{H^+}^{CH_3})$, where $k_{H^+}^R$ and $k_{H^+}^{CH_3}$ are the rate constants for acid hydrolysis of R-substituted alkyl benzoate, $C_6H_5CO_2R$, in water.^[56] To estimate the values of the steric substituent constants, E_s^B , for $R = CH_2CF_3$, CH_2CCl_3 , CH_2CHCl_2 and *ortho*- CO_2CH_3 (Tables S4 and S2), the corresponding second-order rate constants k ($dm^3 mol^{-1} s^{-1}$) for alkaline hydrolysis of esters of benzoic acid ($C_6H_5CO_2R$, $C_6H_5CO_2C_6H_4-X$ where $X = 2-CO_2CH_3$) in aqueous 0.5 M Bu_4NBr at 25 °C were measured in the present work (Table S5).

The results of correlations of the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , for phenyl esters of substituted benzoic acids, $X-C_6H_4CO_2C_6H_5$, substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4-X$, and for alkyl benzoates, $C_6H_5CO_2R$, (Tables 1-3) with Eqns (1)-(3) are listed in Table 4. For comparison, the correlations of the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , for *ortho*-, *meta*- and *para*-substituted ethyl benzoates, methyl benzoates and phenyl acetates based mainly on the δ_{CO} values published in literature (Table 3 and Table S3) with Eqns (1) and (2) are shown in Tables 4 as well. The values of δ_{CO} for non-substituted derivatives, $(\delta_{CO})_H$, used in correlations were calculated as arithmetic mean values when the $(\delta_{CO})_H$ values in Tables 1, 3 and S3 were involved. The values of the substituent constants σ_I and E_s^B for alkyl substituents R used to correlate the data for alkyl benzoates, $C_6H_5CO_2R$, are given in Table S4.

To compare of the substituent effects in alkaline hydrolysis and in the infrared stretching frequencies of carbonyl group, $(\nu_{CO})_X$, with those in the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , in substituted phenyl benzoates, $X-C_6H_4CO_2C_6H_5$, $C_6H_5CO_2C_6H_4-X$, and substituted alkyl benzoates, $C_6H_5CO_2R$ the following relationships were used:

$$\log k_{m,p,ortho} = \log k_H + a_{1(m,p,ortho)}(\Delta\delta_{CO})_X + a_{2(m,p,ortho)}\sigma_R + a_{3(ortho)}E_s^B \quad (4)$$

$$(\nu_{CO})_{m,p,ortho} = (\nu_{CO})_H + a_{1(m,p,ortho)}(\Delta\delta_{CO})_X + a_{2(m,p,ortho)}\sigma_R + a_{3(ortho)}E_s^B \quad (5)$$

$$\log k_{Alk}((\nu_{CO})_{Alk}) = \log k_{CH_3}((\nu_{CO})_{CH_3}) + a_{1(Alk)}(\Delta\delta_{CO})_{Alk} + a_{3(Alk)}E_s^B \quad (6)$$

where $(\Delta\delta_{CO})_X = (\delta_{CO})_X - (\delta_{CO})_H$ and $(\Delta\delta_{CO})_{Alk} = (\delta_{CO})_R - (\delta_{CO})_{CH_3}$

In correlations using Eqns (4) and (6), the $\log k$ values for alkaline hydrolysis of phenyl esters of substituted benzoic acids, $X-C_6H_4CO_2C_6H_5$, substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4-X$, and substituted alkyl benzoates in water, 0.5 M Bu_4NBr and 2.25 M Bu_4NBr at 25 °C have been reported previously.^[1-5,8,40,56,57] The IR stretching frequencies of the carbonyl group, ν_{CO} , used in correlations with Eqns (5) and (6) were reported earlier.^[7] 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 (4)-(6) are listed in Table 5. For the data processing a multiple-parameter linear least-squares (LLSQ) procedure^[58] was used.

DISCUSSION

The carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , for phenyl esters of *meta*-, *para*- and *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 good correlations with Eqns (1) and (2) (Table 4):

$$(\delta_{\text{CO}})_{\text{m}} = (165.11 \pm 0.10) - (2.91 \pm 0.22)_{\text{m}}\sigma_{\text{I}} - (1.64 \pm 0.22)_{\text{m}}\sigma_{\text{R}} \quad (7)$$

$$R = 0.992, s = 0.126, n/n_0 = 6/6$$

$$(\delta_{\text{CO}})_{\text{p}} = (165.00 \pm 0.10) - (2.18 \pm 0.20)_{\text{p}}\sigma_{\text{I}} - (1.00 \pm 0.26)_{\text{p}}\sigma_{\text{R}} \quad (8)$$

$$R = 0.972, s = 0.154, n/n_0 = 9/9$$

$$(\delta_{\text{CO}})_{\text{ortho}} = (165.32 \pm 0.22) - (5.08 \pm 0.37)_{\text{ortho}}\sigma_{\text{I}} + (1.58 \pm 0.42)_{\text{ortho}}\sigma_{\text{R}} - (4.33 \pm 0.51)_{\text{ortho}}E_{\text{s}}^{\text{B}} \quad (9)$$

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

The calculated sensitivities of chemical shifts, δ_{CO} , for *meta*, *para* and *ortho* derivatives towards the substituents inductive effect, $(\rho_{\text{I}})_{\text{m}}$, $(\rho_{\text{I}})_{\text{p}}$, $(\rho_{\text{I}})_{\text{ortho}}$, resonance $(\rho_{\text{R}})_{\text{m}}$, $(\rho_{\text{R}})_{\text{p}}$, $(\rho_{\text{R}})_{\text{ortho}}$, and the steric effect, δ_{ortho} , (Table 4) were approximately the same in case of the δ_{CO} values determined in the present work (Tables 1 and 2) only were included or the δ_{CO} values available in literature (Table S3) were involved in correlations as well. The data treatment with Eqn (2) gave nearly the identical results using two steric scales for *ortho* substituents: E_{s}^{B} and the modified Charton ν constants (Table 4). The sensitivities of the chemical shifts, δ_{CO} , towards the inductive effect, $(\rho_{\text{I}})_{\text{m}}$, $(\rho_{\text{I}})_{\text{p}}$, $(\rho_{\text{I}})_{\text{ortho}}$, resonance $(\rho_{\text{R}})_{\text{m}}$, $(\rho_{\text{R}})_{\text{p}}$, $(\rho_{\text{R}})_{\text{ortho}}$, and the steric effect δ_{ortho} , in methyl and ethyl esters of substituted benzoic acids shown in Table 4 are nearly the same as represented by Eqns (7)-(9) for phenyl esters of *meta*-, *para*- and *ortho*-substituted benzoic acids. The contribution of the inductive effect from *para* position to the chemical shifts, δ_{CO} , in phenyl esters of substituted benzoic acids found in the present work, $(\rho_{\text{I}})_{\text{p}} = -2.18$, is slightly weaker as that in Ref. [9] ($(\rho_{\text{F}})_{\text{p}} = -2.50$). In methyl esters of *meta*- and *para*-substituted benzoic acids the susceptibilities of the chemical shifts, δ_{CO} , towards the inductive effect $(\rho_{\text{I}})_{\text{m}} = -3.11$, $(\rho_{\text{I}})_{\text{p}} = -2.41$, and resonance, $(\rho_{\text{R}})_{\text{m}} = -1.10$, $(\rho_{\text{R}})_{\text{p}} = -1.04$, estimated in the present paper (Table 4) agree well with those reported in Ref. [18] (in Ref. [18] $(\rho_{\text{I}})_{\text{m}} = -3.33$, $(\rho_{\text{R}})_{\text{m}} = -1.06$, $(\rho_{\text{I}})_{\text{p}} = -2.43$, and $(\rho_{\text{R}})_{\text{p}} = -1.12$).

It follows from Table 4 that in substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, containing substituents in phenyl moiety the influence of *meta*, *para* and *ortho* substituent effects to the carbonyl carbon chemical shifts, δ_{CO} , could be expressed by Eqns (10)-(12):

$$(\delta_{\text{CO}})_{\text{m}} = (165.13 \pm 0.03) - (0.95 \pm 0.07)_{\text{m}}\sigma_{\text{I}} - (0.22 \pm 0.08)_{\text{m}}\sigma_{\text{R}} \quad (10)$$

$$R = 0.988, s = 0.046, n/n_0 = 7/7$$

$$(\delta_{\text{CO}})_{\text{p}} = (165.16 \pm 0.02) - (1.10 \pm 0.04)_{\text{p}}\sigma_{\text{I}} - (1.48 \pm 0.06)_{\text{p}}\sigma_{\text{R}} \quad (11)$$

$$R = 0.994, s = 0.053, n/n_0 = 25/26$$

$$(\delta_{\text{CO}})_{\text{ortho}} = (164.90 \pm 0.07) - (1.56 \pm 0.13)_{\text{ortho}}\sigma_{\text{I}} + (0.33 \pm 0.14)_{\text{ortho}}\sigma_{\text{R}} - (0.72 \pm 0.11)_{\text{ortho}}E_{\text{s}}^{\text{B}} \quad (12)$$

$$R = 0.978, s = 0.103, n/n_0 = 12/13$$

In *meta*- and *para*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4-X$, (Eqns (10)-(12)) and acetic acid, $CH_3CO_2C_6H_4-X$, containing substituents in phenyl moiety, the estimated susceptibilities towards the inductive effect from *meta* and *para* position are approximately equal to each other ($(\rho_I)_m \approx (\rho_I)_p$). The corresponding calculated $(\rho_I)_m$ and $(\rho_I)_p$ values are -0.95 , -1.16 and -1.10 , -1.27 , respectively (Table 4). At the same time in substituted phenyl esters of benzoic acid and acetic acids the contribution of the resonance effect from *para* position to the carbonyl carbon chemical shifts, δ_{CO} , surpasses that from *meta* position essentially ($(\rho_R)_m \ll (\rho_R)_p$).

The determined carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , in Table 1 show that electron-withdrawing substituents in *meta* and *para* position both in the benzoyl and phenyl part of an ester cause an upfield shift of the carbonyl carbon resonance indicating increased shielding at the $C=O$ carbon. The electron-donating substituents have an opposite effect showing the downfield shift and deshielding of the carbonyl carbon as compared to the carbonyl carbon in the unsubstituted ester. The negative values of ρ_I and ρ_R for all the examined *meta*- and *para*-substituted series prove a reverse substituent effect that operates through the polar and the resonance pathways of the electronic effects of substituents. The reverse polar effect has often been explained on the basis of the through-space polarization of the π -system induced by the substituent dipole^[9,11,16,19] (localized polarization). Due to π -polarization the electron-withdrawing substituents shifts the π -electrons in $C=O$ group towards the carbonyl carbon making the carbonyl group less polar with increase in the strength of the $C=O$ bond as compared to unsubstituted derivative. Lately the influence of the substituent-induced inductive and resonance effects on the carbonyl carbon ^{13}C NMR chemical shifts in esters^[9,16,37] was explained in terms of the contribution of different resonance structures.^[9,16,37] The electron-withdrawing substituents were found to destabilize the resonance structure $R_1(C^{\delta+}-O^{\delta-})OR_2$ to a greater extent. This increases the importance of the less polar structure $R_1(C=O)OR_2$ with an increased shielding of the carbonyl carbon (the upfield ^{13}C NMR chemical shifts).^[9,16,37]

The contribution of the inductive effect from the *meta* position to the carbonyl carbon chemical shifts, δ_{CO} , surpasses that from *para* position in phenyl esters as well as in methyl and ethyl esters of substituted benzoic acids i.e. $(\rho_I)_m > (\rho_I)_p$. This could be interpreted in terms of a shorter distance between the substituent and the carbonyl carbon.

Unexpectedly, it appeared (Table 4) that there is no difference between contributions of resonance effects from *meta* and *para* position to the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , in phenyl, methyl and ethyl esters of substituted benzoic acids. The corresponding $(\rho_R)_m$ and $(\rho_R)_p$ values are -1.64 , -1.10 , -1.23 and -1.00 , -1.04 , -1.23 , respectively (Table 4). Contrary to expectation, in substituted phenyl benzoates the resonance contribution of *para* substituents to chemical shifts, δ_{CO} , from phenyl side was found to be stronger (1.4 times) compared to that from the benzoyl side. It was suggested,^[9,11] that the resonance effect in the case of *para* substituents in benzoyl part could consist of the two competitive resonance types. The normal direct resonance effect between the substituent and the carbonyl group which $\rho_R > 0$ and the substituent-induced reverse resonance effect explained as the resonance induced polar effect ($\rho_R < 0$).^[9,11,16,19] In the case of *para* substituents in the benzoyl part the contribution of the normal direct resonance makes the summary resonance, ρ_R , less negative as the ρ_R values for the resonance induced polar effect (reverse resonance effect).

In the alkyl part of esters, $C_6H_5CO_2R$, the substituent-induced effect on the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , was found to be described by the reverse inductive and steric effects as shown by Eqn (13)(Table 4):

$$(\delta_{CO})_{Alk} = (166.62 \pm 0.21) - (4.59 \pm 0.42)_{Alk}\sigma_I - (1.39 \pm 0.56)\delta_{Alk}E_s^B \quad (13)$$

$R = 0.966$, $s = 0.188$, $n/n_0 = 15/15$

We obtained nearly the same results as shown by Eqn (13) (Table 4) when to correlate data for alkyl substituted benzoates, $C_6H_5CO_2R$, with Eqn (3) the Charton steric ν constants for alkyl substituent R (Table S4) were used.

Effects induced by *ortho* substituents

We found the influence of *ortho* substituents to the carbonyl carbon chemical shifts, δ_{CO} , in phenyl, methyl and ethyl benzoates containing *ortho* substituents in benzoyl moiety as well as in phenyl benzoates and phenyl acetates with *ortho* substituents in phenyl ring (Eqns (9) and (12), Table 4) to be described by the reverse inductive effect ($(\rho_I)_{ortho} < 0$), the normal resonance effect ($(\rho_R)_{ortho} > 0$) and the steric effect with the negative sign of the transmission coefficient (the values of E_s^B are negative). 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. Thus in the *ortho*-substituted esters the carbonyl carbon is shielded by the $-I$ and $+R$ substituent effects and deshielded by the $+I$ and $-R$ effects as well as by steric effects of *ortho* substituents.

In the case of substituents in the benzoyl moiety the estimated susceptibilities towards the inductive effect from the *ortho* position, were in range $-5.00 < (\rho_I)_{ortho} < -5.48$ (Table 4). Approximately the same value for $(\rho_I)_{ortho}$ was found for *ortho*-substituted benzoic acids ($(\rho_I)_{ortho} = 5.08^{[26]}$). The influence of the *ortho* inductive effect was found to be approximately 1.7 times higher than the corresponding influences from the *meta* position in both esters containing substituents in the benzoyl moiety and in the phenyl part. The ratio $(\rho_I)_{ortho}/(\rho_I)_{meta}$ was ca. 2.0 in the case of infrared stretching frequencies, ν_{CO} ,^[7] and $(\rho_I)_{ortho}/(\rho_I)_{meta} \approx 1.5$ for the alkaline hydrolysis of substituted phenyl benzoates in water for both series containing the substituents in benzoyl and in the phenyl component of benzoates.^[4] In the case of *ortho* and *meta* substituents in the benzoyl moiety, the inductive influence to the carbonyl carbon chemical shifts, δ_{CO} , surpasses by a factor of three the corresponding influence when in the phenyl ring (Table 4). The inductive effect of *para* substituents from the benzoyl side is ca. twice (2.1 times) as strong as that from the phenyl side. This is in accordance with the generally accepted views that in the substituted benzoyl derivatives the inductive effect is increased due to shorter distance between the substituent and carbonyl carbon atom relative to when the substituents are in the phenyl side.

Results of correlations in Eqns (9) and (12), and Table 4 show that due to the steric requirements of *ortho* substituents the chemical shift of the carbonyl carbon, δ_{CO} , increases (downfield shift) and the carbonyl carbon is deshielded more as compared to unsubstituted derivative. It could be considered that due to the bulky *ortho* substituents the π -electron density around the CO carbon 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^[27,34]).

In the case of phenyl, methyl and ethyl esters of *ortho*-substituted benzoic acids we found that *ortho* substituents exert the normal substituent-induced resonance effect ($\rho_R > 0$) on the carbonyl carbon ^{13}C NMR chemical shifts, which is different from that for *meta*- and *para*-substituted esters ($\rho_R < 0$) (Table 4). In the case of *ortho* substituents in the phenyl part, the resonance effect was negligible. Earlier,^[4,7] on the bases of the kinetic data for the alkaline hydrolysis, the IR stretching frequencies, ν_{CO} , and calculations with the Density Functional Theory (DFT) method we found that in phenyl esters of *ortho*-substituted benzoic acids the resonance between carbonyl group and the *ortho*-substituted phenyl ring is inhibited by the bulky *ortho* substituents. Therefore we suggest that the effect of the direct conjugation between the carbonyl group, where $\rho_R > 0$ in the esters considered, is suppressed and the observed substituent-induced positive resonance effect in *ortho*-substituted esters is caused by the normal conjugation between the *ortho* substituent and phenyl ring. Due to the reduced resonance effect between the phenyl ring and the carbonyl group, the resonance stabilization within the carbonyl group is increased. This is associated with an increase in the electron density at the carbon atom where the measurement is made. It was shown that for compounds with a less polarized carbonyl bond the normal substituent-induced resonance effect is favored (similar to acetophenones).^[11,19]

Correlation of the rates of the alkaline hydrolysis and IR carbonyl stretching frequencies, ν_{CO} , with the carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{\text{CO}}$

The rates of the alkaline hydrolysis for the phenyl esters of *ortho*- *meta* -and *para*-substituted benzoic acids, $\text{X}-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, *ortho*-, *meta* -and *para*-substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, and substituted alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, in water, 0.5 M Bu_4NBr and 2.25 M Bu_4NBr aqueous solutions as well as the IR carbonyl stretching frequencies, ν_{CO} , with Eqns (4)-(6) showed a good correlation with the corresponding carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{\text{CO}}$ ($0.960 < R < 0.999$, Table 5). The correlation equations obtained in Table 5 enable one to predict the reaction rates for the alkaline hydrolysis and the IR stretching frequencies using the carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{\text{CO}}$, for the esters considered.

The log k values of alkaline hydrolysis and the IR stretching frequencies were correlated well with the corresponding chemical shifts, $\Delta\delta_{\text{CO}}$, and in the case for *meta*- and *para*-substituted derivatives with the additional resonance term and for *ortho* derivatives with the additional resonance and steric terms. In the case of alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, the log k values gave a good correlation with the $(\Delta\delta_{\text{CO}})_{\text{Alk}}$ values when an additional steric term for alkyl substituents was included. The slope a_1 in Eqn (4) for *ortho*, *meta* and *para* derivatives as well as for alkyl derivatives in Eqn (6) represents the ratio of the inductive effects in alkaline hydrolysis and in the corresponding chemical shifts, $\Delta\delta_{\text{CO}}$. Similarly, the slope a_1 in Eqn (5) for *ortho*, *meta* and *para* derivatives as well as for alkyl derivatives in Eqn (6) represents the ratio of the inductive effects in the IR carbonyl stretching frequencies, ν_{CO} , and in the corresponding carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{\text{CO}}$.

The log k values of the alkaline hydrolysis for the phenyl esters of *ortho*-substituted benzoic acids in water were correlated with the corresponding substituent chemical shifts, $\Delta\delta_{\text{CO}}$, as follows (Table 5):

$$\log k_{\text{ortho}} = (-0.334 \pm 0.163) - (0.457 \pm 0.056)\Delta\delta_{\text{CO}} + (0.92 \pm 0.32)\sigma_{\text{R}} + (0.99 \pm 0.41)E_{\text{s}}^{\text{B}} \quad (14)$$

$R = 0.960, n = 11$

The correlation between the IR carbonyl stretching frequencies, ν_{CO} , and the corresponding substituent chemical shifts, $\Delta\delta_{\text{CO}}$, for the phenyl esters of *ortho*-substituted benzoic acids is shown by Eqn (15) (Table 5):

$$(\nu_{\text{CO}})_{\text{ortho}} = (1743.5 \pm 1.3) - (2.91 \pm 0.54)\Delta\delta_{\text{CO}} + (8.03 \pm 2.81)\sigma_{\text{R}} - (39.1 \pm 3.4)E_{\text{s}}^{\text{B}} \quad (15)$$

$R = 0.971, n = 10$

The magnitudes of the parameters a_1 , a_2 and a_3 in Table 5 calculated with Eqns (4)-(6) coincide quite well with the following relations: $a_1 = \rho_1(\text{AH})/\rho_1(\text{NMR})$, $a_2 = \rho_{\text{R}}(\text{AH}) - a_1\rho_{\text{R}}(\text{NMR})$, $a_3 = \delta(\text{AH}) - a_1\delta(\text{NMR})$ and $a_1 = \rho_1(\text{IR})/\rho_1(\text{NMR})$, $a_2 = \rho_{\text{R}}(\text{IR}) - a_1\rho_{\text{R}}(\text{NMR})$, $a_3 = \delta(\text{IR}) - a_1\delta(\text{NMR})$ where alkaline hydrolysis is denoted by (AH), the carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{\text{CO}}$, by (NMR) and the infrared stretching frequencies, ν_{CO} , by (IR). Using for the alkaline hydrolysis of the phenyl esters of substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\rho_1(\text{AH})_{\text{ortho}} = 2.13$, $\rho_{\text{R}}(\text{AH})_{\text{ortho}} = 0.31$ and $\delta(\text{AH})_{\text{ortho}} = 2.67$ in water at $25^\circ\text{C}^{[4,8]}$ as well as $\rho_1(\text{NMR})_{\text{ortho}} = -5.0$, $\rho_{\text{R}}(\text{NMR})_{\text{ortho}} = 1.43$ and $\delta(\text{NMR})_{\text{ortho}} = -4.1$ (Table 5) we obtained the values of $a_1 = -0.420$, $a_2 = 0.90$ and $a_3 = 0.82$ which are approximately the same as shown by Eqn (14).

The parameter a_1 in Eqn (4) found for *ortho* derivatives in all media studied (pure water, aqueous 0.5 M and 2.25 M Bu_4NBr) are lower as compared to the parameter a_1 for *para* and *meta* derivatives. Therefore, in the case of *ortho* derivatives, the ratio of the susceptibilities to the inductive effect in the alkaline hydrolysis and in the corresponding carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{\text{CO}}$, is lower compared with the same parameter for *para* and *meta* derivatives (Table 5). At the same time the magnitude of a_1 in Table 5 for *meta* and *para* derivatives was found to vary with media to a greater extent as compared to that for the *ortho* derivatives. When going from water to aqueous 2.25 M Bu_4NBr the increase in the a_1 parameter for the phenyl esters of *meta*- and *para*-substituted benzoic acids was by ca. 0.4 units of a_1 (Table 5). In the same change of the solvent the a_1 value for phenyl esters of *ortho*-substituted benzoic acids become larger ca. 0.15 units only. The variation of the parameter a_1 with the media characterizes the increase in the inductive effects in the alkaline hydrolysis of substituted phenyl esters with decreasing of the electrophilic solvating power of the solvent. Earlier^[3] the *ortho* inductive effect was found to vary with solvent ca. three times less as compared to *meta* and *para* polar effect. When going from water to aqueous 0.5 M and 2.25 M Bu_4NBr the increase in the susceptibility to the *meta* and *para* polar effect, $\rho_{\text{m,p}}$, in the alkaline hydrolysis of the phenyl esters of substituted benzoic acids, was found to be 0.34 and 0.99 units of ρ .^[8] In the same change of solvent the inductive effect of *ortho* substituents, $(\rho_1)_{\text{ortho}}$, grows by 0.07 and 0.43 units of ρ_1 only. The negative value of the parameter a_1 shows that the influence of the inductive

effect of substituents on the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , is opposite to that in the alkaline hydrolysis of esters and in the IR carbonyl stretching frequencies, ν_{CO} . With increasing the σ values of substituent the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , were found to diminish, but both the rates of the alkaline hydrolysis and the IR carbonyl stretching frequencies, ν_{CO} , of esters grow when the electron-withdrawing substituents are involved.

The obtained good correlations of the $\log k$ values for the alkaline hydrolysis and the infrared stretching frequencies, ν_{CO} , with the carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{\text{CO}}$, for substituted phenyl benzoates, prove that the same substituent factors (inductive, resonance, steric) are responsible for the substituent effects so in the alkaline hydrolysis as in the infrared stretching frequencies as well as in the carbonyl carbon ^{13}C NMR chemical shifts.

CONCLUSIONS

The influence of the *ortho* substituents on the carbonyl carbon ^{13}C NMR chemical shift, δ_{CO} , in substituted phenyl benzoates ($\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$), methyl benzoates, ethyl benzoates and phenyl acetates was found to be described by the reverse inductive, the normal resonance and the steric effect leading to negative susceptibility constants (the steric substituent constants, E_s^B , are negative). For *meta* and *para* derivatives the reverse substituent-induced inductive and resonance effects were found to be responsible to influence the carbonyl carbon electron density. Due to the inductive effect the electron-withdrawing *ortho*, *meta*, *para* as well as alkyl substituents increase the electron density at the carbonyl carbon while the electron-donating substituents cause the deshielding. The steric effect of *ortho* substituents and alkyl substituents causes the deshielding of the carbonyl carbon. The bulky *ortho* substituents in benzoyl part of esters were considered to twist the plane of the carbonyl group out of the phenyl ring plane causing inhibition of resonance between the carbonyl group and the phenyl ring. Therefore in the case of the *ortho* derivatives the normal resonance between the *ortho* substituent and the benzene ring could occur. The electron-donating *ortho* substituents increase the electron density at the benzene ring and inductively enhance the electron density at the carbonyl carbon. The $\log k$ of alkaline hydrolysis and the IR carbonyl stretching frequencies, ν_{CO} , for *ortho* derivatives show good correlations with the carbonyl carbon ^{13}C NMR substituent chemical shift, $\Delta\delta_{\text{CO}}$, when the additional resonance and steric terms are included.

Supplementary material

The following tables are available as supplementary material deposited with Wiley Interscience: Table S1: ^{13}C NMR spectra for *ortho*-, *meta*- and *para*-substituted phenyl benzoates ($\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$), methyl benzoates and ethyl benzoates; Table S2: The *ortho*, *meta* and *para* substituent constants used in the correlations; Table S3: Literature values for the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , in CDCl_3 for phenyl X-benzoates, methyl X-benzoates, ethyl X-benzoates, X-phenyl benzoates and X-phenyl acetates used in the correlations; Table S4: Values for the alkyl substituent constants and the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , for alkyl benzoates ($\text{C}_6\text{H}_4\text{CO}_2\text{R}$) in CDCl_3 used in the data analysis. Table S5: The second-order

rate constants k ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for alkaline hydrolysis of esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$, in aqueous 0.5 M Bu_4NBr at 25 °C.

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For Peer Review

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Table 1. The carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} (in ppm), in CDCl_3 for phenyl esters of *ortho*-, *meta*- and *para*-substituted benzoic acids, $\text{X-C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$, and substituted phenyl esters of benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-X}$

Substituent X	X-C ₆ H ₄ CO ₂ C ₆ H ₅			C ₆ H ₅ CO ₂ C ₆ H ₄ -X		
	<i>ortho</i> derivatives	<i>meta</i> derivatives	<i>para</i> derivatives	<i>ortho</i> derivatives	<i>meta</i> derivatives	<i>para</i> derivatives
H	165.04	165.04	165.04	165.04	165.04	165.04
CH ₃	165.76 ^[4]	165.33	165.16	164.76	165.16	165.31
OCH ₃	164.38	–	164.81	164.69	–	165.45
F	162.71	–	164.15	164.18	164.73 ^[7]	165.14
Cl	164.05 ^[4]	163.93	164.25	164.19	164.71	164.86
Br	164.54 ^[4]	–	164.44	–	–	–
I	164.74 ^[4]	–	–	164.03	–	–
NO ₂	164.03	163.05	163.27	164.32	164.53	164.21
CN	162.49	–	–	164.01	164.50 ^[7]	164.58
CF ₃	165.23 ^[4]	–	–	164.52	–	–
NH ₂	166.77	–	165.18	–	165.14	–
N(CH ₃) ₂	–	165.80 ^[7]	–	164.84	–	–
C(CH ₃) ₃	–	–	165.13 ^[7]	165.40	–	–
C(O)OCH ₃	–	–	–	165.34	–	–

Table 2. Carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , (in ppm), in CDCl_3 for alkyl benzoates, $\text{C}_6\text{H}_5\text{CO}_2\text{R}$

No.	R	δ_{CO}
1	CH_3	167.03
2	CH_3CH_2	166.55
3	ClCH_2	164.52
4	NCCH_2	165.00
5	$\text{HC}\equiv\text{CCH}_2$	165.69
6	$\text{C}_6\text{H}_5\text{CH}_2$	166.26
7	ClCH_2CH_2	166.14
8	$\text{CH}_3\text{OCH}_2\text{CH}_2$	166.54
9	F_3CCH_2	165.14
10	Cl_3CCH_2	164.87
11	Cl_2HCCH_2	165.53

Table 3. The carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} (in ppm), in CDCl_3 for methyl and ethyl esters of substituted benzoic acids

X	X- $\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$	X- $\text{C}_6\text{H}_4\text{CO}_2\text{CH}_2\text{CH}_3$
H	167.03	166.55
2- NO_2	—	165.33
2-CN	—	164.11
2-Cl	166.19	165.18
2-Br	166.67	—
2-I	167.0	—
2- CF_3	—	166.94

Table 4. Correlation of the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO} , in CDCl_3 with Eqns (1)-(3). The δ_{CO} values in Tables 1-3 and Table S3 used

Nr.	$\delta_{\text{H(calc)}}$	ρ_{I}	ρ_{R}	δ	R^a	R_0^b	s^c	n/n_0^d
Phenyl esters of <i>ortho</i> -substituted benzoic acids, $^e (\delta_{\text{CO}})_\text{H} = 165.17$								
1	165.32 ± 0.30	-5.00 ± 0.50	1.43 ± 0.57	-4.40 ± 0.70	0.959	0.723	0.347	11/11
2	165.36 ± 0.22	-5.20 ± 0.36	1.54 ± 0.41	2.24 ± 0.24	0.980		0.250	11/11 ^f
3	165.32 ± 0.22	-5.08 ± 0.37	1.58 ± 0.42	-4.33 ± 0.51	0.978	0.742	0.257	11/11 ^g
4	165.38 ± 0.19	-5.25 ± 0.37	1.68 ± 0.36	2.15 ± 0.21	0.984		0.221	11/11 ^f
5	165.35 ± 0.14	-5.02 ± 0.37	1.68 ± 0.24	-4.13 ± 0.33	0.980	0.726	0.217	23/26 ^{h,i}
6	165.38 ± 0.13	-5.25 ± 0.21	1.66 ± 0.21	2.10 ± 0.14	0.985		0.190	24/26 ^{f,h}
Methyl esters of <i>ortho</i> -substituted benzoic acids, $^e (\delta_{\text{CO}})_\text{H} = 167.09$								
7	167.50 ± 0.19	-4.99 ± 0.30	1.23 ± 0.35	-3.91 ± 0.46	0.961	0.807	0.312	23/23
8	167.50 ± 0.18	-5.06 ± 0.28	1.33 ± 0.33	-3.92 ± 0.42	0.969		0.287	22/23 ^j
9	167.52 ± 0.14	-5.19 ± 0.22	1.32 ± 0.25	2.04 ± 0.16	0.981		0.220	23/23 ^f
Ethyl esters of <i>ortho</i> -substituted benzoic acids, $^e (\delta_{\text{CO}})_\text{H} = 166.59$								
10	167.14 ± 0.29	-5.37 ± 0.48	1.18 ± 0.56	-4.05 ± 0.69	0.954	0.812	0.394	14/14
11	167.15 ± 0.27	-5.48 ± 0.45	1.31 ± 0.53	-4.01 ± 0.64	0.963		0.366	13/13 ^k
12	167.17 ± 0.23	-5.45 ± 0.38	1.22 ± 0.44	2.04 ± 0.26	0.971		0.313	14/14 ^f
<i>Ortho</i> -substituted phenyl esters of benzoic acid, $^l (\delta_{\text{CO}})_\text{H} = 165.04$								
13	164.78 ± 0.14	-1.52 ± 0.26	0	-0.91 ± 0.24	0.906	0.758	0.205	12/12
14	164.86 ± 0.09	-1.47 ± 0.16	0	-0.62 ± 0.20	0.959		0.123	10/10 ^m
15	164.86 ± 0.08	-1.47 ± 0.15	0	0.31 ± 0.09	0.960		0.121	10/12 ^{f,n}
16	164.90 ± 0.08	-1.57 ± 0.14	0.37 ± 0.16	-0.83 ± 0.13	0.966	0.761	0.116	12/13 ^{o,p}
17	164.88 ± 0.08	-1.48 ± 0.14	0	0.30 ± 0.08	0.963		0.121	11/13 ^{f,n,o}
<i>Ortho</i> -substituted phenyl esters of acetic acid, $^l (\delta_{\text{CO}})_\text{H} = 169.29$								
18	169.18 ± 0.07	-1.50 ± 0.11	0.47 ± 0.19	-0.65 ± 0.12	0.968	0.812	0.110	14/14
19	169.16 ± 0.07	-1.57 ± 0.13	0	0.23 ± 0.09	0.962		0.117	12/14 ^{f,q}
Phenyl esters of <i>para</i> -substituted benzoic acids, $(\delta_{\text{CO}})_\text{H} = 165.17$								
20	165.00 ± 0.10	-2.18 ± 0.20	-1.00 ± 0.26	–	0.972	0.913	0.154	9/9
21	164.99 ± 0.05	-2.17 ± 0.09	-1.13 ± 0.09	–	0.984	0.893	0.121	35/38 ^r
Methyl esters of <i>para</i> -substituted benzoic acids, $(\delta_{\text{CO}})_\text{H} = 167.09$								
22	166.99 ± 0.06	-2.32 ± 0.13	-1.12 ± 0.12	–	0.968	0.896	0.172	42/42
23	167.00 ± 0.04	-2.41 ± 0.10	-1.04 ± 0.09	–	0.984		0.122	36/42 ^s
Ethyl esters of <i>para</i> -substituted benzoic acids, $(\delta_{\text{CO}})_\text{H} = 166.59$								
24	166.54 ± 0.07	-2.53 ± 0.14	-1.13 ± 0.12	–	0.975	0.884	0.171	33/34 ^t
25	166.48 ± 0.05	-2.50 ± 0.11	-1.24 ± 0.10	–	0.987		0.131	30/34 ^u
<i>Para</i> -substituted phenyl esters of benzoic acid, $(\delta_{\text{CO}})_\text{H} = 165.17$								
26	165.16 ± 0.02	-1.10 ± 0.04	-1.48 ± 0.06	–	0.994	0.780	0.053	25/26 ^v
<i>Para</i> -substituted phenyl esters of acetic acid, $(\delta_{\text{CO}})_\text{H} = 169.43$								
27	169.44 ± 0.04	-1.27 ± 0.08	-1.70 ± 0.09	–	0.991	0.714	0.073	17/19 ^w
Phenyl esters of <i>meta</i> -substituted benzoic acids, $(\delta_{\text{CO}})_\text{H} = 165.17$								
28	165.11 ± 0.10	-2.91 ± 0.22	-1.64 ± 0.22	–	0.992	0.887	0.126	6/6 ^x

Methyl esters of <i>meta</i> -substituted benzoic acids, ($\delta_{\text{CO}}\text{H}$) = 167.09									
29	167.16 ± 0.07	-3.11 ± 0.15	-1.10 ± 0.15	–	0.987	0.920	0.138	21/24 ^y	
30	167.14 ± 0.05	-3.04 ± 0.12	-1.04 ± 0.11	–	0.992		0.106	19/24 ^z	
Ethyl esters of <i>meta</i> -substituted benzoic acids, ($\delta_{\text{CO}}\text{H}$) = 166.59									
31	166.60 ± 0.09	-3.21 ± 0.20	-1.23 ± 0.18	–	0.981	0.931	0.185	19/19	
32	166.58 ± 0.07	-3.19 ± 0.16	-0.97 ± 0.16	–	0.987		0.146	17/19 ^{aa}	
<i>Meta</i> -substituted phenyl esters of benzoic acid, ($\delta_{\text{CO}}\text{H}$) = 165.17									
33	165.13 ± 0.03	-0.95 ± 0.07	-0.22 ± 0.08	–	0.988	0.974	0.046	7/7	
34	165.16 ± 0.03	-0.97 ± 0.05	-0.23 ± 0.07	–	0.986	0.972	0.047	14/14	
<i>Meta</i> -substituted phenyl esters of acetic acid, ($\delta_{\text{CO}}\text{H}$) = 169.43									
35	169.48 ± 0.04	-1.16 ± 0.07	-0.35 ± 0.09	–	0.991	0.969	0.045	8/8 ^{bb}	
Alkyl substituted esters of benzoic acid, ($\delta_{\text{CO}}\text{CH}_3$) = 166.9									
36	166.62 ± 0.21	-4.59 ± 0.42	–	-1.39 ± 0.56	0.966	0.956	0.188	15/15 ^{cc}	
37	166.64 ± 0.22	-4.74 ± 0.43	–	-1.51 ± 0.56	0.971	0.955	0.187	14/14 ^{dd}	
38	166.70 ± 0.19	-4.43 ± 0.41	–	1.74 ± 0.75	0.971	0.956	0.195	12/12 ^{ee}	

^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. ^eFor 2-NH₂ derivative $\sigma^{\text{O}}_{\text{R}} = 0$ and for 2-CH₃ derivative $E_s^{\text{B}} = 0$ and $\sigma^{\text{O}}_{\text{R}} = 0$. ^fCharton's modified steric constants, ν , were used (Table S2). ^gFor 2-Br and 2-I derivatives the δ_{CO} values^[59] were used. ^hThe δ_{CO} values from Tables 1 and S3. The values of δ_{CO} for 2-Br derivative (Table 1), 2-OCH₃ derivative^[59] were excluded. ⁱThe $\delta_{\text{CO}} = 165.1$ (Table S3) for 2-I derivative was excluded. ^jThe 2-Br derivative (Table 3) was excluded at confidence level $t = 0.95$. ^kThe 2-Br derivative was omitted. ^lFor 2-CH₃ derivative $E_s^{\text{B}} = 0$, $\sigma_1 = 0$. The average value of steric constants, $E_s^{\text{B}} = -0.881$, for 2-CO₂CH₃ substituent was used. ^mThe 2-CO₂CH₃ and 2-I derivatives were omitted. ⁿThe 2-CO₂CH₃ and 2-I derivatives were excluded at $t = 0.97$. ^oThe alternative δ_{CO} value (Table S3) for 2-CH₃ derivative was added. ^pThe 2-I derivative was excluded. ^qThe 2-CO₂CH₃ derivative and alternative δ_{CO} value for 2-NO₂ derivative were excluded at $t = 0.95$. ^rThe δ_{CO} values (Tables 1 and S3) were included. The 4-NO₂, 4-F, 4-I derivatives^[59] were excluded at $t = 0.97$. ^sThe 4-NO₂ and 4-N(CH₃)₂ derivatives,^[60] 4-Cl, 4-Br, 4-OCH₃ derivatives,^[61] and 4-I derivative^[18] were excluded at $t = 0.95$. ^tThe $\delta_{\text{CO}} = 166.2$ (Table S3) for 4-C(CH₃)₃ derivative was excluded at $t = 0.99$. ^uThe 4-Cl, 4-COCH₃ and 4-CO₂Et derivatives^[62] were excluded at $t = 0.97$. ^vThe 4-CN derivative (Table 1) was excluded. ^wThe 4-C(CH₃)₃ and 4-CH(CH₃)₂ derivatives (Table S3) were excluded. ^xThe δ_{CO} value for 3-OCH₃ derivative (Table S3) was added. ^yFor 3-Cl derivative $\delta_{\text{CO}} = 165.5$ and 3-I derivative $\delta_{\text{CO}} = 165.43$ (Table S3) were excluded at $t = 0.99$. ^zThe 3-N(CH₃)₂ and 3-Br derivatives^[18] were excluded at $t = 0.97$. ^{aa}The 3-NH₂ derivative^[22] and 3-N(CH₃)₂ derivative^[19] were excluded at $t = 0.95$. ^{bb}The δ_{CO} value for 3-C(CH₃)₃ was omitted. ^{cc}The $\delta_{\text{CO}} = 166.9$ ^[63] for derivative R = CH₃ was used. The average values of steric constants, $E_s^{\text{B}} = -0.22$, -0.43 and -0.27 , for F₃CCH₂, Cl₃CCH₂, Cl₂CHCH₂ derivatives, respectively, were used (Table S4). The δ_{CO} values for derivatives R = CH₂CH₃ and R = CH₂CCl₃ (Table S4) were omitted. ^{dd}The δ_{CO} value for derivative R = CH₂C₆H₅ (Table 2) was omitted. ^{ee}The Charton steric constants, ν , for alkyl chain R (Table S4) were used. The δ_{CO} value for derivative R = CH₂Ph (Table 3) was omitted. The δ_{CO} value for derivative R = CH₃ (Table 3) was added.

Table 5. Correlation of the log *k* values for alkaline hydrolysis and IR stretching frequencies of carbonyl group, ν_{CO} , for *ortho*-, *meta*-, and *para*-substituted phenyl benzoates and alkyl benzoates with the carbonyl carbon ^{13}C NMR substituent chemical shifts $(\Delta\delta_{\text{CO}})_{\text{X}} = (\delta_{\text{CO}})_{\text{X}} - (\delta_{\text{CO}})_{\text{H}}$ with Eqns (4)-(6)

Medium/IR	$\log k_{\text{H}}/(\nu_{\text{CO}})_0$	a_1	a_2	a_3	R	R_0	n
Phenyl esters of <i>ortho</i> -substituted benzoic acids ^{a, b, c, d}							
Water	-0.334 ± 0.163	-0.457 ± 0.056	0.92 ± 0.32	0.99 ± 0.41	0.960	0.908	11
0.5 M Bu ₄ NBr	-0.726 ± 0.108	-0.512 ± 0.037	1.53 ± 0.21	1.23 ± 0.27	0.987	0.883	11
2.25M Bu ₄ NBr	-1.058 ± 0.162	-0.591 ± 0.065	2.10 ± 0.31	1.01 ± 0.40	0.972	0.786	10
IR (ν_{CO}) _{ortho}	1743.5 ± 1.5	-2.90 ± 0.60	8.01 ± 3.09	-39.1 ± 3.8	0.968	n.c.	9 ^{e, f, g}
	1743.5 ± 1.3	-2.91 ± 0.54	8.03 ± 2.81	-39.1 ± 3.4	0.971	n.c.	10 ^{f, g, h}
Phenyl esters of <i>para</i> -substituted benzoic acids ^{a, b, i}							
Water	-0.493 ± 0.072	-0.672 ± 0.056	1.25 ± 0.12	—	0.993	0.829	7
0.5 M Bu ₄ NBr	-0.757 ± 0.080	-0.836 ± 0.062	1.25 ± 0.16	—	0.992	0.867	6
2.25M Bu ₄ NBr	-1.180 ± 0.114	-1.119 ± 0.088	1.69 ± 0.23	—	0.991	0.865	6
IR (ν_{CO}) _{para}	1741.7 ± 0.6	-3.29 ± 0.52	7.77 ± 0.84^j	—	0.980	0.698	9
	1742.4 ± 0.4	-2.81 ± 0.33	8.41 ± 0.52^j	—	0.994		8 ^k
Phenyl esters of <i>meta</i> -substituted benzoic acids ^{a, b, l}							
Water	-0.451 ± 0.030	-0.550 ± 0.025	0	—	0.997	0.997	4
0.5 M Bu ₄ NBr	-0.696 ± 0.025	-0.704 ± 0.021	0	—	0.999	0.999	4
2.25M Bu ₄ NBr	-1.176 ± 0.075	-0.917 ± 0.061	0	—	0.993	0.993	4
IR (ν_{CO}) _{meta}	1742.0 ± 0.2	-3.61 ± 0.18	0	—	0.995	0.995	5
Phenyl esters of <i>meta</i> - and <i>para</i> -substituted benzoic acids ^{a, b, l}							
Water	-0.472 ± 0.060	-0.606 ± 0.041	1.25 ± 0.11	—	0.992	0.852	10
0.5 M Bu ₄ NBr	-0.723 ± 0.065	-0.763 ± 0.044	1.25 ± 0.15	—	0.992	0.891	9
2.25M Bu ₄ NBr	-1.193 ± 0.112	-1.018 ± 0.077	1.57 ± 0.26	—	0.985	0.899	9
<i>Ortho</i> -substituted phenyl esters of benzoic acid ^{c, l, m, n}							
Water	-0.501 ± 0.114	-0.889 ± 0.098	1.31 ± 0.17	0.66 ± 0.24	0.978	0.787	11
0.5 M Bu ₄ NBr	-0.856 ± 0.126	-0.937 ± 0.108	1.71 ± 0.19	0.93 ± 0.26	0.980	0.731	11
2.25M Bu ₄ NBr	-1.211 ± 0.158	-1.216 ± 0.136	2.35 ± 0.24	0.94 ± 0.33	0.981	0.717	11
IR (ν_{CO}) _{ortho}	1741.3 ± 1.1	-10.63 ± 1.02	4.98 ± 1.88	-5.50 ± 2.23	0.961	0.915	11 ^o
	1741.9 ± 1.0	-11.28 ± 0.95	4.60 ± 1.67	-6.78 ± 2.00	0.969	0.923	11 ^p
<i>Para</i> -substituted phenyl esters of benzoic acid ^{l, m, n}							
Water	-0.475 ± 0.050	-1.171 ± 0.070	-0.63 ± 0.15	—	0.994	0.974	7
0.5 M Bu ₄ NBr	-0.736 ± 0.094	-1.321 ± 0.131	-0.43 ± 0.28	—	0.986	0.982	7
2.25M Bu ₄ NBr	-1.111 ± 0.080	-2.154 ± 0.119	-0.77 ± 0.26	—	0.993	0.985	9 ^q
IR (ν_{CO}) _{para}	1742.6 ± 0.2	-8.30 ± 0.31	-4.52 ± 0.62	—	0.998	0.966	6 ^r
<i>Meta</i> -substituted phenyl esters of benzoic acid ^{l, m, n}							
Water	-0.446 ± 0.057	-1.139 ± 0.107	0.24 ± 0.13	—	0.983	0.974	7 ^s
	-0.503 ± 0.049	-1.227 ± 0.114	0	—	0.975		7 ^s
0.5 M Bu ₄ NBr	-0.808 ± 0.042	-1.435 ± 0.079	0.38 ± 0.10	—	0.994	0.978	7 ^s
2.25M Bu ₄ NBr	-0.973 ± 0.110	-1.988 ± 0.209	0.75 ± 0.27	—	0.975	0.949	9 ^t
IR (ν_{CO}) _{para}	1741.7 ± 0.4	-11.3 ± 1.0	0	—	0.977	0.977	7

Alkyl benzoates ^u						
Water	-1.287 ± 0.089	-0.720 ± 0.038	–	0.72 ± 0.27	0.987	0.967 11 ^v
0.5 M Bu ₄ NBr	-1.538 ± 0.170	-0.825 ± 0.078	–	1.24 ± 0.49	0.968	0.933 9 ^v
2.25M Bu ₄ NBr	-1.890 ± 0.131	-0.924 ± 0.060	–	1.03 ± 0.38	0.985	0.956 9 ^v
IR (ν_{CO}) _{meta}	1724.7 ± 2.9	-11.5 ± 1.3	–	18.3 ± 7.0	0.947	0.907 10 ^w
	1726.6 ± 1.8	-11.6 ± 0.8	–	28.8 ± 5.1	0.981	9 ^v

^aRef.^[4] ^bRef.^[8] ^cThe steric constants, E_s^B ,^[4] (Table S2) were used. ^dFor 2-NH₂ derivative $\sigma_R^o = 0$. ^eThe 2-I derivative was omitted. ^fThe 2-NH₂ derivative was omitted. ^gFor 2-CH₃ derivative $E_s^B = 0$ and $\sigma_R^o = 0$. ^hFor 2-I derivative $\nu_{\text{CO}} = 1755.9$ was calculated with relation: $(\nu_{\text{CO}})_{\text{ortho-cis}} = 1742.7 + 16.4\sigma_1 - 22.6E_s^B$.^[8] ⁱThe resonance constants, σ_R ,^[64] were used. ^jThe resonance constants^[65] $\Delta\sigma_R^+ = \sigma_p^+ - \sigma_p^o$ were used. ^kThe 4-C(CH₃)₃ derivative was excluded. ^lThe resonance constants, σ_R^o , were applied. ^mRef.^[56] ⁿRef.^[3] ^oFor 2-CH₃ derivative $E_s^B = 0$. ^pFor unsubstituted derivative $\delta_{\text{CO}} = 165.04$ was used to calculate the $\Delta\delta_{\text{CO}}$ scale. ^qThe log k values for 4-Cl, 4-Br, 4-CN, 4-CH₃, 4-OCH₃ and 4-C(CH₃)₃ derivatives were calculated with Eqn:^[1] $\log k = -1.106 + 2.34\sigma^o$. For 4-Cl derivative $\Delta\delta_{\text{CO}} = -0.22$ (in Table S3 Ref.^[1,3]) was used. ^rThe 4-CN derivative was excluded. ^sThe log k values for 3-CN and 3-F derivatives were calculated with Eqn in Table 1.^[3] ^tThe log k values for 3-F, 3-Br, 3-CN and 3-OCH₃ derivatives were calculated with Eqn in Table 3.^[1] For 3-CH₃ derivative $\Delta\delta_{\text{CO}} = 0.12$ were used (in Table S3 Ref.^[5]). ^uThe log k values for derivatives (R = CH₂CF₃, CH₂CCl₃, CH₂CHCl₂) in water and 2.25 M Bu₄NBr calculated with relations: $\log k = (-1.315 \pm 0.071) + (3.69 \pm 0.14)\sigma_1 + (0.972 \pm 0.190)E_s^B$, $R = 0.995$, $s_0 = 0.101$, $n = 9$; $\log k = (-1.956 \pm 0.116) + (4.67 \pm 0.24)\sigma_1 + (1.172 \pm 0.413)E_s^B$, $R = 0.995$, $s_0 = 0.104$, $n = 7$, respectively, were added. The average values of steric constants, $E_s^B = -0.22$, -0.43 and -0.27 , for F₃CCH₂, Cl₃CCH₂, Cl₂CHCH₂ derivatives, respectively, were used (Table S4). The $E_s^B = -0.41$ for R = CH₂C≡CH was used. ^vThe CH₂CN derivative was excluded. ^wThe ν_{CO} values for derivatives (R = CH₂CF₃, CH₂CCl₃, CH₂CHCl₂) were calculated with Eqn: $\nu_{\text{CO}} = (1726.1 \pm 1.5) + (58.4 \pm 3.4)\sigma_1 + (32.6 \pm 4.1)E_s^B$, $R = 0.991$, $s_0 = 0.138$, $n = 8$.