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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, $\sigma°_R$, and steric, E_s^B, or υ substituent constants. For all the *ortho*-substituted esters containing substituents in the acyl part as well as the phenyl part, the substituent-induced reverse inductive effect ($\rho_I < 0$), the normal resonance effect ($\rho_R > 0$), and the negative steric effect ($\delta_{ortho} < 0$) with the E_s^B were observed. In the case of *ortho* substituents in the phenyl part, the resonance effect was negligible. Due to inductive effect, the *ortho* electron-withdrawing substituents showed an 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 a 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 ($\rho_I < 0$, $\rho_R < 0$) 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 the *ortho*-, *meta*-, and *para*-substituted phenyl benzoates and alkyl benzoates were correlated nicely with the corresponding ^{13}C NMR substituent chemical shifts, $\Delta\delta_{CO}$. Copyright © 2009 John Wiley & Sons, Ltd.

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

INTRODUCTION

The influence of substituent effects, especially the *ortho* effect, on the rates of alkaline hydrolysis (as shown in References [1–6] and the 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 addressed in our earlier studies.

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 those with the rates of the alkaline hydrolysis as well as 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 is 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 ($X\text{-}C_6H_4CO_2C_6H_5$, $C_6H_5CO_2C_6H_4\text{-}X$) are influenced by the inductive, resonance, and the steric effects. For comparison 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 was analyzed as well.

To the best of 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. 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 more thoroughly 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 carboxyl 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 C=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]

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acetonitriles,[31] acetophenones, and benzaldehydes.[32–36] Guy[27] obtained 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 an alkyl chain on the carbonyl carbon ^{13}C NMR chemical shift was studied mainly for the case of esters containing substituents in the acyl part.[37–39]

Earlier (as shown in References [1–6]) we found the log *k* values for the alkaline hydrolysis of phenyl esters of *ortho*-substituted benzoic acids, $X\text{-}C_6H_4CO_2C_6H_5$, and substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4\text{-}X$, to be correlated with the Charton equation using the Taft inductive (σ_I) and resonance ($\sigma^{\circ}{}_R$) 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 the acyl part were 1.5-fold and the steric influence was 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, $X\text{-}C_6H_4CO_2C_6H_5$, in water the resonance term was negligible ($(\rho^{\circ}{}_R)_{ortho}$ *ca.* 0.3). In the case of phenyl esters of *ortho*-substituted benzoic acids, $X\text{-}C_6H_4CO_2C_6H_5$, 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: $(\nu_{CO})_{cis} = (\nu_{CO})_o + 16.4\sigma_I - 22.6E_s^B$ and $(\nu_{CO})_{trans} = (\nu_{CO})_o + 12.6\sigma_p^+ - 11.9E_s^B$.[7] Recently, we found[8] good correlations between the log *k* values of the alkaline hydrolysis of *ortho*-substituted phenyl benzoates and the infrared stretching frequencies of the 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, ($X\text{-}C_6H_4CO_2C_6H_5$,), methyl and ethyl benzoates ($X\text{-}C_6H_4CO_2CH_3$, $X\text{-}C_6H_4CO_2C_2H_5$), phenyl acetates ($CH_3CO_2C_6H_4\text{-}X$), and alkyl benzoates ($C_6H_5CO_2R$) were submitted to a 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, ($X\text{-}C_6H_4CO_2C_6H_5$, $C_6H_5CO_2C_6H_4\text{-}X$), methyl and ethyl benzoates ($X\text{-}C_6H_4CO_2CH_3$, $X\text{-}C_6H_4CO_2C_2H_5$), and alkyl benzoates ($C_6H_5CO_2R$) 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 4.7 T 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 the 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, $X\text{-}C_6H_4CO_2C_6H_5$ (X = 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), $C_6H_5CO_2C_6H_4\text{-}X$ (X = 2-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_2CH_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, $C_6H_5CO_2R$ (R = CH_3, $CH_2C_6H_5$, $CH_2CH_2OCH_3$, CH_2CH_2Cl, $CH_2C{\equiv}CH$, CH_2CF_3, CH_2CHCl_2, CH_2CCl_3, CH_2Cl, CH_2CN), methyl benzoates, $X\text{-}C_6H_4CO_2CH_3$ (X = H, 2-Cl, 2-Br, 2-I), and ethyl benzoates, $X\text{-}C_6H_4CO_2C_2H_5$, (X = H, 2-$NO_2$, 2-CN, 2-Cl, 2-$CF_3$) were recorded (as shown in Table S1). Carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, for phenyl esters of *ortho*-, *meta*-, and *para*-substituted benzoic acids, $X\text{-}C_6H_4CO_2C_6H_5$, *ortho*-, *meta*-, and *para*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4\text{-}X$, substituted alkyl benzoates, $C_6H_5CO_2R$, and methyl and ethyl esters of substituted benzoic acids ($X\text{-}C_6H_4CO_2CH_3$, $X\text{-}C_6H_4CO_2C_2H_5$) are given in Tables 1–3.

Synthesis of compounds

The preparation procedure and characteristics of *ortho*-, *meta*-, and *para*-substituted phenyl benzoates ($X\text{-}C_6H_4CO_2C_6H_5$, $C_6H_5CO_2C_6H_4\text{-}X$) and alkyl benzoates ($C_6H_5CO_2R$) have been previously described.[4,40–42] Methyl 2-chlorobenzoate, methyl 2-bromobenzoate, and methyl 2-iodobenzoate were obtained commercially (Aldrich). Benzyl benzoate was obtained from Sigma and ethyl 2-(trifluoromethyl)benzoate was a reagent from ABCR GmbH & Co. Cyanomethyl benzoate, $C_6H_5CO_2CH_2CN$, 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 (Reference,[43] 152–154 °C/11 mm Hg). IR $\nu_{CO} = 1731.8$ in DMSO. The 2,2,2-trifluoroethyl benzoate, $C_6H_5CO_2CH_2CF_3$, was obtained by the treatment of 2,2,2-trifluoroethanol with benzoyl chloride in pyridine. The yield was 38.4%, b.p. 107–109 °C/27 mm Hg (Reference,[45] 84–86 °C/19 mm Hg, Reference,[46] 50–52 °C/4 mm Hg). IR $\nu_{CO} = 1734.8$ in DMSO. The 2,2,2-trichloroethyl benzoate, $C_6H_5CO_2CH_2CCl_3$, and 2,2-dichloroethyl benzoate, $C_6H_5CO_2CH_2CHCl_2$, were synthesized by the treatment of 2,2,2-trichloroethanol or 2,2-dichloroethanol with benzoyl chloride in pyridine as described for the synthesis of 2,2,2-trifluoroethyl benzoate. 2,2,2-Trichloroethyl benzoate, $C_6H_5CO_2CH_2CCl_3$; yield 84.0%. IR $\nu_{CO} = 1732.3$ in DMSO. 2,2-Dichloroethyl benzoate, $C_6H_5CO_2CH_2CHCl_2$; yield 36.5%, b.p. 185 °C/27 mm Hg. IR $\nu_{CO} = 1726.5$ in DMSO. The 2-CO_2CH_3-phenyl benzoate, $C_6H_5CO_2C_6H_4CO_2CH_3$, was prepared from methyl salicylate and benzoyl chloride in pyridine at 0 °C with stirring. A white solid was obtained by recrystallization from ethanol, m.p. 92 °C (Reference,[47] 92 °C). Ethyl 2-nitrobenzoate, 2-NO_2-$C_6H_4CO_2CH_2CH_3$, was synthesized as previously described.[48] Yield 47.4%, b.p. 179–180 °C/25 mm Hg (Reference,[48] 178–179 °C/23 mm Hg). Ethyl 2-chlorobenzoate, 2-Cl-$C_6H_4CO_2CH_2CH_3$, was prepared as previously described,[48] b.p. 143–148 °C/25 mm Hg (Reference,[49] 122–125 °C/15 mm Hg). Ethyl 2-cyanobenzoate, 2-CN-$C_6H_4CO_2CH_2CH_3$, 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 recrystallization from benzene-pentane: m.p.62–65 °C (Reference,[50] 64.5–66 °C, Reference,[51] 62–65 °C).

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, $X\text{-}C_6H_4CO_2C_6H_5$ and substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4\text{-}X$

	$X\text{-}C_6H_4CO_2C_6H_5$			$C_6H_5CO_2C_6H_4\text{-}X$		
Substituent X	*ortho* derivatives	*meta* derivatives	*para* derivatives	*ortho* derivatives	*meta* derivatives	*para* 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, $C_6H_5CO_2R$

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	$HC{\equiv}CCH_2$	165.69
6	$C_6H_5CH_2$	166.26
7	$ClCH_2CH_2$	166.14
8	$CH_3OCH_2CH_2$	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	$X\text{-}C_6H_4CO_2CH_3$	$X\text{-}C_6H_4CO_2CH_2CH_3$
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

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, $X\text{-}C_6H_4CO_2C_6H_5$, substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4\text{-}X$, and for alkyl benzoates, $C_6H_5CO_2R$, the corresponding δ_{CO} values measured in the present work (Tables 1–3) were correlated with the following Eqns (1)–(3):

$$(\delta_{CO})_{m,p} = (\delta_{CO})_H + (\rho_I)_{m,p}\sigma_I + (\rho_R)_{m,p}\sigma^\circ_R \tag{1}$$

$$(\delta_{CO})_{ortho} = (\delta_{CO})_H + (\rho_I)_{ortho}\sigma_I + (\rho_R)_{ortho}\sigma^\circ_R + \delta_{ortho}E^B_s \tag{2}$$

$$(\delta_{CO})_{Alk} = (\delta_{CO})_H + (\rho_I)_{Alk}\sigma_I + \delta_{Alk}E^B_s \tag{3}$$

Comparison of the measured δ_{CO} values with those of Eqn (1) was performed separately for *meta* and *para* derivatives. In the data processing, the Taft inductive σ_I,[52] resonance constants $\sigma^\circ{}_R$[53] $[\sigma^\circ{}_R = (\sigma^\circ)_p - \sigma_I]$, and the steric constants E^B_s for the *ortho* substituents determined using the kinetic data for the acid hydrolysis of *ortho*-substituted phenyl benzoates, $C_6H_5CO_2C_6H_4\text{-}X$,[54] were employed. For comparison, the Charton steric scale of υ,[55] calculated on the basis of van der Waal's radii, r_v, was used as well (as shown in Table 4). The steric constants, E^B_s, were found to be a nearly linear function of the υ values in the case of monoatomic substituents X = H, F, Cl, Br, and I and X = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, and CF_3.[4] The polyatomic substituents (NO_2, NH_2, $N(CH_3)_2$, CN, OCH_3) deviated from this linearity. Therefore, in correlations for polyatomic *ortho* substituents, the value of υ for the isosterical substituents was used.[4] For the variable alkyl substituent in the alcohol component of esters, $C_6H_5CO_2R$ (Eqn (3)), the steric substituent constants, E^B_s, and the Charton steric scale of υ for alkyl substituents R were used (Table S4). The steric substituent constants, E^B_s, were calculated as follows: $E^B_s = (\log k^R_{H+} - \log k^{CH3}_{H+})$, where k^R_{H+} and k^{CH3}_{H+} 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) from Eqns (1) to (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 the literature (Table 3 and Table S3) with Eqns (1) and (2) are shown in Table 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 of Supporting Information.

To compare 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 the 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:

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

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

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

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, X-$C_6H_4CO_2C_6H_5$, listed in Table 1 showed good correlations with Eqns (1) and (2) (Table 4)

$$(\delta_{CO})_m = (165.11 \pm 0.10) - (2.91 \pm 0.22)_m\sigma_I - (1.64 \pm 0.22)_m\sigma_R^\circ$$
$$R = 0.992,\ s = 0.126,\ n/n_0 = 6/6 \tag{7}$$

$$(\delta_{CO})_p = (165.00 \pm 0.10) - (2.18 \pm 0.20)_p\sigma_I - (1.00 \pm 0.26)_p\sigma_R^\circ$$
$$R = 0.972,\ s = 0.154,\ n/n_0 = 9/9 \tag{8}$$

$$(\delta_{CO})_{ortho} = (165.32 \pm 0.22) - (5.08 \pm 0.37)_{ortho}\sigma_I + (1.58 \pm 0.42)_{ortho}\sigma_R^\circ - (4.33 \pm 0.51)_{ortho}E_s^B \tag{9}$$
$$R = 0.978,\ s = 0.257,\ n/n_0 = 11/11$$

The calculated sensitivities of chemical shifts, δ_{CO}, for *meta*, *para*, and *ortho* derivatives toward the substituents inductive effect $(\rho_I)_m$, $(\rho_I)_p$, $(\rho_I)_{ortho}$, resonance $(\rho_R)_m$, $(\rho_R)_p$, $(\rho_R)_{ortho}$, and the steric effect, δ_{ortho} (Table 4) were approximately the same in the case of the δ_{CO} values determined in the present work (Tables 1 and 2); the δ_{CO} values available in the literature (Table S3) were involved in correlations as well. The data treatment with Eqn (2) gave nearly identical results using two steric scales for the *ortho* substituents: E_s^B and the modified Charton υ constants (Table 4). The sensitivities of the chemical shifts, δ_{CO}, toward the inductive effect, $(\rho_I)_m$, $(\rho_I)_p$, $(\rho_I)_{ortho}$, resonance $(\rho_R)_m$, $(\rho_R)_p$, $(\rho_R)_{ortho}$, and the steric effect δ_{ortho}, in methyl and ethyl esters of substituted benzoic acids shown in Table 4 are nearly the same as presented in Eqns (7)–(9) for the phenyl esters of *meta*-, *para*-, and *ortho*-substituted benzoic acids. The contribution of the inductive effect from the *para* position to the chemical shifts, δ_{CO}, in phenyl esters of substituted benzoic acids found in the present work, $(\rho_I)_p = -2.18$, is slightly weaker than that in Reference [9] ($(\rho_F)_p = -2.50$). In methyl esters of *meta*- and *para*-substituted benzoic acids, the susceptibilities of the chemical shifts, δ_{CO}, toward the inductive effect $(\rho_I)_m = -3.11$, $(\rho_I)_p = -2.41$, and resonance, $(\rho_R)_m = -1.10$, $(\rho_R)_p = -1.04$, estimated in the present paper (Table 4) agree well with those reported in Reference [18] (in Reference [18] $(\rho_I)_m = -3.33$, $(\rho_R)_m = -1.06$, $(\rho_I)_p = -2.43$, and $(\rho_R)_p = -1.12$).

It follows from Table 4 that in substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, containing substituents in phenyl moiety, the influence of *meta*, *para*, and *ortho* substituent effects on the carbonyl carbon chemical shifts, δ_{CO}, could be expressed by the following equations:

$$(\delta_{CO})_m = (165.13 \pm 0.03) - (0.95 \pm 0.07)_m\sigma_I - (0.22 \pm 0.08)_m\sigma_R^\circ$$
$$R = 0.988,\ s = 0.046,\ n/n_0 = 7/7 \tag{10}$$

$$(\delta_{CO})_p = (165.16 \pm 0.02) - (1.10 \pm 0.04)_p\sigma_I - (1.48 \pm 0.06)_p\sigma_R^\circ$$
$$R = 0.994,\ s = 0.053,\ n/n_0 = 25/26 \tag{11}$$

$$(\delta_{CO})_{ortho} = (164.90 \pm 0.07) - (1.56 \pm 0.13)_{ortho}\sigma_I + (0.33 \pm 0.14)_{ortho}\sigma_R^\circ - (0.72 \pm 0.11)_{ortho}E_s^B \tag{12}$$
$$R = 0.978,\ s = 0.103,\ n/n_0 = 12/13$$

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 toward the inductive effect from *meta* and *para* positions 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,

Table 4. Correlation of the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, in $CDCl_3$ from Eqns (1) to (3)

Nr.	$\delta_{H(calc)}$	ρ_I	ρ_R	δ	R[a]	R_0[b]	s[c]	n/n_0[d]
Phenyl esters of *ortho*-substituted benzoic acids,[e] $(\delta_{CO})_H = 165.17$								
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[hi]
6	165.38 ± 0.13	−5.25 ± 0.21	1.66 ± 0.21	2.10 ± 0.14	0.985		0.190	24/26[fh]
Methyl esters of *ortho*-substituted benzoic acids,[e] $(\delta_{CO})_H = 167.09$								
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 *ortho*-substituted benzoic acids,[e] $(\delta_{CO})_H = 166.59$								
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]
Ortho-substituted phenyl esters of benzoic acid,[l] $(\delta_{CO})_H = 165.04$								
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[fn]
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[op]
17	164.88 ± 0.08	−1.48 ± 0.14	0	0.30 ± 0.08	0.963		0.121	11/13[fno]
Ortho-substituted phenyl esters of acetic acid,[l] $(\delta_{CO})_H = 169.29$								
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[fq]
Phenyl esters of *para*-substituted benzoic acids, $(\delta_{CO})_H = 165.17$								
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 *para*-substituted benzoic acids, $(\delta_{CO})_H = 167.09$								
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 *para*-substituted benzoic acids, $(\delta_{CO})_H = 166.59$								
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]
Para-substituted phenyl esters of benzoic acid, $(\delta_{CO})_H = 165.17$								
26	165.16 ± 0.02	−1.10 ± 0.04	−1.48 ± 0.06	—	0.994	0.780	0.053	25/26[v]
Para-substituted phenyl esters of acetic acid, $(\delta_{CO})_H = 169.43$								
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 *meta*-substituted benzoic acids, $(\delta_{CO})_H = 165.17$								
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 *meta*-substituted benzoic acids, $(\delta_{CO})_H = 167.09$								
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 *meta*-substituted benzoic acids, $(\delta_{CO})_H = 166.59$								
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]
Meta-substituted phenyl esters of benzoic acid, $(\delta_{CO})_H = 165.17$								
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
Meta-substituted phenyl esters of acetic acid, $(\delta_{CO})_H = 169.43$								
35	169.48 ± 0.04	−1.16 ± 0.07	−0.35 ± 0.09	—	0.991	0.969	0.045	8/8[bb]

(*Continues*)

Table 4. (Continued)

Nr.	$\delta_{H(calc)}$	ρ_I	ρ_R	δ	R^a	$R_0{}^b$	s^c	$n/n_0{}^d$
			Alkyl substituted esters of benzoic acid, $(\delta_{CO})_{CH_3} = 166.9$					
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]

The δ_{CO} values in Tables 1–3 and Table S3 used.

[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.

[e] For a 2-NH$_2$ derivative $\sigma^\circ{}_R = 0$ and for a 2-CH$_3$ derivative $E_s^B = 0$ and $\sigma^\circ{}_R = 0$.

[f] Charton's modified steric constants, υ, were used (Table S2).

[g] For 2-Br and 2-I derivatives, the δ_{CO} values[59] were used.

[h] The δ_{CO} values from Tables 1 and S3. The values of δ_{CO} for a 2-Br derivative (Table 1) and 2-OCH$_3$ derivative[59] were excluded.

[i] The $\delta_{CO} = 165.1$ (Table S3) for the 2-I derivative was excluded.

[j] The 2-Br derivative (Table 3) was excluded at the confidence level $t = 0.95$.

[k] The 2-Br derivative was omitted.

[l] For the 2-CH$_3$ derivative, $E_s^B = 0$ and $\sigma_I = 0$. The average value of steric constants, $E_s^B = -0.881$, was used for the 2-CO$_2$CH$_3$ substituent.

[m] The 2-CO$_2$CH$_3$ and 2-I derivatives were omitted.

[n] The 2-CO$_2$CH$_3$ and 2-I derivatives were excluded at $t = 0.97$.

[o] The alternative δ_{CO} value (Table S3) for 2-CH$_3$ derivative was added.

[p] The 2-I derivative was excluded.

[q] The 2-CO$_2$CH$_3$ derivative and the alternative δ_{CO} value for 2-NO$_2$ derivative were excluded at $t = 0.95$.

[r] The δ_{CO} values (Tables 1 and S3) were included. The 4-NO$_2$, 4-F, and 4-I derivatives[59] were excluded at $t = 0.97$.

[s] The 4-NO$_2$ and 4-N(CH$_3$)$_2$ derivatives,[60] 4-Cl, 4-Br, 4-OCH$_3$ derivatives,[61] and the 4-I derivative[18] were excluded at $t = 0.95$.

[t] The $\delta_{CO} = 166.2$ (Table S3) for the 4-C(CH$_3$)$_3$ derivative was excluded at $t = 0.99$.

[u] The 4-Cl, 4-COCH$_3$ and 4-CO$_2$Et derivatives[62] were excluded at $t = 0.97$.

[v] The 4-CN derivative (Table 1) was excluded.

[w] The 4-C(CH$_3$)$_3$ and 4-CH(CH$_3$)$_2$ derivatives (Table S3) were excluded.

[x] The δ_{CO} value for the 3-OCH$_3$ derivative (Table S3) was added.

[y] For the 3-Cl derivative $\delta_{CO} = 165.5$ and for the 3-I derivative $\delta_{CO} = 165.43$ (Table S3) were excluded at $t = 0.99$.

[z] The 3-N(CH$_3$)$_2$ and 3-Br derivatives[18] were excluded at $t = 0.97$.

[aa] The 3-NH$_2$ derivative[22] and 3-N(CH$_3$)$_2$ derivative[19] were excluded at $t = 0.95$.

[bb] The δ_{CO} value for 3-C(CH$_3$)$_3$ was omitted.

[cc] The $\delta_{CO} = 166.9$[63] for the derivative R = CH$_3$ was used. The average values of steric constants, $E_s^B = -0.22$, -0.43, and -0.27, for F$_3$CCH$_2$, Cl$_3$CCH$_2$, Cl$_2$CHCH$_2$ derivatives, respectively, were used (Table S4). The δ_{CO} values for the derivatives R = CH$_2$CH$_3$ and R = CH$_2$CCl$_3$ (Table S4) were omitted.

[dd] The δ_{CO} value for the derivative R = CH$_2$C$_6$H$_5$ (Table 2) was omitted.

[ee] The Charton steric constants, υ, for the alkyl chain R (Table S4) were used. The δ_{CO} value for the derivative R = CH$_2$Ph (Table 3) was omitted. The δ_{CO} value for derivative R = CH$_3$ (Table 3) was added.

in substituted phenyl esters of benzoic 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 ($(\rho_R)_m << (\rho_R)_p$).

The determined carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, in Table 1 show that electron-withdrawing substituents in *meta* and *para* positions, both in the benzoyl and phenyl parts 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 imply a reverse substituent effect that operates through the polar and resonance pathways for 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 shift the π-electrons in the C=O group toward the carbonyl carbon making the carbonyl group less polar with increase in the strength of the C=O bond as compared to the 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] have been explained in terms of the contribution of different resonance structures.[9,16,37] The electron-withdrawing substituents were found to destabilize the resonance structure

Table 5. Correlation of the log *k* values for alkaline hydrolysis and IR streching 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 $(\Delta\delta_{CO})_X = (\delta_{CO})_X - (\delta_{CO})_H$ from Eqns (4) to (6)

Medium/IR	log $k_H/(\nu_{CO})_0$	a_1	a_2	a_3	*R*	R_0	*n*
Phenyl esters of *ortho*-substituted benzoic acids[abcd]							
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_4NBr	−0.726 ± 0.108	−0.512 ± 0.037	1.53 ± 0.21	1.23 ± 0.27	0.987	0.883	11
2.25 M Bu_4NBr	−1.058 ± 0.162	−0.591 ± 0.065	2.10 ± 0.31	1.01 ± 0.40	0.972	0.786	10
IR $(\nu_{CO})_{ortho}$	1743.5 ± 1.5	−2.90 ± 0.60	8.01 ± 3.09	−39.1 ± 3.8	0.968	n.c.	9[efg]
	1743.5 ± 1.3	−2.91 ± 0.54	8.03 ± 2.81	−39.1 ± 3.4	0.971	n.c.	10[fgh]
Phenyl esters of *para*-substituted benzoic acids[abi]							
Water	−0.493 ± 0.072	−0.672 ± 0.056	1.25 ± 0.12	—	0.993	0.829	7
0.5 M Bu_4NBr	−0.757 ± 0.080	−0.836 ± 0.062	1.25 ± 0.16	—	0.992	0.867	6
2.25 M Bu_4NBr	−1.180 ± 0.114	−1.119 ± 0.088	1.69 ± 0.23	—	0.991	0.865	6
IR $(\nu_{CO})_{para}$	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 *meta*-substituted benzoic acids[abl]							
Water	−0.451 ± 0.030	−0.550 ± 0.025	0	—	0.997	0.997	4
0.5 M Bu_4NBr	−0.696 ± 0.025	−0.704 ± 0.021	0	—	0.999	0.999	4
2.25 M Bu_4NBr	−1.176 ± 0.075	−0.917 ± 0.061	0	—	0.993	0.993	4
IR $(\nu_{CO})_{meta}$	1742.0 ± 0.2	−3.61 ± 0.18	0	—	0.995	0.995	5
Phenyl esters of *meta*- and *para*-substituted benzoic acids[abl]							
Water	−0.472 ± 0.060	−0.606 ± 0.041	1.25 ± 0.11	—	0.992	0.852	10
0.5 M Bu_4NBr	−0.723 ± 0.065	−0.763 ± 0.044	1.25 ± 0.15	—	0.992	0.891	9
2.25 M Bu_4NBr	−1.193 ± 0.112	−1.018 ± 0.077	1.57 ± 0.26	—	0.985	0.899	9
Ortho-substituted phenyl esters of benzoic acid[clmn]							
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_4NBr	−0.856 ± 0.126	−0.937 ± 0.108	1.71 ± 0.19	0.93 ± 0.26	0.980	0.731	11
2.25 M Bu_4NBr	−1.211 ± 0.158	−1.216 ± 0.136	2.35 ± 0.24	0.94 ± 0.33	0.981	0.717	11
IR $(\nu_{CO})_{ortho}$	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]
Para-substituted phenyl esters of benzoic acid[lmn]							
Water	−0.475 ± 0.050	−1.171 ± 0.070	−0.63 ± 0.15	—	0.994	0.974	7
0.5 M Bu_4NBr	−0.736 ± 0.094	−1.321 ± 0.131	−0.43 ± 0.28	—	0.986	0.982	7
2.25 M Bu_4NBr	−1.111 ± 0.080	−2.154 ± 0.119	−0.77 ± 0.26	—	0.993	0.985	9[q]
IR $(\nu_{CO})_{para}$	1742.6 ± 0.2	−8.30 ± 0.31	−4.52 ± 0.62	—	0.998	0.966	6[r]
Meta-substituted phenyl esters of benzoic acid[lmn]							
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_4NBr	−0.808 ± 0.042	−1.435 ± 0.079	0.38 ± 0.10	—	0.994	0.978	7[s]
2.25 M Bu_4NBr	−0.973 ± 0.110	−1.988 ± 0.209	0.75 ± 0.27	—	0.975	0.949	9[t]
IR $(\nu_{CO})_{para}$	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_4NBr	−1.538 ± 0.170	−0.825 ± 0.078	—	1.24 ± 0.49	0.968	0.933	9[v]
2.25 M Bu_4NBr	−1.890 ± 0.131	−0.924 ± 0.060	—	1.03 ± 0.38	0.985	0.956	9[v]
IR $(\nu_{CO})_{meta}$	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]

[a] Reference.[4]

[b] Reference.[8]

[c] The steric constants, E_s^B,[4] (Table S2) were used.

[d] For 2-NH_2 derivative $\sigma^\circ_R = 0$.

[e] The 2-I derivative was omitted.

[f] The 2-NH_2 derivative was omitted.

(*Continues*)

Table 5. (Continued)

[g] For the 2-CH_3 derivative $E_s^B = 0$ and $\sigma^\circ_R = 0$.

[h] For the 2-I derivative $\nu_{CO} = 1755.9$ was calculated with the relation: $(\nu_{CO})_{\text{ortho-cis}} = 1742.7 + 16.4\sigma_I - 22.6E_s^B$.[8]

[i] The resonance constants, σ_R,[64] were used.

[j] The resonance constants[65] $\Delta\sigma^+_R = \sigma^+_p - \sigma^\circ_p$ were used.

[k] The 4-C(CH_3)$_3$ derivative was excluded.

[l] The resonance constants, σ°_R, were applied.

[m] Reference.[56]

[n] Reference.[3]

[o] For the 2-CH_3 derivative $E_s^B = 0$.

[p] For unsubstituted derivative $\delta_{CO} = 165.04$ was used to calculate the $\Delta\delta_{CO}$ scale.

[q] The log *k* values for 4-Cl, 4-Br, 4-CN, 4-CH_3, 4-OCH_3, and 4-C(CH_3)$_3$ derivatives were calculated with the equation: log $k = -1.106 + 2.34\sigma^\circ$. For the 4-Cl derivative $\Delta\delta_{CO} = -0.22$ (in Table S3 Reference[1,3]) was used.

[r] The 4-CN derivative was excluded.

[s] The log *k* values for 3-CN and 3-F derivatives were calculated with the equation in Table 1.[3]

[t] The log *k* values for 3-F, 3-Br, 3-CN, and 3-OCH_3 derivatives were calculated with the equation in Table 3.[1] For the 3-CH_3 derivative, $\Delta\delta_{CO} = 0.12$ was used (Table S3, Reference[5]).

[u] The log *k* values for derivatives (R = CH_2CF_3, CH_2CCl_3, CH_2CHCl_2) in water and 2.25 M Bu_4NBr calculated with the relations: log $k = (-1.315 \pm 0.071) + (3.69 \pm 0.14)\sigma_I + (0.972 \pm 0.190)E_s^B$, $R = 0.995$, $s_0 = 0.101$, $n = 9$; log $k = (-1.956 \pm 0.116) + (4.67 \pm 0.24)\sigma_I + (1.172 \pm 0.413)E_s^B$, $R = 0.995$, $s_0 = 0.104$, $n = 7$, respectively, were added. The average values of steric constants, $E_s^B = -0.22$, -0.43 and -0.27, for F_3CCH_2, Cl_3CCH_2, Cl_2CHCH_2 derivatives, respectively, were used (Table S4). The $E_s^B = -0.41$ for R = $CH_2C{\equiv}CH$ was used.

[v] The CH_2CN derivative was excluded.

[w] The ν_{CO} values for derivatives (R = CH_2CF_3, CH_2CCl_3, CH_2CHCl_2) were calculated with the equation: $\nu_{CO} = (1726.1 \pm 1.5) + (58.4 \pm 3.4)\sigma_I + (32.6 \pm 4.1)E_s^B$, $R = 0.991$, $s_0 = 0.138$, $n = 8$.

$R_1(C^{\delta+}{-}O^{\delta-})OR_2$ to a great 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 the *para* position in phenyl esters as well as in methyl and ethyl esters of substitued 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 the contributions of resonance effects from *meta* and *para* positions to the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, in the 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 the 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 the benzoyl part could consist of two competitive resonance types. The normal direct resonance effect between the substituent and the carbonyl group for 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 compared to 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 follows (Table 4):

$$
\begin{aligned}
(\delta_{CO})_{Alk} = {} & (166.62 \pm 0.21) - (4.59 \pm 0.42)_{Alk}\sigma_I \\
& - (1.39 \pm 0.56)\delta_{Alk}E_s^B \qquad (13) \\
R = 0.966,\ & s = 0.188,\ n/n_0 = 15/15
\end{aligned}
$$

We obtained nearly the same results as from Eqn (13) (Table 4) as the correlated data for alkyl substituted benzoates, $C_6H_5CO_2R$, were fitted to Eqn (3), and the Charton steric υ constants for alkyl substituent R (Table S4) were used.

Effects induced by *ortho* substituents

We found the influence of *ortho* substituents on the carbonyl carbon chemical shifts, δ_{CO}, in the phenyl, methyl, and ethyl benzoates containing *ortho* substituents in benzoyl moiety as well as in phenyl benzoates and phenyl acetates with *ortho* substituents in the 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 υ constants were used, susceptibility to the steric effect, δ_{ortho}, was positive and approximately twice smaller as compared to the δ_{ortho} value obtained by 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 toward the inductive effect from the *ortho* position, were in the 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 the 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 on 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 view that in the substituted benzoyl derivatives, the inductive effect is increased due to the 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 the 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 the substituent increases in 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 the *ortho* substituents in the phenyl part, the resonance effect was negligible. In previous studies,[4,7] on the basis of the kinetic data for alkaline hydrolysis, 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 the carbonyl group and the *ortho*-substituted phenyl ring was 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 the 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 alkaline hydrolysis and IR carbonyl stretching frequencies, ν_{CO}, with the carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{CO}$

The rates of alkaline hydrolysis for the phenyl esters of *ortho*-, *meta*-, and *para*-substituted benzoic acids, $X\text{-}C_6H_4CO_2C_6H_5$, *ortho*-, *meta*-, and *para*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4\text{-}X$, and substituted alkyl benzoates, $C_6H_5CO_2R$, 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, $\Delta\delta_{CO}$ ($0.960 < R < 0.999$, 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, $\Delta\delta_{CO}$, for the esters considered.

The log *k* values of alkaline hydrolysis and the IR stretching frequencies were correlated well with the corresponding chemical shifts, $\Delta\delta_{CO}$, 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, $C_6H_5CO_2R$, the log *k* values gave a good correlation with the $(\Delta\delta_{CO})_{Alk}$ values when an additional steric term for alkyl substituents was included. The slope a_1 in Eqn (4) for the *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, $\Delta\delta_{CO}$. 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, $\Delta\delta_{CO}$.

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, $\Delta\delta_{CO}$, as follows (Table 5):

$$\begin{aligned} \log k_{ortho} &= (-0.334 \pm 0.163) - (0.457 \pm 0.056)\Delta\delta_{CO} \\ &\quad + (0.92 \pm 0.32)\sigma^{\circ}_{R} + (0.99 \pm 0.41)\,E^{B}_{s} \qquad (14) \\ R &= 0.960,\ n = 11 \end{aligned}$$

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

$$\begin{aligned} (\nu_{CO})_{ortho} &= (1743.5 \pm 1.3) - (2.91 \pm 0.54)\Delta\delta_{CO} \\ &\quad + (8.03 \pm 2.81)\sigma^{\circ}_{R} - (39.1 \pm 3.4)E^{B}_{s} \qquad (15) \\ R &= 0.971, n = 10 \end{aligned}$$

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: $a_1 = \rho_I(AH)/\rho_I(NMR)$, $a_2 = \rho_R(AH) - a_1\rho_R(NMR)$, $a_3 = \delta(AH) - a_1\delta(NMR)$ and $a_1 = \rho_I(IR)/\rho_I(NMR)$, $a_2 = \rho_R(IR) - a_1\rho_R(NMR)$, $a_3 = \delta(IR) - a_1\delta(NMR)$ where alkaline hydrolysis is denoted by (AH), the carbonyl carbon ^{13}C NMR substituent chemical shifts, $\Delta\delta_{CO}$, by (NMR) and the infrared stretching frequencies, ν_{CO}, by (IR). Using the alkaline hydrolysis of the phenyl esters of substituted benzoic acids, $X\text{-}C_6H_4CO_2C_6H_5$, $\rho_I(AH)_{ortho} = 2.13$, $\rho_R(AH)_{ortho} = 0.31$, and $\delta(AH)_{ortho} = 2.67$ in water at 25 °C,[4,8] as well as $\rho_I(NMR)_{ortho} = -5.0$, $\rho_R(NMR)_{ortho} = 1.43$, and $\delta(NMR)_{ortho} = -4.1$ (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 the *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, $\Delta\delta_{CO}$, 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 unit 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 by *ca.* 0.15 unit 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 decrease in the electrophilic solvating power of the solvent. In a previous study,[3] the *ortho* inductive effect was found to vary with solvent by *ca.* three times less as compared to *meta* and *para* polar effects. 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 effects, $\rho_{m,p}$, 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] For the same change in the solvent, the inductive effect of *ortho* substituents, $(\rho_I)_{ortho}$, grows by 0.07 and 0.43 units of ρ_I 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 the esters and in the IR carbonyl stretching frequencies, ν_{CO}. With increase in the σ values of substituents, the carbonyl carbon ^{13}C NMR chemical shifts, δ_{CO}, were found to diminish, but the rates of both alkaline hydrolysis and 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, $\Delta\delta_{CO}$, 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 ($X\text{-}C_6H_4CO_2C_6H_5$, $C_6H_5CO_2C_6H_4\text{-}X$), methyl benzoates, ethyl benzoates, and phenyl acetates was found to be described by the reverse inductive, the normal resonance, and the steric effects 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 in influencing 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 the 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, $\Delta\delta_{CO}$, 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 ($X\text{-}C_6H_4CO_2C_6H_5$, $C_6H_5CO_2C_6H_4\text{-}X$), 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 ($C_6H_4CO_2R$) in $CDCl_3$ used in the data analysis; Table S5: The second-order rate constants *k* ($dm^3\,mol^{-1}\,s^{-1}$) for alkaline hydrolysis of esters of benzoic acid, $C_6H_5CO_2R$, in aqueous 0.5 M Bu_4NBr at 25 °C.

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