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Influence of substituents on the infrared stretching frequencies of carbonyl group in esters of benzoic acid

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ABSTRACT: Infrared spectra of 25 substituted phenyl esters of benzoic acid $C_6H_5CO_2C_6H_4$-X (X=H, 3-Cl, 3-F, 3-CN, 3-NO_2, 3-CH_3, 3-OH, 3-NH_2, 4-Cl, 4-F, 4-NO_2, 4-CN, 4-OCH_3, 4-CH_3, 4-NH_2, 2-Cl, 2-F, 2-I, 2-NO_2, 2-CF_3, 2-CN, 2-CH_3, 2-OCH_3, 2-N$(CH_3)_2$, 2-C$(CH_3)_3$), 8 alkyl benzoates $C_6H_5CO_2R$ (X=CH_3, CH_2CH_3, CH_2Cl, CH_2CN, $CH_2C{\equiv}CH$, CH_2CH_2Cl, $CH_2CH_2OCH_3$, $CH_2C_6H_5$), and 22 phenyl esters of substituted benzoic acids X-$C_6H_4CO_2C_6H_5$ (X=3-Cl, 3-NO_2, 3-CH_3, 3-N$(CH_3)_2$, 4-F, 4-Cl, 4-Br, 4-NO_2, 4-CH_3, 4-C$(CH_3)_3$, 4-OCH_3, 4-NH_2, 2-Cl, 2-F, 2-Br, 2-I, 2-NO_2, 2-CN, 2-CF_3, 2-CH_3, 2-OCH_3, 2-NH_2) were recorded in tetrachloromethane in the region of 400–4000 cm^{-1}. Carbonyl stretching frequencies ν_{CO} for *meta*- and *para*-substituted phenyl esters of benzoic acid and phenyl esters of *meta*-substituted benzoic acids were shown to correlate with the substituent constants σ^o. The influence of the through resonance effect on ν_{CO} was found to be important in the case of $+R$ *para* substituents in the benzoyl part of phenyl benzoates as well. The carbonyl stretching frequencies of *ortho* derivatives in phenoxy part were shown to correlate with the inductive substituent constant σ_I only. In the benzoyl part of the esters the carbonyl stretching frequencies of *cis* and *trans* conformers (relative to the carbonyl group) of *ortho* derivatives were nicely described by dual parameter equations: $(\nu_{CO})_{cis} = (\nu_{CO})_o + c_1\sigma_I + c_3 E_s^B$ and $(\nu_{CO})_{trans} = (\nu_{CO})_o + c_1\sigma_p^+ + c_3 E_s^B$ ($R = 0.99$). The *trans* isomers of phenyl esters of *ortho*-substituted benzoic acids showed direct resonance similar to that for *para* derivatives. The positive steric term found for both the *cis* and *trans* conformers could be considered as measure of the steric inhibition of resonance between the phenyl ring and the carboxy-group caused by bulky *ortho* substituents. The existence of *cis*/*trans* conformations was supported by frequency calculations with Density Functional Theory (DFT) method at B3LYP/6-311+G** level for the *ortho*-substituted benzoates. In the case of alkyl benzoates good correlations of ν_{CO} values were obtained when both the Taft σ^* and the steric E_s^B constants were used. For *meta*- and *para*-substituted phenyl benzoates *s-trans* conformation where the plane of the benzene ring in the benzoyl part of the ester is coplanar with the carbonyl bond plane and the plane of the benzene ring in the phenoxy part is twisted nearly perpendicular relative to the carbonyl bond plane was supported. Copyright © 2006 John Wiley & Sons, Ltd.
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KEYWORDS: phenyl benzoates; alkyl benzoates; infrared spectra; substituent effects; DFT calculations

INTRODUCTION

In our previous papers[1–5] the influence of the substituent effects on the kinetics of the alkaline hydrolysis of *meta-*, *para-*, and *ortho*-substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, alkyl benzoates, $C_6H_5CO_2R$, in various media and phenyl esters of *meta-*, *para-*, and *ortho*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, in pure water has been studied. In the present paper we extended the study of substituent effects to the infrared absorption of these esters. To check up which of the substituent descriptors could be used to correlate the infrared carbonyl stretching frequencies ν_{CO} in *ortho-*, *meta-*, and *para*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, and alkyl-substituted esters of benzoic acid, $C_6H_5CO_2R$, in the present work the infrared spectra for 55 esters were recorded in tetrachloromethane solution.

The influence of substituents on the infrared carbonyl-stretching frequencies $\nu_{C=O}$ of esters RCO_2R' involving

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a variable substituent has been studied for methyl benzoates,[6–10] ethyl benzoates,[11–13] *t*-butyl benzoates,[9] phenyl acetates,[14–18] phenyl and alkyl esters of hydrocinnamic acid,[19–20] and phenyl dichloroacetates.[21]

We could find only a few publications providing data on the infrared carbonyl stretching frequencies of substituted phenyl benzoates including data for *ortho*-, *meta*-, and *para*-substituted derivatives in the same series[17,22] and for alkyl benzoates, $C_6H_5CO_2R$, with electronegative substituents.[23]

Freedman[14] observed that the carbonyl-stretching frequencies of phenyl acetates failed to correlate with σ or σ^- for the *para*-substituents and suggested that the frequency $\nu_{C=O}$ is dependent only on the inductive component of σ. Cohen and Takahashi[20] obtained the excellent correlation using σ° constants to correlate the infrared carbonyl stretching frequencies for 48 mono- and polysubstituted phenyl hydrocinnamates for the *meta* and *para* benzene ring substituents. In the case of *ortho* substituents, the same authors[20] used substituent constants $\sigma^0_o = \sigma^0_p + 0.39\sigma^*$ (RCH_2), assuming that the inductive effect from *ortho* position exceeds that of *para* substituents. In the case of the alkyl substituted esters of 3-phenylpropionic acids it was demonstrated[20] that excellent correlations exist between carbonyl stretching frequencies and σ^* constants for a large number of esters.

Methyl esters of *ortho*-halogeno and *ortho*-methoxy substituted benzoic acids and esters of α-substituted acetic acids exhibit a split of carbonyl bands which was attributed to the presence of two different *cis* and *trans* (*gauche*) conformations.[6,18,24–26] In the case of carbonyl compounds, a strong non-bonding interaction is considered to operate across the space between two nearly parallel oriented dipoles of the C═O and another polar bond situated in a mutually vicinal position. Previously[6,24–26] the lower wave number band was assigned to the less polar *trans* (*gauche*) conformation and the higher wave number to more polar *cis* conformation exhibiting the dipole field effect known as Corey effect.[27]

To the best of our knowledge, there are no sufficient data on IR absorption of carbonyl bond for *ortho-*, *meta-*, and *para*-substituted phenyl benzoates and alkyl benzoates in literature enabling a thorough study of the influence of substituent effects on IR carbonyl stretching frequencies $\nu_{C=O}$. Therefore in the present work the infrared spectra were recorded for the following substituted phenyl benzoates in tetrachloromethane solution: $C_6H_5CO_2C_6H_4$-X (X═H, 3-Cl, 3-F, 3-CN, 3-NO_2, 3-CH_3, 3-OH, 3-NH_2, 4-Cl, 4-F, 4-NO_2, 4-CN, 4-OCH_3, 4-CH_3, 4-NH_2, 2-Cl, 2-F, 2-I, 2-NO_2, 2-CF_3, 2-CN, 2-CH_3, 2-OCH_3, 2-$N(CH_3)_2$, 2-$C(CH_3)_3$), alkyl benzoates, $C_6H_5CO_2R$ (R═CH_3, CH_2CH_3, CH_2Cl, CH_2CN, $CH_2C{\equiv}CH$, $CH_2C_6H_5$, CH_2CH_2Cl, $CH_2CH_2OCH_3$), and X-$C_6H_4CO_2C_6H_5$ (X═3-Cl, 3-NO_2, 3-CH_3, 3-$N(CH_3)_2$, 4-F, 4-Cl, 4-Br, 4-NO_2, 4-CH_3, 4-$C(CH_3)_3$, 4-OCH_3, 4-NH_2, 2-Cl, 2-F, 2-Br, 2-I, 2-NO_2, 2-CN, 2-CF_3, 2-CH_3, 2-OCH_3, 2-NH_2).

One of the purposes of the current study was to check the influence of substituent effects on IR carbonyl stretching frequencies $\nu_{C=O}$ of *ortho*-, *meta*-, and *para*-substituted phenyl and alkyl benzoates, and propose conformations for the esters studied on the grounds of correlation analysis. To confirm the conclusions derived from the correlation analysis the DFT calculations were also employed.

The accent of our work was mainly on *ortho* substituents. It is known that Hammett type relationships are mostly applied to *meta*- and *para*-substituted derivatives while *ortho* derivatives usually do not obey Hammett type equations very well and the problem is more complicated. In the very beginning of the study of 'the *ortho* effect,' the infrared frequencies often used to calculate so-called polar substituent constants for *ortho* substituents as the infrared frequencies of *ortho* derivatives were found to be independent of steric effects.[28] Nowadays it is accepted that the polar influence of *ortho* substituents is only very seldom equal to that of *para* substituents (i.e., the absence of '*ortho* effect') and the inductive and resonance components for *ortho* substituents usually vary depending on the processes and conditions.

EXPERIMENTAL

The spectra of 25 substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, 8 alkyl benzoates, $C_6H_5CO_2R$, and 22 phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, were recorded in the region 400–4000 cm^{-1} on Interspectrum PFS 2020 FT-IR spectrometer in approximately 0.013 M solution of tetrachloromethane (Fluka, for IR-spectroscopy). A KrS_5 cell with path length 1.02 mm was used. The wavelength scale of the spectrometer was calibrated using polystyrene film (0.013 mm thick). The day-to-day reproducibility of the absorption maxima was $\pm 0.3\ cm^{-1}$.

The preparation procedure and characteristics of substituted phenyl and alkyl benzoates (Refs 1–5, 29–33 and references cited therein) as well as the ^1H and ^{13}C NMR spectra for phenyl 4-*tert*-butylbenzoate, phenyl 3-dimethylaminobenzoate, 3-fluorophenyl benzoate, and 3-cyanophenyl benzoate are available in the supplementary material. The purity of some of the compounds, X-$C_6H_4CO_2C_6H_5$ (X═2-F, 2-Cl, 2-Br, 2-I, 2-OCH_3, 2-CF_3, H), first of all those that showed two peaks in the carbonyl stretching region of the IR spectra—was additionally checked using GC-MS method. The mass spectrum of the non-substituted phenyl benzoate[34] served as the reference spectrum in the interpretation of the mass spectra of the substituted phenyl benzoates (see supplementary material).

CALCULATIONS

Energies, the absorption frequencies of the C═O group, ν_{CO}, and the dipole moments, μ, for 12 *trans* and *cis*

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conformers of *ortho*-substituted phenyl benzoates, 2-X-$C_6H_4CO_2C_6H_5$, (H, CH_3, NH_2, CN, NO_2, OCH_3, Cl, F, Br, CF_3, $C(CH_3)_3$, 2,6-$(CH_3)_2$) and *meta*- and *para*-substituted phenyl benzoates, X-$C_6H_5CO_2C_6H_5$ (X═4-NO_2, 4-NH_2, 4-OCH_3, 3-Cl) were calculated by the DFT method at the B3LYP/6-311+G** level (Table S1). The geometry optimizations, and frequency calculations and rotational barrier calculations for 10 *trans* and *cis* conformers of *ortho*-substituted methyl benzoates, 2-X-$C_6H_4CO_2CH_3$ (X═H, Cl, F, Br, NO_2, CN, CF_3, CH_3, OCH_3, NH_2) were performed by the DFT method at the B3LYP/6-31+G** level (Table S2). The Gaussian 03 program[35] was used. The smaller 6-31+G** basis set was chosen for the more computation-intensive rotational barrier calculations. It gives good agreement with the experimental results for unsubstituted phenyl benzoate, and the results obtained with the larger 6-311+G** basis set are not significantly different (See also reference 36.) Since methyl and phenyl esters of substituted benzoic acid show very similar behavior in the correlation analysis, the smaller system (methyl benzoate) was chosen instead of bulky phenyl benzoate for the calculations of rotational barriers in the *ortho*-substituted esters. This approach is valid because the barrier height is mainly determined by the steric interaction of the *ortho* substituent and the O═C—O moiety. The influence of the alkyl part of the ester is small. The rotational barriers were calculated by constrained optimizations of the dihedral angle (O═C—C═C) at 15° increments from 0 to 180°. This was done in such a way that all remaining geometry parameters were allowed to be optimized. The existence of the hydrogen bond in the *cis*-2-NH_2-benzoate was checked with the Atoms In Molecules (AIM) approach at the same level of theory. Geometry optimizations were also performed for unsubstituted and 2-Cl-phenyl hydrocinnamate and 2-Cl-phenyl benzoate.

RESULTS

C═O stretching frequencies

The infrared carbonyl stretching frequencies ν_{CO} for *meta*-, *para*-, and *ortho*-substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, X-$C_6H_4CO_2C_6H_5$ and alkyl benzoates, $C_6H_5CO_2R$, recorded in tetrachloromethane, are listed in Tables S3 and S4.

The splitting of the carbonyl band was observed for the following esters: $C_6H_5CO_2C_6H_4$-X (X═3-OH) and X-$C_6H_4CO_2C_6H_5$ (X═2-OCH_3, 2-F, 2-Cl, 2-Br 2-I, 2-CF_3). In order to get more accurate estimates of the carbonyl stretching frequencies deconvolution of the carbonyl bands using Igor Pro[37] was performed. (Voigt profiles showed better fit to the experimental data than the Gaussian or Lorenzian profiles.) The results are shown in Table S1. Using the deconvolution approach it was also possible to obtain the $(\nu_{CO})_{max}$ values for the *cis* and *trans* conformers of 2-CN and 2-NO_2 phenyl benzoates for which no splitting of the carbonyl band was observable in the spectra.

The observed range of the $(\nu_{CO})_{max}$ values (Tables S3 and S4) is 1709–1758 cm^{-1} for *ortho*-, *meta*-, and *para*-substituted phenyl benzoates and 1724–1748 cm^{-1} for alkyl benzoates.

Data analysis

The values of $\nu_{C=O}$ for substituted phenyl and alkyl benzoates were treated according to the following equations:

$$(\nu_{CO})_{m,p,ortho} = (\nu_{CO})_o + c_{1(m,p)}\sigma^o + c_{2(ortho)}\sigma_I + c_{3(ortho)}\sigma_R^o + c_{4(ortho)}\left(E_s^B\right)_{ortho} \quad (1)$$

$$(\nu_{CO})_p = (\nu_{CO})_o + c_1\sigma \quad (2)$$

$$(\nu_{CO})_p = (\nu_{CO})_o + c_1\sigma_p^+ \quad (3)$$

$$(\nu_{CO})_{ortho} = (\nu_{CO})_o + c_1\sigma_I + c_2\sigma_R^+ + c_3\left(E_s^B\right)_{ortho} \quad (4)$$

$$(\nu_{CO})_{ortho-trans} = (\nu_{CO})_o + c_1\sigma_p^+ + c_3\left(E_s^B\right)_{ortho} \quad (5)$$

$$(\nu_{CO})_R = (\nu_{CO})_o + c_1\sigma^* + c_2\left(E_s^B\right)_{Alk} \quad (6)$$

$$(\nu_{CO})_R = (\nu_{CO})_o + c_1\sigma_I + c_2\left(E_s^B\right)_{Alk} \quad (7)$$

The carbonyl stretching frequencies ν_{CO} of *meta*-, *para*-, and *ortho*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, and the phenyl esters of *meta*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, were treated according to Eqn (1). The ν_{CO} values in the phenyl esters of *para*-substituted benzoic acids and the phenyl esters of *ortho*-substituted benzoic acids were correlated according to Eqns (2)–(5). The carbonyl stretching frequencies ν_{CO} of substituted alkyl esters of benzoic acid, $C_6H_5CO_2R$, were analyzed with Eqns (6) and (7).

The Taft' s polar σ°,[38,39] inductive σ_I,[40] the resonance σ_R^o $[\sigma_R^o = (\sigma^\circ)_{para} - \sigma_I]$,[41] and steric $(E_s^B)_{ortho}$ scales[1,5] were used with Eqns (1), (4), and (5). $(E_s^B)_{ortho} = \log k_{H^+}^X - \log k_{H^+}^H$, where $k_{H^+}^X$ and $k_{H^+}^H$ are the rate constants for the acidic hydrolysis of *ortho*-substituted and unsubstituted phenyl benzoates in water at 50°C. σ and σ_p^+ in Eqns (2)–(3) are the Hammett and Brown and Okamoto substituent constants, respectively.[39] σ_R^+ in Eqn (5) is the resonance substituent constant, characteristic of through-resonance ($\sigma_R^+ = R^+$).[39] The unsubstituted phenyl benzoate (X═H) was also included in the data treatment of the *ortho*-substituted derivatives according to Eqn (1).

To correlate the ν_{CO} values of substituted alkyl esters of benzoic acid, $C_6H_5CO_2R$, (Eqns (6) and (7)) both the Taft σ^* substituent constants[42,43] and the induction constants σ_I[44] were used as the polar substituent parameter. The σ_I scale was chosen in order to compare the influence of the induction effect of the aliphatic substituents —CH_2X and

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that of *meta*- and *para*-substituted phenyls —C_6H_4X. Steric substituent constants for the variable substituent in the alkyl component of the ester, $(E_s^B)_{Alk}$ were calculated as follows: $(E_s^B)_{Alk} = (\log k_{H+}^R - \log k_{H+}^{CH_3})$, where k_{H+}^R and $k_{H+}^{CH_3}$ are the rate constants for the acidic hydrolysis of R-substituted and CH_3-substituted alkyl benzoate or acetate in water.[2]

The data treatment was carried out using a multiple parameter linear least squares (LLSQ) procedure.[45] Exclusion of significantly deviating points was performed at confidence level 0.99.

The results of the statistical data treatment according to Eqns (1)–(7) for the carbonyl stretching frequencies ν_{CO} of the esters $C_6H_5CO_2C_6H_4$-X, X-$C_6H_4CO_2C_6H_5$, and $C_6H_5CO_2R$ are listed in Table 1.

For comparison the carbonyl stretching frequencies ν_{CO} taken from the literature for *meta*-, *para*-, and *ortho*-substituted methyl benzoates,[6] 3-phenyl propioanates,[19] benzoic acids,[46–49] alkyl esters of benzoic acid,[23] $C_6H_5CO_2R$ and ethyl acetates,[24] $XCH_2CO_2CH_2CH_3$, were correlated via Eqns (1)–(7) as well (Table S5). The substituent constants used for the correlations are listed in Table S6 and Table S7.

Figure 1 illustrates the relationship between the ν_{CO} values and σ^o or $(\sigma_I)_{ortho}$ constants for substituted phenyl esters of benzoic and 3-phenylpropionic acids. The relationships between the $\nu_{CO} - c(E_s^B)_{ortho}$ values and σ_p^+, $(\sigma_I)_{ortho\text{-}cis}$ and $(\sigma_p^+)_{ortho\text{-}trans}$, for phenyl esters of *para*- and *ortho*-substituted benzoic acid are shown in Fig. 2.

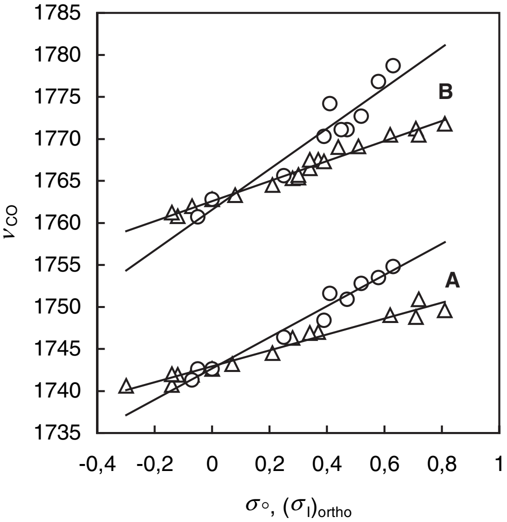

Figure 1. Relationship between the ν_{CO} values and σ^o or $(\sigma_I)_{ortho}$ constants for substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, (A) and 3-phenylpropionic acids, $C_6H_5(CH_2)_2CO_2C_6H_4$-X, (B). For *meta* and *para* substituents (Δ) σ^o and for *ortho* substituents (○) σ_I were used.

Computational results

The DFT calculations show the existence of *cis*- and *trans*-conformations (with respect to the carbonyl group) for nearly all *ortho*-substituted benzoates as confirmed by energy minima and absence of imaginary vibrations. The computed carbonyl absorption frequencies $(\nu_{CO})_{calc}$ of *cis*

Table 1. Results of the treatment of the ν_{CO} values for substituted phenyl and alkyl esters of benzoic acid with Eqns (1)–(7)

Ester	Eqn	$(\nu_{CO})_o$	c_1	c_2	c_3	n/n_0[a]	R	s_o
$C_6H_5CO_2C_6H_4$-X	1	1743.3 ± 0.2	8.19 ± 0.40	—	—	14/15[b]	0.984	0.174
	1	1742.6 ± 0.3	18.7 ± 0.8	0	0	11/11[c]	0.985	0.173
	1	1743.3 ± 0.2	8.21 ± 0.40	18.1 ± 0.5	2.0 ± 0.7[d]	23/25	0.991	0.130
X-$C_6H_4CO_2C_6H_5$	1	1741.7 ± 0.2	11.6 ± 1.1	—	—	5/5[e]	0.983	0.186
	2	1740.3 ± 0.6	10.6 ± 1.4	—	—	8/9[f]	0.944	0.330
	3	1742.3 ± 0.3	7.41 ± 0.34	—	—	8/9[f]	0.993	0.122
	4	1740.0 ± 1.5	22.0 ± 2.5	0	-21.5 ± 3.3	10/10[g]	0.971	0.239
	4	1741.5 ± 0.9	18.4 ± 1.7	0	-23.2 ± 1.8	8/8[g,h]	0.991	0.133
	4	1740.6 ± 0.6	0	14.1 ± 0.7	-8.38 ± 1.70	7/8[i]	0.994	0.108
	5	1734.0 ± 0.6	12.6 ± 0.6	—	-11.9 ± 1.6	7/7[i,j]	0.995	0.104
$C_6H_5CO_2R$	6	1725.8 ± 1.6	25.9 ± 1.7	30.8 ± 4.4	—	8/8	0.989	0.150
	7	1725.9 ± 1.8	57.6 ± 3.9	30.7 ± 4.7		8/8	0.987	0.160
	6	1726.6 ± 1.5	25.5 ± 1.3	32.5 ± 3.7	—	7/7[k]	0.993	0.133
	7	1726.7 ± 1.7	56.8 ± 3.6	32.2 ± 4.4		7/7[k]	0.993	0.160

[a] n_o, the total number of data subjected to the regression data treatment; n, the number of points left after exclusion of significantly deviating points, confidence level 0.99.

[b] Only *meta*- and *para*-substituted derivatives included.

[c] *Ortho*-substituted derivatives included.

[d] $c_4 = 0$.

[e] Only *meta*-substituted derivatives were included.

[f] Included *para*-substituted derivatives. 4-F derivative excluded.

[g] ν_{CO} values for *cis* isomers (with respect to the carbonyl group) of phenyl esters of 2-substituted benzoic acids calculated by deconvolution of carbonyl bands as well as unsubstituted derivative and 2-CH_3 derivative (X=H, NO_2, F, Cl, Br, I, OCH_3, CN, CF_3, CH_3) were included (Table 1).

[h] 2-CH_3 and 2-I derivatives omitted.

[i] ν_{CO} values for *trans* isomers calculated by deconvolution of carbonyl bands (NO_2, F, Cl, Br, I, OCH_3, CN, CF_3) included (Table 1). 2-NO_2 derivative excluded during data treatment.

[j] 2-NO_2 derivative omitted.

[k] The CH_3CH_2 derivative was omitted before data processing.

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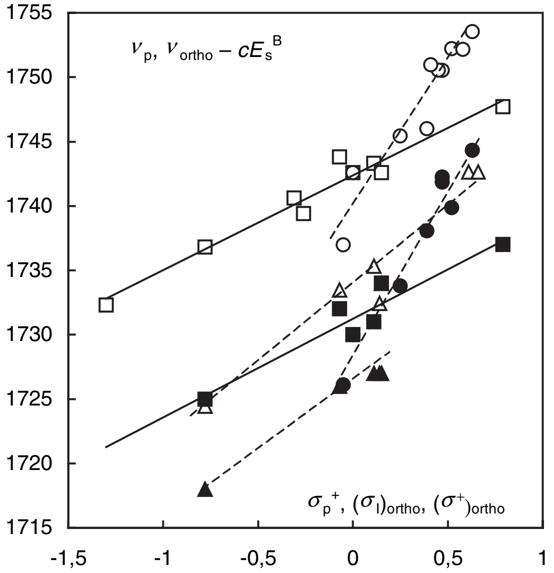

Figure 2. Relationship between the ν_{CO} and $(\nu_{CO}-cE_s^B)_{ortho}$ values and substituent constants for phenyl (□, ○, △) and methyl esters (■, ●, ▲) of *para*- and *ortho*-substituted benzoic acids. For *para* substituents σ_p^+ (□, ■), *ortho cis* derivatives $(\sigma_I)_{ortho}$ (○, ●) and for *ortho trans* derivatives (△, ▲) $(\sigma_p^+)_{ortho}$ were used.

and *trans* conformers for phenyl esters of *ortho*-substituted benzoic acid, X-$C_6H_4CO_2C_6H_5$, are presented in Table S1. Those for *ortho*-substituted methyl benzoates X-$C_6H_4CO_2CH_3$ are presented in Table S2. Both computed frequencies were found to be linearly correlated with the corresponding experimental ν_{CO} values for the *cis* and *trans* conformers (Tables S3). For phenyl esters of substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, we found:

$$(\nu_{CO})_{calc} = (-0.0005 \pm 0.0080) + (1.302 \pm 0.046)\nu_{CO} \tag{8}$$

$$R = 0.989,\ s_0 = 0.15,\ n/n_0 = 20/21,$$
$$X = trans-2-CN \text{ excluded}$$

The same relationship for methyl esters of substituted benzoic acids, X-$C_6H_4CO_2CH_3$, is expressed as follows:

$$(\nu_{CO})_{calc} = (-0.0006 \pm 0.0001) + (1.357 \pm 0.078)\nu_{CO} \tag{9}$$

$$R = 0.982,\ s_0 = 0.188,\ n/n_0 = 11/12,$$
$$X = trans-2-Br \text{ excluded}$$

In agreement with the experiment, the computed ν_{CO} frequencies for the *trans* rotamers are lower than those for the *cis* rotamers (except 2-NH_2 phenyl benzoate). The wave number difference between the two forms was of 5–48 cm^{-1}, with the smallest differences in frequency values for 2-NO_2-, 2-CH_3-, and 2-CN-rotamers (5, 7, and 23 cm^{-1}, respectively).

The energy calculations by the DFT method confirmed that *trans* conformers are more stable than the corresponding *cis* conformers in both the phenyl and methyl esters of *ortho*-substituted benzoic acids for the following substituents: X═CN, OCH_3, F, CF_3, NO_2, Cl, Br (for phenyl 2-chloro- and 2-bromobenzoates $\Delta G_{trans/cis} = 0$), whereas alkyl substituents X═CH_3, $C(CH_3)_3$ are preferably located near to the carbonyl group (Tables S1 and S2).

Relatively low rotational barriers of the ester group with respect to the aromatic ring plane found for *ortho*-substituted methyl benzoates (Table S2) and the small energy differences of the *cis* and *trans* conformations indicate that both conformations should be well enough populated. The calculations reveal a trend of the rotational barrier to depend on the size of substituents: the larger substituents tend to decrease the barrier to the rotation and it is the highest for the unsubstituted methyl benzoate (~6.6 kcal/mol). The exception is 2-NH_2-benzoate, the *cis* form of which forms a hydrogen bond with the carbonyl oxygen. Therefore, this configuration is significantly stabilized, in comparison to the *trans* form, and its rotational barrier (~10.6 kcal/mol) is almost twice as high as that for the unsubstituted ester.

In both the phenyl and methyl esters of *ortho*-substituted benzoic acids (Tables S1 and S2) the carboxyl groups plane was found to be nearly coplanar with the benzene ring plane for the smallest substituents CN (the steric parameter $E^B_{s\ ortho} = -0.03$) and F ($E^B_{s\ ortho} = -0.15$) in both *cis* and *trans* isomers. For the bulkiest *ortho* substituents 2-CF_3 ($E^B_{s\ ortho} = -0.593$) and 2-$C(CH_3)_3$ ($E^B_{s\ ortho} = -0.604$) in both *cis* and *trans* isomers the carboxyl group was out of the aromatic ring plane by about 38° and 53°, respectively. The difference in the values of dihedral angle O═C—C═C calculated for phenyl esters and methyl esters of *ortho*-substituted benzoic acids is in the range 5–10° in the case of substituents X═CH_3, CN, NH_2, Cl, F, OCH_3, CF_3, NO_2 (Tables S1 and S2).

The values of the dihedral angle O═C—C═C for the phenyl esters of *ortho*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$, and methyl benzoates, X-$C_6H_4CO_2CH_3$ (the values of the dihedral angle are shown in brackets) for *cis* and *trans* forms were: 2-CH_3: 4.2°, (0°), 175.4°, (180°); 2-NH_2: 0.4°, (0°), 175.5°, (180°); 2-CN: 2.2°, (0°), 162.9°, (180°); 2-Cl: 26.2°, (24.0°), 147.7°, (153.7°); 2-F: 10.8°, (0°), 172.2°, (180°); 2-OCH_3: 28.3°, (17.8°), 153.1°, (166.1°); 2-CF_3: 37.6°, (36.4°), 140.2°, (142.3°); 2-NO_2: 81.6°, 134.8°, (137.8°), 2-Br: 29.1°, (0°), 144.6°, (180°); 2-$C(CH_3)_3$: 52.8°, 125.9°.

The dihedral angle (═C—O—C═C—) between the ester group's plane and the aromatic ring plane of the phenoxy part of esters for 2-H-, 2-Cl-phenyl hydrocinnamate and 2-H-, 2-Cl-phenyl benzoate was computed to be 63.3°, 86.45°, 63.7°, and 90.5°, respectively.

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The hydrogen bond was proved for methyl *ortho*-NH_2-benzoate according to criteria given in Ref. [50] by $=$O..H— bond distance, electron density and Laplacian (1.937 Å, 0.029 and 0.094 au, respectively). This result is well in line with the high rotational barrier of the carbonyl bond in respect to the aromatic ring plane of benzoate in this molecule.

DISCUSSION

Influence of substituents

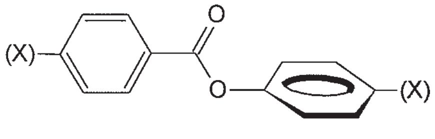
The ν_{CO} frequencies increase with increasing σ values of the corresponding substituent (Tables 1, S3 and S4). It means that electron-withdrawing substituents increase and electron-donating substituents decrease ν_{CO} values, which is similar to the findings of previous works in this field. Since the stretching frequencies are proportional to the bond force constants, higher wave numbers indicate higher formal bond orders of the carbonyl bond. The electron-withdrawing substituents are considered to suppress the polarization of the C$=$O bond or diminish the C$=$O bond resonance forms stabilization.[21,25,25,51]

Carbonyl stretching frequencies ν_{CO} for *meta*- and *para*-substituted phenyl esters of benzoic and propionic acids as well as phenyl and methyl esters of *meta*-substituted benzoic acids showed good correlation with the σ^o constants ($R > 0.980$). The influence of the through resonance effect to ν_{CO} was found to be also important in the phenyl esters of *para*-substituted benzoic acids. It was found that the carbonyl stretching frequencies ν_{CO} of phenyl and methyl benzoates in the case of $+R$ *para* substituents in the acyl group correlated better with the Okamoto and Brown σ_p^+ constants in comparison to the Hammett σ constants (Tables 1 and S5).

The polar influence of *meta*, *para*, and *ortho* substituents in the benzoyl part of the ester on the carbonyl stretching frequencies ν_{CO} was found to be only about 1.3 times stronger than in the case of substituents in the aroxy part of the esters. The magnitudes of c_1 calculated according to Eqn (1) for *meta*- and *para*-substituted phenyl benzoates in the case of substituents in the aroxy part and in the case of substituents in the benzoyl part were found to be 8.19 and 11.6, respectively. In the case of *ortho* substituents, the corresponding values of c_1 found from Eqns (1) and (4) appeared to be 18.1 and 22.0 (Table 1) giving the ratios $(c_I)_{ortho}/(c_I)_{m,p} \approx 2.0$ for both series. The same ratio was nearly 1.5 for the alkaline hydrolysis of substituted phenyl benzoates in water.[1,5]

The inductive influence of substituents X in the alkyl chain CH_2X of $C_6H_5CO_2CH_2X$ on the carbonyl stretching frequencies ν_{CO} was found to be 6.7 times stronger than that of substituents in *meta* and *para* positions in the corresponding aromatic series and 3.1 times stronger than the influence of *ortho* substituents from aroxy part of the esters. For the alkaline hydrolysis of the same esters in water, the inductive effect of substituents X in the alkyl chain CH_2X appeared to be approximately four times stronger than that in *meta* and *para* positions of the aromatic ring.[2]

A good correlation of the carbonyl stretching frequencies ν_{CO} with σ^o for *para*-substituted phenyl esters of benzoic acid shows the absence of the through-resonance between the electron-donating substituents and carbonyl group. This is in agreement with Exner[52] and Cohen[19] who proposed *s-trans* conformation for phenyl esters where the carbonyl group in the phenyl ester is nearly perpendicular to the aroxy plane (Structure 1), which is also confirmed by the calculations. One of the primary requirements for the resonance interaction between two groups is mutual coplanarity of these groups. The carbonyl stretching frequencies ν_{CO} for phenyl and methyl esters of *para*-substituted benzoic acid show correlation with σ_p^+ substituent constants in the case of electron-donor substituents. Thus, the presence of the resonance between $+R$ substituents and the carbonyl group indicates that the benzene ring in the benzoyl part of the ester is coplanar with the carboxyl group (Structure 1):



Structure 1

The split of the experimental carbonyl stretching bands (Table S3) in the case of some phenyl esters of *ortho*-substituted benzoic acids can be explained by conformational isomerism, which is supported by the calculations. At the same time the possibility of a Fermi resonance cannot be excluded.

In the case of substituents in the aroxy part of the esters, ($C_6H_5CO_2C_6H_4$-X, $C_6H_5CO_2R$) (except X$=$3-OH) the splitting of the carbonyl absorption maximum was not observed. Due to the rotation of the aromatic plane in the phenoxy part out of the carbonyl plane by nearly 90°, there is essentially only one conformation for the *ortho* derivatives possible.

The carbonyl stretching frequencies, $\nu_{CO,}$ for *ortho*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X (X$=$H, NO_2, CN, CF_3, $N(CH_3)_2$, F, Cl, I, OCH_3, CH_3, $C(CH_3)_3$), showed a good correlation only with the inductive constant σ_I, while resonance and steric factors appeared to be insignificant (Fig. 1, Table 1):

$$\begin{aligned}(\nu_{CO})_{m,p,ortho} &= \\ (1743.3 \pm 0.2) &+ (8.21 \pm 0.4)_{m,p}\sigma^o \\ &+ (18.1 \pm 0.5)_{ortho}\sigma_I + (2.0 \pm 0.7)_{ortho}\sigma_R^o\end{aligned} \tag{10}$$

$R = 0.991,\ s_0 = 0.130,\ n/n_0 = 23/25$

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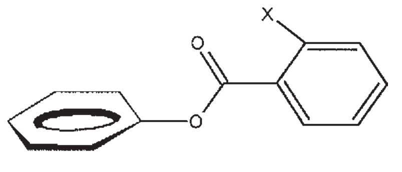
However, in addition to σ_I inductive constants, resonance σ_R^o constants were also required to correlate the ν_{CO} values for *ortho*-substituted phenyl esters of 3-phenyl propionic acid (Table S5).

Similar to methyl benzoates[7] the lower carbonyl stretching frequency for *meta*-hydroxyphenyl benzoate $\nu_{CO} = 1716.2\,cm^{-1}$ could be ascribed to dimers or trimers, which are formed by the intermolecular H-bond between carbonyl oxygen and hydrogen of the *meta*-hydroxyl substituent. In the hydroxyl absorption region the spectrum of the *meta*-hydroxyphenyl benzoate shows a band at $3606\,cm^{-1}$ and also a broad band with the maximum at $\nu_{CO} = 3441 cm^{-1}$ that could be ascribed to hydrogen bonded associates.

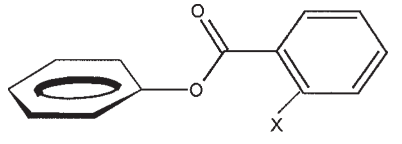
In the case of the *ortho* substituents X═Cl, F, Br I, OCH_3, CF_3 in the benzoyl part of phenyl benzoates, 2-X-$C_6H_4CO_2C_6H_5$, the split of the carbonyl experimental stretching bands was observed. The experimental ν_{CO} values of phenyl esters of *ortho*-substituted benzoic acid show only one carbonyl stretching band in the carbonyl stretching region in the case of strong electron-acceptor substituents (–*I* and –*R* substituents: NO_2, CN), strong electron repelling substituents (+*R* substituent: NH_2) and for substituents showing weak substituent effect (CH_3). Two carbonyl bands were found for substituents, which exhibit both the relatively strong inductive and resonance effects. According to the frequency calculations there are two conformations possible in the case of all *ortho* substituents (Tables S1 and S2).

Due to the existence of the hydrogen bond for *cis*-2-NH_2-benzoate, the high rotational barrier and energetically less favorable *trans*-configuration may result in a very poor population of the *trans* form. Separation of the experimental carbonyl bands by deconvolution gave two very close bands for phenyl 2-nitro- and 2-CN-benzoates as well. There is also a good agreement with the conformations of the corresponding *ortho*-substituted methyl esters and benzoic acids.[6,46]

On the grounds of the infrared spectra, correlation analysis and DFT calculations we assume that phenyl and methyl esters of *ortho*-substituted benzoic acids can exist in two conformations: *ortho* substituents in *cis* and *trans* positions relative to the carbonyl group (Structures 2 and 3) whereas the lower frequency component corresponds to the *trans* rotamer and the higher frequency component may be attributed to the *cis* rotamer.



Structure 2 *cis* conformer



Structure 3 *trans* conformer

Correlation analysis using Eqns (4) and (5) showed that both the inductive and the steric scales were essential to correlate the ν_{CO} values of the *cis* rotamers in the phenyl esters of *ortho*-substituted benzoic acids, 2-X-$C_6H_4CO_2C_6H_5$ (X═H, CH_3, NO_2, CN, Cl, F, Br, I, OCH_3, CF_3), while the resonance term appeared to be insignificant and was excluded during the data processing (Fig. 2, Table 1):

$$(\nu_{CO})_{cis-ortho} = (1740.0 \pm 1.5) + (22.0 \pm 2.5)_{ortho}\sigma_I - (21.5 \pm 3.3)_{ortho}E_s^B \qquad (11)$$

$R = 0.971,\ s_0 = 0.239,\ n/n_0 = 10/10$

Correlation becomes better if 2-CH_3 and 2-I derivatives were omitted:

$$(\nu_{CO})_{ortho-cis} = (1741.5 \pm 0.9) + (18.4 \pm 1.7)_{ortho}\sigma_I - (23.2 \pm 1.8)_{ortho}E_s^B \qquad (12)$$

$R = 0.991,\ s_0 = 0.133,\ n/n_o = 8/8$

The *trans* conformers in the phenyl esters of *ortho*-substituted benzoic acids (X═CN, CF_3, OCH_3, F, Cl, I, Br) are very well described by the dual parameter Eqn (5) (Table 1):

$$(\nu_{CO})_{ortho-trans} = (1734.0 \pm 0.6) + (12.6 \pm 0.6)_{ortho}\sigma_p^+ - (11.9 \pm 1.6)_{ortho}E_s^B \qquad (13)$$

$R = 0.995,\ s_0 = 0.104,\ n/n_0 = 7/7$

The ν_{CO} value for *trans* conformation of phenyl 2-nitrobenzoate was omitted as it was excluded during the data treatment.

The correlations similar to Eqns (12) and (13) were obtained for *cis* and *trans* isomers in *ortho*-substituted methyl benzoates and benzoic acids (Table S5).

The strong inductive effect ($c_1 = 22.0$) of the *ortho* substituents in *cis* position with respect to the carbonyl group diminishes the C═O bond resonance forms stabilization thus increasing essentially the carbonyl stretching frequencies compared to the non-substituted ester. The *trans* isomers of phenyl and methyl esters of *ortho*-substituted benzoic acids showed direct polar resonance effect to nearly the same extent as in the case of +*R para* substituents (Tables 1 and S5, Fig. 2).

The positive steric term, found for both the *cis* and *trans* conformers could be considered as measure of the steric inhibition of resonance between the phenyl ring in

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benzoyl part and the carbonyl group caused by *ortho* substituents. It is in accordance with the values of the corresponding dihedral angles calculated for the phenyl and methyl esters of *ortho*-substituted benzoic acids (Tables S1 and S2) and benzoic acids.[46] In the case of bulky CF_3 group in *ortho* position the carbonyl groups plane was found to be more twisted out of the benzene ring plane (by 38°) compared to that for the smallest ones CN and F (in phenyl esters by 2° and 11°, respectively, and in methyl esters by 0° in both cases). In *cis* isomers the steric inhibition of resonance between of phenyl ring and carbonyl group was found to be about twice larger than in trans isomers (Eqns (12) and (13)).

The through $+R$ resonance in the case of *para* and *trans ortho* substituents in acyl part of the esters stabilizes the resonance form of carbonyl bond $C^+—O^-$ decreasing the corresponding carbonyl stretching frequencies ν_{CO}. Inductive effect of the electronegative substituents increases the bond order of the C═O bond and therefore the carbonyl stretching frequencies ν_{CO} become higher compared to unsubstituted derivative. In Fig. 2 the points for the *trans ortho* substituents do not fall on the same straight line with *para* substituents. It has been proposed[53] that in the case of *trans* isomers an additional through space interaction between the negatively charged heteroatom of the *ortho* substituent and the positively charged C atom of the carbonyl group could stabilize the resonance form of the carbonyl bond. Furthermore, in the case of *trans* rotamers of phenyl esters of *ortho*-substituted benzoic acids the additional through space interaction appeared to surpass the inductive influence of the *ortho* substituents from *trans* position.

In the case of the phenyl ester of *ortho*-amino benzoic acid only one carbonyl band was observed ($\nu_{CO} = 1709.8\,cm^{-1}$). Very low value of ν_{CO} shows strong interaction between the *ortho* NH_2 substituent and the carbonyl CO group. Similar to acetophenones[54] this could be explained by the intramolecular NH…O hydrogen bond that depresses the ν_{CO} value considerably. This hypothesis is also supported by the DFT calculations.

As was mentioned above, another alternative explanation for the splitting of the carbonyl band, namely Fermi resonance, cannot be excluded.[25,26] The Aryl–C stretch appears to be at around 850–870 cm^{-1}. When the overtone of this vibration happens to be at the similar frequency to the C═O stretch vibration, the C═O stretch band splits resulting in the higher and lower stretching frequency compared to the fundamental carbonyl stretching bands. At the molecular level, this interaction is due to an overlapping of the *p* orbitals. This overlapping forms an extended system where electrons are delocalized. The lower stretching frequencies are considered to be caused by expanded conjugation effects. The introduction of a C═C bond adjacent to the carbonyl group results in the electron delocalization in the carbonyl double bond. Resonance increases the single bond character of the C═O bond and consequently, lowers its force constant resulting in the lower frequency of carbonyl absorption.

We propose that the split of the experimental carbonyl stretching bands in the phenyl esters of *ortho*-substituted benzoic acids (Table S3) could be ascribed to the conformational isomerism rather than to Fermi resonance. The existence of *cis*/*trans* conformations was supported by frequency calculations with Density Functional Theory (DFT) method (Table S1). Between the computed frequencies, $(\nu_{CO})_{calc}$, for *cis* and *trans* rotamers, and the corresponding experimental ν_{CO} values was found an excellent correlation (Eqn (8), $R = 0.989$). Similarly, earlier[6,9] study of the variation of the ν_{CO} values with solvent and temperature proved that in *ortho*-substituted methyl and *t*-butyl benzoates the split of the split carbonyl stretching bands has been attributed to *cis* and *trans* isomers but not to Fermi resonance.

The carbonyl stretching frequencies ν_{CO} for substituted alkyl benzoates, $C_6H_5CO_2R$, and for ethyl esters of substituted acetic acids,[24] $XCH_2CO_2C_2H_5$, were found to be dependent on both the inductive and the steric effects of substituents (Tables 1 and S5). The stronger electron-acceptor substituents in alkyl benzoates shift the carbonyl stretching frequencies ν_{CO} towards higher values. However, due to the steric consequences the influence of the inductive effect is suppressed and the carbonyl stretching frequencies of the substituted alkyls appeared to be lower than expected.

CONCLUSIONS

Substituted phenyl benzoates with *ortho*, *meta*, and *para* substituents as well as alkyl substituents in the ester part ($C_6H_5CO_2C_6H_4$-X, $C_6H_5CO_2R$) showed experimentally a single infrared carbonyl stretching band. In the case of *ortho* substituents (X═Cl, Br, I, F, OCH_3, CF_3) in benzoyl part in substituted phenyl benzoates, X-$C_6H_4CO_2C_6H_5$, doublet infrared carbonyl stretching bands were observed. Calculations with the DFT method and correlation analysis proved for *meta*- and *para*-substituted phenyl benzoates *s-trans* conformation where the plane of the benzene ring in the benzoyl part of the ester is coplanar with the carbonyl bond plane and the plane of the benzene ring in the phenoxy part is twisted nearly perpendicular relative to the carboxyl bond plane. The calculations with DFT method at the B3LYP/6-311+G** and 6-31+G* levels and correlation analysis support the existence of *cis* and *trans* conformations with respect to the carbonyl bond for the phenyl and methyl esters of *ortho*-substituted benzoic acids. The *ortho* substituent effect on ν_{CO} for *cis* rotamers in benzoyl part of esters was described by the inducive σ_I and the steric E_s^B scales. To correlate the substituent effect in *trans* isomers both the σ_p^+ scale characteristic of the direct polar

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resonance and steric E_s^B scale were significant. In both *cis* and *trans* conformers the aromatic plane in benzoyl part of the esters was twisted out of coplanarity with respect to the carbonyl bond plane due to the steric hindrance of *ortho* substituents.

Supplementary material

The following supplementary material is available in Wiley Interscience:

Table S1, the results of DFT B3LYP/6-311+G** calculations of electronic energies *E*, Gibbs energies *G* (at 298 K), IR frequencies ν_{CO}, and dipole moments μ for substituted phenyl benzoates; Table S2, results of DFT calculations for methyl esters of 2-substituted benzoic acids; Table S3, infrared carbonyl stretching frequencies ν_{CO} for substituted phenyl esters of benzoic acid and phenyl esters of substituted benzoic acids in CCl_4; Table S4, infrared carbonyl stretching frequencies ν_{CO} for substituted alkyl benzoates, $C_6H_5CO_2R$ in CCl_4; Table S5, results of the literature ν_{CO} values treatment according to Eqns (1)–(7) for substituted phenyl esters of 3-phenylpropionic acid, methyl esters of benzoic acids, benzoic acids, alkyl esters of benzoic acid, and alkyl esters of acetic acid; Table S6, the substituent constants for *meta*-, *para*-, and *ortho*-substituents used in correlations; Table S7, the substituent constants for alkyl substituents used in correlations. The preparation procedure and analyses of substituted phenyl and alkyl benzoates; the ^1H and ^{13}C NMR spectra for phenyl 4-*tert*-butylbenzoate, phenyl 3-dimethylamino benzoate, 3-fluoro- and 3-cyanophenyl benzoates are available as supplementary material. This material is available at the epoc website at http://www.wiley.com/epoc. at Wiley Interscience.

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