^{17}O NMR STUDY OF *ortho* AND ALKYL SUBSTITUENT EFFECTS IN SUBSTITUTED PHENYL AND ALKYL ESTERS OF BENZOIC ACIDS

Vilve NUMMERT[1], Vahur MÄEMETS[2], Mare PIIRSALU[3], Signe VAHUR[4] and Ilmar A. KOPPEL[5,*]

Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia;
e-mail: [1] vilve.nummert@ut.ee, [2] vahur.maemets@ut.ee, [3] mare.piirsalu@ut.ee,
[4] signe.vahur@ut.ee, [5] ilmar.koppel@ut.ee

Received May 9, 2011
Accepted August 10, 2011

---

^{17}O NMR spectra for 44 *ortho*-, *meta*- and *para*-substituted phenyl and alkyl benzoates ($C_6H_5CO_2C_6H_4$-X, $C_6H_5CO_2R$) at natural abundance in acetonitrile were recorded. Substituent effects on the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, of the carbonyl oxygen and the single-bonded phenoxy (OPh) and alkoxy (OR) oxygens have been studied. The $\delta(^{17}O)$ values of the carbonyl oxygen for *para* derivatives showed a good correlation with the $\sigma°$ constants. The $\delta(^{17}O)$ values of carbonyl oxygen for *ortho* derivatives were found to be described well with the Charton equation containing the inductive, σ_I, resonance, $\sigma°_R$, and steric, E_s^B, substituent constants in case the data treatment was performed separately for electron-donating +*R* and electron-attracting –*R* substituents. The electron-donating +*R* *ortho* and *para* substituents in substituted benzoates caused shielding and the electron-withdrawing –*R* substituents produced deshielding of the O signal. The steric interaction of *ortho* substituents with the ester group decreased the electron density at the carbonyl oxygen. In alkyl benzoates the $\delta(^{17}O)$ values were found to be described well with the inductive, σ_I, and the steric, E_s^B, substituent constants.

Keywords: NMR spectroscopy; Substituent effects; Structure–activity relationships; ^{17}O NMR spectra; *ortho* Effect; Phenyl benzoates; Alkyl benzoates.

We have previously investigated the contribution of the inductive, resonance and steric effects of *ortho*, *meta*, *para* and alkyl substituents into the rates of the alkaline hydrolysis in various media (as shown in refs[1–11]), the carbonyl carbon ^{13}C NMR chemical shifts[12], δ_{CO}, and the infrared stretching frequencies of the carbonyl group[13], ν_{CO}, in substituted phenyl benzoates, X-$C_6H_4CO_2C_6H_5$, $C_6H_5CO_2C_6H_4$-X, and alkyl benzoates, $C_6H_5CO_2R$. In the recent paper[14] we studied the *ortho* substituent effect on the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, of the carbonyl oxygen and the

Collect. Czech. Chem. Commun. 2011, Vol. 76, No. 12, pp. 1737–1763

doi:10.1135/cccc2011100

single-bonded phenoxy oxygen in substituted phenyl benzoates, containing substituents in benzoyl moiety, X-$C_6H_4CO_2C_6H_5$.

For comparison, in the present paper we report ^{17}O NMR spectra for 44 *ortho*-, *meta*- and *para*-substituted phenyl esters, $C_6H_5CO_2C_6H_4$-X, and alkyl esters, $C_6H_5CO_2R$, of benzoic acid containing substituents in phenyl and alkyl components (Chart 1).

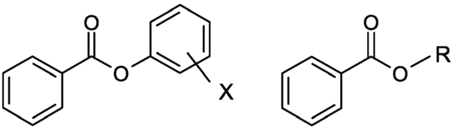

CHART 1

On the bases of determined ^{17}O NMR chemical shifts, $\delta(^{17}O)$, the influence of the substituent inductive, resonance and steric effects on the carbonyl and single-bonded oxygen ^{17}O NMR chemical shifts, $\delta(^{17}O)$, from the phenyl and alkyl components was studied.

The studies regarding the investigation of the *ortho*, *meta* and *para* as well as alkyl substituents effects on the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, using correlation equations for phenyl benzoates and alkyl benzoates involving substituents in phenyl and alkyl moiety appear to be missing in the literature. To the best of our knowledge there are practically no data on the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, except unsubstituted phenyl benzoate[14–18], X = H, available in the literature. One could find in the literature the values of the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, only for phenyl acetates[15,16,19,20], $CH_3CO_2C_6H_4$-X, with X = H, 4-NO_2, 4-OCH_3, 2-CH_3, 2,6-$(CH_3)_2$, phenyl formate[21] ($HCO_2C_6H_4$-X), with X = H, *meta*-substituted phenyl naphthoates[22], and *para*-substituted phenylthiol acetates[23], containing variable substituents in phenoxy part (OPh). In substituted phenyl benzoates the influence of the substituent effects from the aryl moiety on the carbonyl carbon ^{13}C NMR chemical shifts more thoroughly was investigated in refs[24–27]. There are only few chemical shifts, $\delta(^{17}O)$, for substituted alkyl benzoates, ($C_6H_5CO_2R$), involving electronegative substituents available. In the case of alkyl benzoates[15,16,28–33], ($C_6H_5CO_2R$), the chemical shifts, $\delta(^{17}O)$, have been reported for only R = CH_3, CH_2CH_3, $C(CH_3)_3$, CH_2Ph and CH_2CF_3. The influence of substituents on the chemical shifts, $\delta(^{17}O)$, of the oxygen attached to the phenyl group have been studied in the case of *para* substituents for substituted phenols[34–36], anisoles[36–39], vinyl aryl ethers[39], phenoxyethyl derivatives[40] and trialkoxysilanes[41]. The influence of the electronegative substituents on the chemical shifts, $\delta(^{17}O)$, of the single-bonded oxygen attached to the alkyl group was investigated for alcohols[42–46], alkoxygermanes[46] and alkoxysilanes[43]. The $\delta(^{17}O)$ values in alkoxysilanes were found to be dependent on the inductive and steric substituent constants and showed a good linear relationship with the $\delta(^{17}O)$ values for the corresponding alcohols[43]. It was found that the substituent-induced chemical shifts of the single-bonded oxygen in ethers ROR′ correlate well with the ^{13}C chemical shifts for the methylene groups of the corresponding alkanes[39,47,48] RCH_2R' and the substituent-dependent chemical shifts of the double-bonded oxygen in carbonyl group depend on the same factors as the ^{13}C chemical shifts of the β-carbon of alkenes[28,48,49]. The behavior of the ether oxygen atoms (2p level) was found to be similar to that of sp^3 carbons, whereas carbonyl oxygen atoms exhibit the same trends as sp^2 carbon atoms[28,48,49].

In the previous paper[14] in substituted phenyl benzoates, containing substituents in benzoyl moiety, ($X-C_6H_4CO_2C_6H_5$), we studied the influence of the *ortho*, *meta* and *para* substitutent effects on the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, of the carbonyl oxygen and the single-bonded phenoxy oxygen. The $\delta(^{17}O)$ values for *para* and *meta* derivatives with substiuents in benzoyl moiety gave good correlation with the σ^+ and σ_m constants, respectively. The $\delta(^{17}O)$ values for the *ortho*-substituted phenyl benzoates, $X-C_6H_4CO_2C_6H_5$, as well as *ortho*-substituted nitrobenzenes, acetophenones and benzoyl chlorides showed excellent correlation with the Charton equation[50] using the inductive, σ_I, resonance, σ^+_R, and steric, E_s^B, substituent constants in case the data treatment was performed separately for derivatives containing the electron-donating $+R$ substituents and electron-attracting $-R$ substituents[14].

Following our studies on the *ortho* effect in the current work we check the applicability of the Charton equation[50] to describe the influence of *ortho* substituents on the chemical shifts, $\delta(^{17}O)$, in substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4-X$. It was of interest to compare the contributions of the inductive, resonance and steric effects to the $\delta(^{17}O)$ values in phenyl benzoates containing substituents in phenoxy part, $C_6H_5CO_2C_6H_4-X$, with those containing substituents in benzoyl moiety ($X-C_6H_4CO_2C_6H_5$). Similarly, it was of interest to compare the substituent effects in the carbonyl oxygen $\delta(^{17}O)$ values for substituted phenyl benzoates, $C_6H_5CO_2C_6H_4-X$, and alkyl benzoates, $C_6H_5CO_2R$, with the corresponding substituent-induced carbonyl ^{13}C NMR chemical shifts[12], $\Delta\delta_{CO}$, the infrared stretching frequencies[13], $\Delta\nu_{CO}$, and the rates of the alkaline hydrolysis[5,51,52], $\Delta\log k$.

To estimate the steric substituent constants E_s^B for alkyl substituents R = CH_2CF_3, CH_2CCl_3, CH_2CHCl_2, CH_2CH_2Br, the infrared stretching frequencies of the carbonyl group, ν_{CO}, for corresponding substituted alkyl benzoates, $C_6H_5CO_2R$, were determined.

EXPERIMENTAL

NMR Measurements

^{17}O NMR spectra for 32 *ortho*-, *meta*- and *para*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X (X = 4-NO_2, 4-CN, 4-SO_2CH_3, 4-CF_3, 4-F, 4-Cl, 4-CH_3, 4-OCH_3, 4-NH_2, 3-NO_2, 3-CN, 3-CF_3, 3-F, 3-Cl, 3-Br, 3-CH_3, 3-NH_2, 3-$N(CH_3)_2$, 2-NO_2, 2,6-$(NO_2)_2$, 2-CN, 2-CF_3, 2-SO_2CH_3, 2-F, 2-Cl, 2-Br, 2-OCH_3, 2-CH_3, 2-$C(CH_3)_3$, 2,6-$(CH_3)_2$, 2-CO_2CH_3, 2-$COCH_3$), and 12 R-substituted alkyl esters of benzoic acid, $C_6H_5CO_2R$ (R = CH_3, CH_2CH_3, CH_2Cl, CH_2CN, CH_2CF_3, $CH_2C_6H_5$, $CH_2C\equiv CH$, CH_2CHCl_2, CH_2CCl_3, $CH_2CH_2OCH_3$, CH_2CH_2Cl, CH_2CH_2Br), were recorded at natural abundance in acetonitrile (Tables I and II). NMR spectra were recorded on a Bruker Avance II 200 spectrometer equipped with 10 mm BBO for ^{17}O or 5 mm QNP-z probe for ^1H and ^{13}C NMR spectra. For ^{17}O NMR the benzoates were dissolved in the mixture of 1 ml CD_3CN and 2 ml CH_3CN. Acetonitrile-d_3 'Special HOH' 99.8 atom % D (Aldrich) and Acetonitrile SPECTRANAL® (Riedel-de Haën) were used, respectively. Resonance frequency for ^{17}O measurements was 27.13 MHz. Depending on the type of the benzoate, the concentration of the benzoate varied between 0.3 and 1 molal. Temperature of the measurements was 50 °C, and water at 50 °C was used as an external reference (^{17}O chemical shift was taken 0 ppm). Other measurement parameters were the same as described in previous work[14]. The standard ^1H and proton-decoupled ^{13}C NMR spectra were recorded at a room temperature in $CDCl_3$ solution (with 1% TMS added for the spectral referencing) at 200.13 and 50.33 MHz, correspondingly. 2D HSQC and HMBC spectra were also recorded for assignment of the ^1H and ^{13}C chemical shifts of some benzoates.

IR Measurements

The IR spectra of 4 alkyl-substituted phenyl esters, $C_6H_5CO_2R$ (R = CH_2CH_2Br, CH_2CF_3, CH_2CHCl_2, CH_2CCl_3) were registered in the region 225–4000 cm^{-1} on Nicolet 6700 FT-IR spectrometer in approximately 0.013 M solution of tetrachloromethane (Aldrich 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). Thermo Electron's OMNIC software for FT-IR spectrometer was used to collect and process IR spectrum. The day-to-day reproducibility of the adsorption maxima was ±0.3 cm^{-1}. The values of $(\nu_{CO})_{max}$ for esters $C_6H_5CO_2R$ (R = CH_2CH_2Br, CH_2CF_3, CH_2CHCl_2, CH_2CCl_3) are shown in Table II.

Synthesis of Compounds

The preparation procedure and characteristics for the most *ortho*-, *meta*- and *para*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, and alkyl esters of benzoic acid, $C_6H_5CO_2R$, have been previously described[9,52–55]. The phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, (X = 2-SO_2CH_3, 2-$COCH_3$, 2-CF_3, 3-Cl, 4-SO_2CH_3, 4-CF_3) were prepared by the addition of benzoyl chloride to the corresponding substituted phenol in pyridine with stirring at 0 °C (the Einhorn method)[56–58]. The phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, (X = 3-Br, 3-$N(CH_3)_2$, 3-CF_3, 2-Br) and 2,6-dimethylphenyl benzoate, were prepared by addition the benzoyl chloride to the mixture of the corresponding substituted phenol in aqueous 10% sodium hydroxide (the Schotten–Baumann method)[59,60]. 2,6-Dinitrophenyl benzoate was synthesized by the addition of the thionyl chloride to the mixture of benzoic acid and 2,6-dinitrophenol in pyridine with stirring at 0 °C [61,62]. Purity of synthesized phenyl benzoates, $C_6H_5CO_2C_6H_4$-X (X = 2-SO_2CH_3, 2-$COCH_3$, 2-CF_3, 2-Br, 2,6-$(CH_3)_2$, 2,6-$(NO_2)_2$, 3-Cl, 3-Br, 3-$N(CH_3)_2$, 3-CF_3, 4-SO_2CH_3, 4-CF_3) and 2,2,2-trichloroethyl benzoate was confirmed by ^{1}H and ^{13}C NMR spectroscopy in deuterated chloroform at 25 °C (see Supplementary material).

DATA PROCESSING AND RESULTS

The values of chemical shifts, $\delta(^{17}O)$, for the carbonyl oxygen and the single-bonded oxygen in the *ortho*-, *para*- and *meta*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, given in Table I were treated according to the Taft and Charton equations using the Taft $\sigma°$ [63,64], inductive σ_I [64,65] and the resonance $\sigma°_R$ ($\sigma°_R = \sigma_P - \sigma_I$)[64,66] substituent constants[12] (see Supplementary material). In the case of *ortho* substituents, two steric scales were employed: the E_s^B constants[6,12,67] and the Charton scale[68–70] of υ. The steric constants, E_s^B, determined on the basis of the acid hydrolysis of *ortho*-substituted phenyl benzoates[67], $C_6H_5CO_2C_6H_4$-X, in the case of substituents X = H, F, Cl, Br, I, CH_3, $C(CH_3)_3$, CF_3, were found to be nearly linear function of the υ values, calculated on the bases of van der Waals radii, r_v.

In the case of the carbonyl and single-bonded oxygen chemical shifts, $\delta(^{17}O)$, for alkyl benzoates, $C_6H_5CO_2R$, given in Table II, Eq. (*1*) was applied.

$$\delta(^{17}O)_{Alk} = \delta(^{17}O)_H + (\rho_I)_{Alk}\,\sigma_I + \delta_{Alk}(E_s^B)_{Alk} \qquad (1)$$

The steric substituent constants[10,12], E_s^B, for the variable alkyl substituent in the alcohol component of esters, $C_6H_5CO_2R$, (Eq. (*1*)) were calculated as follows: $E_s^B = (\log k_{H+}^R - \log k_{H+}^{CH3})$, where k_{H+}^R and k_{H+}^{CH3} are the rate constants for acid hydrolysis of R-substituted alkyl benzoates, $C_6H_5CO_2R$, in water[71].

The results of correlations of the carbonyl oxygen and the single-bonded oxygen $\delta(^{17}O)$ values for *ortho*-, *meta*- and *para*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, and alkyl benzoates, $C_6H_5CO_2R$ (given in Tables I and II) with the Taft and Charton equations (see Supplementary material, Eqs (*1*)–(*5*)), are listed in Table III.

TABLE I
^{17}O NMR chemical shifts, $\delta(^{17}O)$, (in ppm) of the carbonyl oxygen, the single-bonded oxygen and the oxygen in substituent X for substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, in CH_3CN at 50 °C

X	$\delta(^{17}O)_{C=O}$	$\delta(^{17}O)_{OPh}$	$\delta(^{17}O)_X$	$c_{ester}{}^a$ (m)	$\delta(^{13}C)_{C=O}{}^b$	log k^c
4-NO_2	348.6	188.4	570.5	0.3		0.524
4-CN	347.9	190.1		0.5		0.320
4-SO_2CH_3	349.1	188.5	156.0	0.5	165.72	0.29^d
4-CF_3	348.3	187.9		0.5	164.66	–0.015^d
4-F	346.1	183.4		0.5		–0.507
4-Cl	346.3	184.6		0.5		–0.389
4-CH_3	345.5	185.5		0.5		–0.886
4-OCH_3	345.7	183.8	48.5	0.5		–0.857
4-NH_2	344.0	182.9		0.3		–1.215
H	345.7^e	187.3^e				–0.775
	345.8^e	187.5^e		0.4		
3-NO_2	346.9	185.7	573.9	0.5		0.230
3-CN	346.9	185.6		0.5		0.145^d
3-CF_3	346.8	185.7		0.5	164.78	–0.116^d
3-F	346.8	186.8		0.5		0.441^d
3-Cl	347.7	186.6		1.0		–0.260
	346.7	185.7		0.5		
3-Br	346.9	186.4		0.5	164.66	0.496^d
3-CH_3	345.4	187.3				–0.866
3-NH_2	344.9	187.6		0.5		–0.955
3-$N(CH_3)_2$	345.2	188.8		0.5	165.24	–1.028^d
2-NO_2	347.5	178.0	600.1			–0.060
2,6-$(NO_2)_2$	350.2	166.1	607.5		163.21	0.791^d
2-CN	349.5	185.5				0.320
2-CF_3	348.6	180.0				–0.406
2-SO_2CH_3	348.6	179.9	161.0	0.3	164.37	–0.533^d
2-F	347.6	169.2				–0.481
2-Cl	349.6	183.3				–0.613

TABLE I
(Continued)

X	$\delta(^{17}O)_{C=O}$	$\delta(^{17}O)_{OPh}$	$\delta(^{17}O)_X$	$c_{ester}{}^{a}$ (m)	$\delta(^{13}C)_{C=O}{}^{b}$	log k^c
2-Br	349.5	189.2			164.13	–0.635[d]
2-OCH_3	346.1	173.8	37.8			–1.309
2-CH_3	345.4	184.6				–1.226
2,6-$(CH_3)_2$	347.4	183.3			164.31	–1.891[d]
2-$C(CH_3)_3$	347.7	189.5				–1.740
2-CO_2CH_3	347.5	184.7	354; 135.8			–1.03[f]
2-$COCH_3$	345.7	183.1	574.0		165.1	–0.528[d]

[a] Approximately 1 molal solutions of *ortho*, *meta* and *para* derivatives in mixture of CH_3CN and CD_3CN (2 ml + 1 ml) were used, except where shown otherwise. [b] The carbonyl carbon ^{13}C NMR chemical shift (in ppm) in $CDCl_3$. [c] Unpublished kinetic data for the alkaline hydrolysis of $C_6H_5CO_2C_6H_4$-X in aqueous 0.5 M Bu_4NBr at 25 °C. [d] The log *k* values calculated from equations[5] $\log k_{m,p} = -0.754 + 1.45\sigma°$ and $\log k_{ortho} = -0.727 + 1.61\sigma_I + 1.37\sigma°_R + 1.38E_s{}^B$. [e] Data from ref.[14] [f] Supporting information for ref.[12]

DISCUSSION

Influence of para and meta Substituents

The carbonyl oxygen chemical shifts, $\delta(^{17}O)$, for the *para*- and *meta*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X (Table I), correlated well so with the single parameter treatment using the Taft σ° as the dual substituent method using the Taft σ_I and $\sigma°_R$ (see Supplementary material).

$$\delta(^{17}O)_{para} = (345.8 \pm 0.2) + (3.74 \pm 0.40)\sigma° \qquad (2)$$

$$R = 0.952,\ s = 0.507,\ n/n_0 = 10/10$$

$$\delta(^{17}O)_{para} = (346.1 \pm 0.4) + (3.25 \pm 0.72)\sigma_I + (4.34 \pm 0.76)\sigma°_R \qquad (3)$$

$$R = 0.951,\ s = 0.507,\ n/n_0 = 10/10$$

$$\delta(^{17}O)_{meta} = (345.6 \pm 0.1) + (2.43 \pm 0.32)\sigma^\circ \qquad (4)$$

$$R = 0.929,\ s = 0.301,\ n/n_0 = 10/10$$

TABLE II
^{17}O NMR chemical shifts, $\delta(^{17}O)$, (in ppm) of the carbonyl oxygen, the single-bonded oxygen and the oxygen in substituent R for substituted alkyl esters of benzoic acid, $C_6H_5CO_2R$, in CH_3CN at 50 °C

R	$\delta(^{17}O)_{C=O}$	$\delta(^{17}O)_{OR}$	$\delta(^{17}O)_R$ and ν_{CO}[a]	σ_I[b]	E_s^{B}[c]
CH_3[d]	338.5	128.1		0	0
CH_2CH_3[e]	338.2	158.4		–0.05	0
CH_2Cl	349.2	165.7		0.47	–0.17
CH_2CN	345.9	134.8		0.58	–0.55
CH_2CF_3[f]	342.0	128.2	ν_{CO} = 1743.4	0.41	–0.214[g]
$CH_2C_6H_5$	339.7	156.3		0.11	–0.17
$CH_2C{\equiv}CH$	342.3	148.1		0.27	–0.27
CH_2CH_2Cl	339.6	148.2		0.17	–0.23
CH_2CH_2Br	339.6	151.3	ν_{CO} = 1729.3	0.17	–0.22[h]
$CH_2CH_2OCH_3$	338.1	148.1	–24	0.07	–0.20
CH_2CHCl_2	340.8	146.7	ν_{CO} = 1733.2	0.31	–0.348[i]
CH_2CCl_3	341.3	149.4	ν_{CO} = 1741.2	0.41	–0.413[j]

[a] The IR stretching frequency of carbonyl group (in cm^{-1}) in tetrachloromethane. [b] Data from ref.[66]. [c] Data from refs[11,12]. [d] $\delta(^{17}O)_{C=O}$ = 340 and $\delta(^{17}O)_{OR}$ = 128 in acetonitrile at 75 °C [33]; $\delta(^{17}O)_{C=O}$ = 337.3 and $\delta(^{17}O)_{OR}$ = 127.7 in acetonitrile at 40 °C [28]; $\delta(^{17}O)_{C=O}$ = 337.3 and $\delta(^{17}O)_{OR}$ = 127.7 in acetonitrile at 40 °C [31]. [e] $\delta(^{17}O)_{C=O}$ = 339 and $\delta(^{17}O)_{OR}$ = 159 in acetonitrile at 75 °C [16]; $\delta(^{17}O)_{C=O}$ = 337.0 and $\delta(^{17}O)_{OR}$ = 157.4 in acetonitrile at 40 °C [31]. [f] $\delta(^{17}O)_{C=O}$ = 340.3 and $\delta(^{17}O)_{OR}$ = 126.6 in deuterochloroform at 40 °C [15]. [g] For R = CH_2CF_3 derivative $E_s^B = -0.214$ was calculated as the average value from $E_s^B = -0.231$[12], -0.207[12] and -0.205; $E_s^B = -0.205$ was calulated from equation[13] $(\nu_{CO}) = 1743.4 = 1726.7 + 56.8\sigma_I + 32.2E_s^B$. [h] For R = CH_2CH_2Br derivative $E_s^B = -0.22$ was calculated from equation[13] $(\nu_{CO}) = 1729.3 = 1726.7 + 56.8\sigma_I + 32.2E_s^B$. [i] For R = CH_2CHCl_2 derivative $E_s^B = -0.348$ was calculated as the average value from $E_s^B = -0.350$[12] and -0.345; $E_s^B = -0.345$ was calculated from equation[13] $(\nu_{CO}) = 1733.2 = 1726.7 + 56.8\sigma_I + 32.2E_s^B$. [j] For R = CH_2CCl_3 derivative $E_s^B = -0.413$ was calculated as the average value from $E_s^B = -0.518$[12] and -0.308; $E_s^B = -0.308$ was calculated from equation[13] $(\nu_{CO}) = 1741.2 = 1726.7 + 56.8\sigma_I + 32.2E_s^B$.

$$\delta(^{17}\mathrm{O})_{\mathrm{meta}} = (345.6 \pm 0.2) + (2.47 \pm 0.47)\sigma_{\mathrm{I}} + (0.93 \pm 0.48)\sigma^{\circ}_{\mathrm{R}} \qquad (5)$$

$$R = 0.913,\ s = 0.330,\ n/n_0 = 10/10$$

The calculated positive sensitivities towards the substituent-induced inductive (ρ_I) and resonance (ρ_R) effects (Eqs (*2*)–(*5*), Table III) for the carbonyl oxygen chemical shifts, $\delta(^{17}O)$, indicate that the electron-withdrawing substituents cause high-frequency shift of the ^{17}O signal showing deshielding effect of the carbonyl O atom. The electron-donating substituents induce an opposite effect resulting in low-frequency shift and shielding of the O atom. This is in accord with the reverse substituent-induced inductive and resonance effects observed in the carbonyl carbon ^{13}C NMR chemical shifts, (δ_{CO}), for substituted phenyl benzoates where the electron-withdrawing substituents increased and the electron-donating substituents decreased the electron density at the carbonyl carbon[12]. Consequently, the substituent effects so in the carbonyl oxygen chemical shifts, $\delta(^{17}O)$, as in the carbonyl carbon ^{13}C chemical shifts, (δ_{CO}), prove the increased double bond character of the carbonyl group produced by an electron-withdrawing groups and an increase in single bond character resulting from the electron-donating substituents[48,72–76]. In substituted phenyl benzoates the increased double bond character of the carbonyl group due to electron-withdrawing substituents was proved earlier by the increased infrared stretching frequencies of the carbonyl group, ν_{CO} [13], as well.

In the carbonyl oxygen chemical shifts, $\delta(^{17}O)$, the susceptibility to the inductive effect of *para* substitutents from the phenyl side ($\rho_I = 3.74$, $\rho_I = 3.25$; Eqs (*2*) and (*3*), Table III) was found to be ca. 2.3 times weaker than that from the benzoyl side ($\rho^+ = 9.07$, $\rho_I = 7.21$[14]). Similarly, the magnitude of the *para* inductive term for the carbonyl carbon ^{13}C NMR chemical shifts, (δ_{CO}), from the phenyl side ($\rho_I = -1.10$ [12]) was twice smaller, compared to that from the benzoyl moiety ($\rho_I = -2.18$ [12]). In the alkaline hydrolysis of *para*- and *meta*-substituted phenyl benzoates in water the polar influence from the phenyl side was ca. 1.6 times weaker than the corresponding influence from the benzoyl moiety i.e. $(\rho_I)_{PhCO}/(\rho_I)_{PhO} = 1.6$ [6]. With the generally accepted views in the substituted benzoyl derivatives, inductive effect increased due to shorter distance between the substituent and carbonyl carbon atom, compared to that in phenyl side. Similar to the inductive effect, the contribution of the *para* substituent resonance effect to

TABLE III
Correlation of the ^{17}O NMR chemical shifts, $\delta(^{17}O)$, of the carbonyl oxygen and single-bonded oxygen with the Taft and Charton equations

Scale	$\delta(^{17}O)_H$	ρ_I or ρ°	ρ°_R	δ	R^a	$(R_0^2)^b$	s^c	n/n_0^d
		ortho-substituted phenyl benzoates						
	C=^{17}O		+*R* substituents					
σ_I, σ°_R, E_s^B	345.6±0.5	9.10±0.82	9.36±1.41	–5.74±0.88	0.977	0.286	0.362	7/8[e]
	345.6±0.5	8.84±0.89	9.03±1.54	–6.16±0.91	0.968	0.286	0.401	8/8[f]
σ_I, σ°_R, υ	345.5±0.5	8.08±0.81	7.66±1.44	2.85±0.91	0.969	0.286	0.390	8/8[f]
			–*R* substituents					
σ_I, σ°_R, E_s^B	346.1±1.4	8.94±1.57	–19.0±5.2	0	0.942	0.618	0.585	7/7[g,h]
	346.2±1.7	7.53±1.78	–14.8±6.1	0	0.889	0.617	0.741	8/8[h]
	$^{17}OC_6H_5$		+*R* substituents					
σ_I, σ°_R, E_s^B	187.1±0.7	5.35±1.25	43.6±1.9	–10.1±1.2	0.996	0.056	0.468	6/6[i,j]
	187.0±5.2	9.28±8.11	57.1±14.5	–16.0±9.1	0.848	0.088	3.88	8/8[j]
σ_I, σ°_R, υ	187.1±0.6	4.34±1.23	41.8±1.9	4.75±0.56	0.996	0.056	0.481	6/6[i,j]
	186.7±4.7	7.83±7.17	54.1±13.1	7.85±3.93	0.866	0.088	3.66	8/8[j]
			–*R* substituents					
σ_I, σ°_R, E_s^B	188.5±0.8	–17.0±1.2	0	0	0.985		1.18	7/8[k]
	C=^{17}O	*para*-substituted phenyl benzoates						
σ°_p	345.8±0.2	3.74±0.40	–	–	0.952	–	0.507	10/10
σ_I, σ°_R	346.1±0.4	3.25±0.72	4.34±0.76	–	0.951	0.531	0.507	10/10
	$^{17}OC_6H_5$							
σ°_p	185.0±0.6	4.80±1.27	–	–	0.773	–	1.61	10/10
σ_I, σ°_R	187.3±0.3	0	9.86±1.14	–	0.944	0.071	0.832	10/10
	187.0±0.2	0	9.00±0.74	–	0.974	–	0.510	9/10[l]
	C=^{17}O	*meta*-substituted phenyl benzoates						
σ°	345.6±0.1	2.43±0.32	–	–	0.929	–	0.301	10/10
σ_I, σ°_R	345.6±0.2	2.47±0.47	0.93±0.48	–	0.913	0.776	0.330	10/10
	$^{17}OC_6H_5$							
σ°	187.5±0.2	–3.07±0.54	–	–	0.881	–	0.509	10/10
	187.2±0.2	–2.53±0.41	–	–	0.907	–	0.348	9/10[m]
σ_I, σ°_R	187.2±0.3	–2.48±0.69	–2.14±0.69	–	0.894	0.579	0.482	10/10

TABLE III
(*Continued*)

Scale	$\delta(^{17}O)_H$	ρ_I or $\rho°$	$\rho°_R$	δ	R^a	$(R_0^2)^b$	s^c	n/n_0^d
	$C{=}^{17}O$	*R*-substituted alkyl benzoates						
σ_I, E_s^B	339.1±0.7	27.4±1.6	–	17.1±2.1	0.987	0.771	0.572	10/10[n]
	^{17}OR							
σ_I, E_s^B	163.0±3.4	35.4±7.2	–	85.1±9.5	0.958	–0.010	2.49	9/9[o]

[a] *R* – correlation coefficient. [b] R_0 – zeroth correlation coefficient (*R* for correlation with one descriptor σ_I). [c] *s* – standard deviation (in ppm). [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] The 2,6-$(CH_3)_2$ derivative was excluded. [f] For 2,6-$(CH_3)_2$ derivative, double values of resonance and steric constants were used and the inductive constant was equal to zero. [g] The 2-CO_2CH_3 derivative was omitted before data treatment. [h] For 2-$COCH_3$ substituent $\sigma°_R$ = 0.16 and 2-CO_2CH_3 $\sigma°_R$ = 0.14 were used. [i] The 2-F and 2-Br derivatives were omitted. [j] For 2,6-$(CH_3)_2$ derivative, double values of inductive, resonance and steric constants were used. [k] The 2-CN derivative was excluded. [l] The 4-CN derivative was excluded. [m] The 3-NH_2 derivative was excluded. [n] Benzoates with R = CH_2CF_3 and R = CH_2CCl_3 were omitted. The inductive and steric constants from Table II were used. [o] Benzoates with R = CH_2CF_3, R = CH_2CCl_3 and R = CH_3 were omitted.

the carbonyl $\delta(^{17}O)$ values from the phenyl side was about 2.5 times smaller than the corresponding influence from the benzoyl side ($(\rho_R)_{PhCO}/(\rho_R)_{PhO}$ = 9.71 [14]/4.34 = 2.24; Table III). A good correlation obtained for the carbonyl oxygen chemical shifts, $\delta(^{17}O)$, with $\sigma°$, σ_I and $\sigma°_R$ constants (Eqs (*2*) and (*3*), Table III) for *para*-substituted esters, $C_6H_5CO_2C_6H_4$-X, indicated the absence of the through-resonance between substituents in the phenyl moiety and the carbonyl oxygen. In phenyl benzoates containing *para*-substituents in the benzoyl side, X-$C_6H_4CO_2C_6H_5$, the contribution of the through-conjugation between substituent and the carbonyl oxygen (or carbonyl group) was found to be significant so to the carbonyl oxygen as in the single-bonded chemical shifts[14], $\delta(^{17}O)$, the infrared stretching frequencies of the carbonyl group[13], ν_{CO}, and the log *k* values of the alkaline hydrolysis[6]. This once more prove that in phenyl benzoates the benzene ring in benzoyl part of the ester is coplanar with the carbonyl bond plane while the aromatic plane in the phenoxy part is twisted nearly perpendicular relative to the carboxyl bond plane[13,77–81]. In contrast to this for phenyl benzoate and benzoates with *ortho* substituents in phenoxy moiety nearly planar conformers were proved as well[82–84]. The primary condition for the resonance interaction between two groups is the mutual coplanarity of these groups.

In *meta*-substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, the contribution of the inductive effect to the carbonyl oxygen chemical shifts, $\delta(^{17}O)$, from the phenyl side was about one unit lower ($(\rho_I)_m = 2.47$; Eq. (*5*), Table III), compared to that for *para* substituents ($(\rho_I)_p = 3.25$; Eq. (*3*), Table III). The influence of the *meta* inductive effect from the phenyl side was approximately 2.4 times weaker than the same effect from the benzoyl component ($(\rho_I)_m = 6.16$ [14]).

Influence of ortho Substituents

The carbonyl oxygen $\delta(^{17}O)$ values measured for fourteen *ortho*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X (Table I), except CH_3, showed high frequency shift of the ^{17}O signal relative to unsubstituted phenyl benzoate, $C_6H_5CO_2C_6H_5$. The carbonyl oxygen chemical shifts, $\delta(^{17}O)$, for *ortho*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, estimated in the present work (Table I) correlated well with the Charton equation in case the data treatment was carried out separately for derivatives with +*R* substituents and with –*R* substituents. In the case of +*R* substituents (X = H, 2-OCH_3, 2-CH_3, 2,6-$(CH_3)_2$, 2-$C(CH_3)_3$, 2-F, 2-Cl, 2-Br), the influence of *ortho* substituents to the carbonyl ^{17}O NMR chemical shifts, $\delta(^{17}O)$, was expressed as follows (Table III).

$$(\delta^{17}O)_{ortho} = (345.6 \pm 0.5) + (9.10 \pm 0.82)\sigma_I + (9.36 \pm 1.91)\sigma^\circ_R - (5.74 \pm 0.88)E_s^B \qquad (6)$$

$$R = 0.977,\ s = 0.362,\ n/n_0 = 7/8$$

It follows from Eq. (*6*) that in the case of *ortho* derivatives with +*R* substituents, the carbonyl oxygen is deshielded due to the –*I* inductive and steric effects and shielded by the +*I* inductive and +*R* resonance effects of *ortho* substituents.

For *ortho*-substituted phenyl esters of benzoic acid containing electron-withdrawing –*R* substituents (X = H, 2-NO_2, 2-CN, 2-CF_3, 2-SO_2CH_3, 2-CO_2CH_3, 2-$COCH_3$, 2,6-$(NO_2)_2$), the steric factor appeared to be insignificant (Table III).

$$(\delta^{17}\mathrm{O})_{\mathrm{ortho}} = (346.1 \pm 1.4) + (8.94 \pm 1.57)\sigma_\mathrm{I} - (19.0 \pm 5.2)\sigma^\circ_\mathrm{R} \qquad (7)$$

$$R = 0.942,\ s = 0.585,\ n/n_0 = 7/7$$

Unexpectedly, for *ortho* derivatives with –*R* substituents in the phenyl moiety the negative resonance effect ρ < 0 was obtained. In the case of –*R* substituents the carbonyl oxygen appeared to be deshielded by the inductive effect but shielded by resonance effect similar to that for the *ortho* derivatives containing +*R* substituents. The oxygens of the *ortho* NO_2 groups also revealed the deshielding effect, compared to oxygens in the *para* NO_2 group (Table I).

The correlation using the modified Charton steric constants, υ, gave nearly the same results as with the steric constants E_s^B. In the case of the Charton steric constants, υ, the susceptibility to the steric effect, δ_{ortho}, was positive and the magnitude of δ_{ortho} was ca. twice smaller, compared to the δ_{ortho} value obtained with the E_s^B steric constants ($E_s^B < 0$). For phenyl benzoates with *ortho* +*R* substituents, we obtained Eq. (*8*) (Table III).

$$(\delta^{17}\mathrm{O})_{\mathrm{ortho}} = (345.5 \pm 0.5) + (8.08 \pm 0.81)\sigma_\mathrm{I} + (7.66 \pm 1.44)\sigma^\circ_\mathrm{R} + (2.85 \pm 0.91)\upsilon \qquad (8)$$

$$R = 0.969,\ s = 0.390,\ n/n_0 = 8/8$$

The influence of the *ortho* inductive effect in the case of +*R* substituents ($\rho_\mathrm{I} = 9.10$) and –*R* substituents ($\rho_\mathrm{I} = 8.94$) was found to be approximately twice higher than the corresponding influence from the *para* position (ρ_I = 3.74, 3.25) (Table III). In the case of *ortho* substituents in phenyl moiety similar to *para* and *meta* derivatives the inductive effect appeared to be ca. twice weaker than that in the case of *ortho* substituents in benzoyl moiety ($\rho_\mathrm{I} = 17.3$ [14]).

Results of correlations (see Table III) show that the steric requirements of *ortho* +*R* substituents ($\delta_{\mathrm{ortho}}E_s^B > 0$) caused an increase in the carbonyl oxygen $\delta(^{17}\mathrm{O})$ values (high frequency shift). Due to the steric effect of substituents in phenyl moiety, carbonyl oxygen is more deshielded, compared to the unsubstituted derivative. In the case of +*R* substituents in the phenyl moiety, the steric influence on the carbonyl oxygen $\delta(^{17}\mathrm{O})$ values was reduced ca. 13.5 times, compared to that involving substituents in the benzoyl moiety (δ_{ortho} = –81.2 [14]). We suggested that the observed steric effects of *ortho* +*R* substituents in phenyl moiety are caused by the van der Waals deshielding effect[85–88]. In this mechanism the π-electron density around the CO oxygen in an *ortho*-substituted ester would be reduced by electrostatic repulsion between the orbitals of X and those of the carbonyl CO bond with the effect increasing as X increases in size.

Influence of Substituents on the δ(^{17}O) values of Single-Bonded Phenoxy Oxygen

The substituent effects on the δ(^{17}O) values of the single-bonded phenoxy oxygen in phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, from the phenyl side appeared to be different from those found for the carbonyl oxygen chemical shifts, δ(^{17}O), and from the substituent effects from the benzoyl moiety. The substituent effects from the benzoyl part of esters on the δ(^{17}O) values of the single-bonded phenoxy oxygen were found to be ca. twice smaller than that on the chemical shifts, δ(^{17}O), of carbonyl oxygen[14].

In *para*-substituted phenyl benzoates, the positive value of ρ_R = 9.00 (Eq. (*9*), Table III) indicated that due to resonance effect of the *para* electron-donating substituents, the single-bonded phenoxy oxygen is shielded and the electron-withdrawing substituents are deshielded it, compared to the unsubstituted derivative.

$$\delta(^{17}\mathrm{O})_{para} = (187.0 \pm 0.2) + (9.00 \pm 0.74)\sigma^{\circ}_{R} \qquad (9)$$

$$R = 0.974,\ s = 0.510,\ n/n_0 = 9/10$$

Similar resonance effect exerted *para* substituents on the carbonyl oxygen chemical shifts, δ(^{17}O), only the resonance effect on the carbonyl oxygen chemical shifts, δ(^{17}O), was more than twice weaker (ρ_R = 4.34; Eq. (*3*), Table III), compared to that on the single-bonded oxygen (ρ_R = 9.00). Due to the resonance and inductive effects, the oxygen of the *para* NO_2 substituent in phenyl benzoate, $C_6H_5CO_2C_6H_4$-NO_2, (δ(^{17}O) = 570.5; Table I) appeared to be shielded, compared to that for unsubstituted nitrobenzene, C_6H_5-NO_2 (δ(^{17}O) = 573.3 [14]).

Due to polar effect, the electron-withdrawing *meta* substituents in the phenyl side attract electrons from the carbonyl oxygen, increasing the electron density at the carbonyl carbon[12] and the single-bonded phenoxy oxygen, compared to the unsubstituted derivative (Table III).

$$\delta(^{17}\mathrm{O})_{\mathrm{meta}} = (187.2 \pm 0.2) - (2.53 \pm 0.41)\sigma^\circ \qquad (10)$$

$$R = 0.907,\ s = 0.348,\ n/n_0 = 9/10$$

For *ortho*-substituted phenyl benzoates with +*R* substituents we found Eq. (*11*).

$$(\delta^{17}\mathrm{O})_{\mathrm{ortho}} = (187.1 \pm 0.7) + (5.35 \pm 1.25)\sigma_{\mathrm{I}} + (43.6 \pm 1.9)\sigma^\circ_{\mathrm{R}} - (10.1 \pm 1.2)E_{\mathrm{s}}^{\mathrm{B}} \qquad (11)$$

$$R = 0.996,\ s = 0.468,\ n/n_0 = 6/6$$

It follows from Eq. (*11*) that in the case of the electronegative +*R* *ortho* substituents capable of electron-withdrawal by inductive effect (I-effect > 0), the inductive effect and the steric effect ($E_s^B < 0$) deshielded single-bonded phenoxy oxygen atom while the resonance effect shielded it ($\sigma^\circ_R < 0$). The contribution of the *ortho* resonance term to the single-bonded oxygen chemical shifts was ca. five times stronger than that to the carbonyl oxygen $\delta(^{17}O)$ ($\rho_R = 9.36$; Eq. (*6*), Table III). An increased sensitivity of the $\delta(^{17}O)$ values to the resonance effect of substituents was detected also in anisoles and aromatic ethers[39] ($\rho_R >> \rho_I$). The influence of the steric term of *ortho* substituents on the single-bonded oxygen chemical shifts, $\delta(^{17}O)$, was ca. twice stronger, compared to that on the carbonyl oxygen $\delta(^{17}O)$ ($\delta_{ortho} = -5.74$; Table III).

In *ortho*-substituted phenyl benzoates with electron-attracting –*R* substituents in phenyl moiety increase the shielding of the single-bonded oxygen by the substituent inductive effect only (Eq. (*12*), Table III).

$$(\delta^{17}\mathrm{O})_{\mathrm{ortho}} = (188.5 \pm 0.8) - (17.0 \pm 1.2)\sigma_{\mathrm{I}} \qquad (12)$$

$$R = 0.985,\ s = 1.18,\ n/n_0 = 7/8$$

Influence of Substituents on the Phenyl ipso-Carbon ^{13}C MNR Chemical Shifts

We found that in substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X, substituents in *para*, *meta* and *ortho* positions in phenyl moiety induced the charge at the phenyl *ipso*-carbon (C-1) similarly as it was found previously in the case of the adjacent single-bonded phenoxy oxygen.

The *ipso*-carbon (C-1) in phenyl moiety is shielded with the *para* electron-donor substituents and deshielded when the electron-attracting –*R* substituents were involved (Eq. (*13*)).

$$\delta(\text{C-1})_{\text{para}} = (150.81 \pm 0.24) + (3.26 \pm 0.47)\sigma_I + (16.24 \pm 0.55)\sigma^\circ_R \qquad (13)$$

$$R = 0.997,\ s = 0.317,\ n/n_0 = 8/8$$

In the case of *para* substituents the resonance affects the electron density at the adjacent single-bonded phenoxy oxygen in the same way (Eq. (*9*), Table III).

The substituents in the *meta* position in phenyl moiety show very small effects on the phenyl *ipso*-carbon ^{13}C MNR chemical shifts, whereas the resonance operates in the opposite sign to those for the corresponding *para* substituents.

$$\delta(\text{C-1})_{\text{meta}} = (151.12 \pm 0.13) + (0.67 \pm 0.26)\sigma_I - (1.68 \pm 0.26)\sigma^\circ_R \qquad (14)$$

$$R = 0.905,\ s = 0.425,\ n/n_0 = 10/10$$

The adjacent single-bonded phenoxy oxygen was found to be affected by the reverse resonance effect of *meta* substituents as well (Eq. (*10*)).

In the case of electron-donating *ortho* +*R* substituents in phenyl moiety due to the inductive effect a decrease in the electron density at *ipso*-carbon (C-1) was observed while the resonance effect increased it.

$$\delta(\text{C-1})_{\text{ortho}} = (152.24 \pm 0.88) + (4.65 \pm 1.85)\sigma_I + (31.5 \pm 3.4)\sigma^\circ_R \qquad (15)$$

$$R = 0.968,\ s = 0.953,\ n/n_0 = 7/7$$

The electron density at the adjacent single-bonded phenoxy oxygen was exerted by inductive and resonance effects of *ortho* +*R* substituents in the same way (Eq. (*11*)). In the case of *ortho* +*R* substituents the contribution of the resonance effect in the shielding effect of the *ipso*-carbon (C-1) was twice stronger than that for *para* substituents.

In the case of *ortho* –*R* substituents in phenyl moiety we obtained Eq. (*16*)

$$\delta(\text{C-1})_{\text{ortho}} = (150.73 \pm 1.45) - (14.4 \pm 1.4)\sigma_{\text{I}} - (8.50 \pm 2.26)E_{\text{s}}^{\text{B}} \qquad (16)$$

$$R = 0.980,\ s = 0.870,\ n/n_0 = 7/8$$

and without the steric factor Eq. (*17*).

$$\delta(\text{C-1})_{\text{ortho}} = (152.6 \pm 1.1) - (10.2 \pm 1.7)\sigma_{\text{I}} \qquad (17)$$

$$R = 0.924,\ s = 1.66,\ n/n_0 = 7/8$$

The electron density at the adjacent of single-bonded oxygen was affected by the *ortho* –*R* substituent inductive effect only (Eq. (*12*)).

The influence of the *ortho* electron-attracting –*R* substituents in the phenyl moiety is different from that for *para* –*R* substituents. The electron-attracting –*R* *para* substituents due to resonance effect reduce the electron density at the *ipso*-carbon (C-1) and the adjacent single-bonded phenoxy oxygen. In the case of –*R* *ortho* substituents, similar to +*R* *ortho* substituents, the increase in the electron density at the phenyl *ipso*-carbon (C-1) and the adjacent single-bonded phenoxy oxygen was observed.

It appeared that –*R* substituents in *ortho* position in substituted acetanilides[89], $CH_3CONHC_6H_4$-X, show the shielding effect on the phenyl *ipso*-carbon C-1 with respect to unsubstituted derivative similarly we found in *ortho*-substituted phenyl benzoates, $C_6H_5CO_2C_6H_4$-X (X = H, CN, COOMe, CF_3, NO_2).

$$\delta(\text{C-1})_{\text{PhCOOC6H4-X}} = (0.825 \pm 0.087)\delta(\text{C-1})_{\text{CH3CONHC6H4-X}} + \\ + (36.38 \pm 12.09) \qquad (18)$$

$$R = 0.978,\ s = 0.677,\ n/n_0 = 5/5$$

Effect of Alkyl Substituents

In substituted alkyl benzoates, $C_6H_5CO_2R$, the substituent-induced effect on the carbonyl oxygen chemical shift, $\delta(^{17}O)$, (Table II) was described by the inductive and steric effects as follows (Table III).

$$(\delta^{17}O)_{Alk} = (339.2 \pm 0.7) + (27.4 \pm 1.6)\sigma_I + (17.1 \pm 2.1)E_s{}^B \qquad (19)$$

$$R = 0.987,\ s = 0.572,\ n/n_0 = 10/10$$

Good correlation (Eq. (*19*)) was obtained when esters with R = CH_2CF_3, CH_2CCl_3 were not included into the data treatment. Similar to the carbonyl oxygen chemical shifts, the single-bonded oxygen chemical shifts, $\delta(^{17}O)$, for $C_6H_5CO_2R$ showed good correlation with the inductive σ_I and steric $E_s{}^B$ substituent constants in case esters with R = CH_3, CH_2CF_3, CH_2CCl_3 were omitted before the data treatment (Table III).

$$(\delta^{17}O)_{Alk} = (163.0 \pm 3.4) + (35.4 \pm 7.2)\sigma_I + (85.1 \pm 9.5)E_s{}^B \qquad (20)$$

$$R = 0.958,\ s = 2.49,\ n/n_0 = 10/10$$

In substituted alkyl benzoates, $C_6H_5CO_2R$, the carbonyl oxygen and single-bonded oxygen are deshielded by –*I* inductive substituent effect and shielded by +*I* inductive and steric substituent effects. We suggested that in the case of substituted alkyl benzoates the steric effect so on the carbonyl oxygen chemical shifts, $\delta(^{17}O)$, as the single-bonded oxygen chemical shifts, $\delta(^{17}O)$, is caused by the attractive van der Waals interaction between the orbitals of the oxygen and substituent with shielding effects[85,86]. The influence of the steric factor on the single-bonded oxygen chemical shifts, $\delta(^{17}O)$, was five times stronger (Eq. (*20*)), compared to the steric contribution to the carbonyl oxygen chemical shifts (Eq. (*19*)). The chemical shifts, $\delta(^{17}O)$, for alkyl benzoates, $C_6H_5CO_2CH_2CF_3$ and $C_6H_5CO_2CH_2CCl_3$, deviate from correlations given by Eqs (*19*) and (*20*). The $E_s{}^B$ values for R = CH_2CF_3 and R = CH_2CCl_3 shown in Table II are too low to correlate the $\delta(^{17}O)$ values with Eqs (*19*) and (*20*). The $E_s{}^B$ values for R = CH_2CF_3 and R = CH_2CCl_3

calculated from Eqs (*19*) and (*20*) are –0.487, –0.582 and –0.526, –0.330, respectively.

We found that the single-bonded oxygen chemical shifts, $\delta(^{17}O)$, for $C_6H_5CO_2R$ could be correlated well with the corresponding $\delta(^{17}O)$ values for substituted alcohols ROH[42,43] when R = CH_3, CH_2CH_3, CH_2Ph, CH_2CH_2Cl, CH_2CF_3, $CH_2C{\equiv}CH$ as follows.

$$\delta(^{17}O)_{PhCO2R} = (150.6 \pm 1.8) + (0.720 \pm 0.098)\delta(^{17}O)_{ROH} \qquad (21)$$

$$R = 0.954,\ s = 3.92,\ n/n_0 = 6/6$$

Correlation of the Carbonyl Oxygen $\delta(^{17}O)$ Values with the Substituent-Induced Carbonyl Carbon ^{13}C NMR Chemical Shifts, $\Delta\delta_{CO}$, and IR Carbonyl Stretching Frequencies, $\Delta\nu_{CO}$, and Rates of the Alkaline Hydrolysis, $\Delta\log k$

The carbonyl oxygen chemical shifts, $\delta(^{17}O)$, for *ortho*-, *para*- and *meta*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, and alkyl benzoates, $C_6H_5CO_2R$, were correlated with the corresponding substituent-induced carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, the IR carbonyl stretching frequencies, $\Delta\nu_{CO}$, and the rates of the alkaline hydrolysis, $\Delta\log k$ in pure water and in aqueous 0.5 M Bu_4NBr (see equations in Supplementary material). In the case of *ortho* derivatives we obtained good correlations with the corresponding substituent-induced carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, IR carbonyl stretching frequencies, $\Delta\nu_{CO}$, and the $\Delta\log k$ values of the alkaline hydrolysis in case the additional resonance and steric terms were involved and the data treatment was carried out separately for esters containing $+R$ substituents and $-R$ substituents (Table IV; $0.983 > R > 0.900$). Correlation equations obtained (Table IV) enables one to predict the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, IR carbonyl stretching frequencies, $\Delta\nu_{CO}$, and the $\Delta\log k$ values of the alkaline hydrolysis using the carbonyl oxygen chemical shifts, $\delta(^{17}O)$, for the esters considered.

For phenyl esters of *ortho*-substituted phenyl benzoates containing $+R$ substituents we obtained Eqs (*22*)–(*24*) (Table IV).

$$(\delta^{17}O)_{ortho} = (345.8 \pm 0.4) - (4.00 \pm 0.34)\Delta\delta_{CO} + \\ + (7.56 \pm 1.07)\sigma^{\circ}_{R} - (6.49 \pm 0.77)E_s^{B} \qquad (22)$$

TABLE IV
Correlation of the carbonyl oxygen ^{17}O NMR chemical shifts, $\delta(^{17}O)$, with the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, the carbonyl IR stretching frequencies, $\Delta\nu_{CO}$ and the $\Delta\log k$ values of the alkaline hydrolysis (see Supplementary material, Eqs (*6*)–(*9*))

Scale	$\delta(^{17}O)_H$	a_1	a_2	a_3	R[a]	s[b]	n/n_0[c]
			ortho-substituted phenyl benzoates				
	$C{=}^{17}O$		+*R* substituents				
$\Delta\delta_{CO}$, σ°_R, E_s^B	345.8±0.4	–4.00±0.34	7.56±1.07	–6.49±0.77	0.983	0.297	6/6[d]
$\Delta\nu_{CO}$, σ°_R, E_s^B	345.5±1.3	0.457±0.130	7.96±3.66	–5.67±2.25	0.827	0.885	6/6[e]
$\Delta\log k^1$, σ°_R, E_s^B	345.5±0.6	5.94±0.67	3.88±1.38	–10.8±1.4	0.965	0.447	7/7[f]
$\Delta\log k^2$, σ°_R, E_s^B	345.2±1.0	5.19±1.03	0	–12.1±2.6	0.897	0.757	7/7[g]
			–*R* substituents				
$\Delta\delta_{CO}$, σ°_R, E_s^B	346.8±0.4	–1.98±0.52	0	0	0.809	0.954	8/8
$\Delta\delta_{CO}$, σ°_R, E_s^B	346.3±0.4	–2.47±0.50	0	0	0.894	0.781	7/7[h]
$\Delta\log k^1$, σ°_R, E_s^B	345.7±0.9	5.60±0.60	–22.5±3.5	–5.56±0.80	0.978	0.364	7/8[i,k]
$\Delta\log k^2$, σ°_R, E_s^B	345.8±0.7	5.18±0.44	–20.6±2.7	–5.49±0.64	0.986	0.292	7/8[j,k]
	$C{=}^{17}O$		*para*-substituted phenyl benzoates				
$\Delta\delta_{CO}$, σ°_R	346.4±0.2	–2.85±0.49	0	–	0.951	0.533	8/8[l]
$\Delta\nu_{CO}$, σ°_R	345.5±0.2	0.353±0.056	0	–	0.920	0.561	8/8[m]
$\Delta\log k^1$, σ°_R	345.6±0.2	3.25±0.41	0	–	0.936	0.581	10/10[n]
$\Delta\log k^2$, σ°_R	345.6±0.2	2.63±0.28	0	–	0.952	0.507	10/10[o]
	$C{=}^{17}O$		*meta*-substituted phenyl benzoates				
$\Delta\delta_{CO}$, σ°_R	345.7±0.1	–2.81±0.35	0	–	0.936	0.285	10/10
	345.8±0.1	–2.52±0.28	0	–	0.954	0.211	9/10[p]
$\Delta\nu_{CO}$, σ°_R	345.5±0.2	0.233±0.024	0	–	0.969	0.203	7/7[q]
$\Delta\log k^1$, σ°_R	345.5±0.2	2.13±0.34	0	–	0.901	0.352	10/10[r]
$\Delta\log k^2$, σ°_R	345.6±0.1	1.65±0.21	0	–	0.933	0.293	10/10[s]

TABLE IV
(*Continued*)

Scale	$\delta(^{17}O)_H$	a_1	a_2	a_3	R^a	s^b	$n/n_0{}^c$
	$C=^{17}O$	*R*-substituted alkyl benzoates					
$\Delta\delta_{CO}$, $E_s{}^B$	336.0±0.9	–4.55±0.67	–	0	0.913	1.49	10/10
$\Delta\nu_{CO}$, $E_s{}^B$	340.0±0.4	0.421±0.048	–	0	0.945	1.20	10/10
$\Delta\log k^1$, $E_s{}^B$	339.9±1.0	7.21±0.76	–	8.99±2.92	0.964	0.974	$10/10^t$
$\Delta\log k^2$, $E_s{}^B$	340.2±1.1	6.10±0.78	–	8.03±3.43	0.948	1.16	$10/10^u$

[a] *R* – correlation coefficient. [b] *s* – standard deviation (in ppm). [c] n_0 reflects the total number of data involved in the correlation; *n* – the number of points remaining after exclusion of significantly deviating points. [d] The 2,6-$(CH_3)_2$ and 2-CH_3 derivatives were omitted. [e] The $\Delta\nu_{CO}$ values for 2,6-$(CH_3)_2$ and 2-Br derivatives were not available. [f] $\Delta\log k^1 = \log k_X - \log k_H$ for the alkaline hydrolysis of $C_6H_5CO_2C_6H_4$-X in water at 25 °C. The $\log k^1$ value in water at 25 °C for 2-Br derivative was calculated from equation[5] $\log k_{ortho} = -0.377 + 1.54\sigma_I + 0.95\sigma°_R + 1.09E_s{}^B$. [g] $\Delta\log k^2 = \log k_X - \log k_H$ for the alkaline hydrolysis of $C_6H_5CO_2C_6H_4$-X in aqueous 0.5 M Bu_4NBr at 25 °C. The $\log k^2$ value in aqueous 0.5 M Bu_4NBr at 25 °C for 2-Br derivative was calculated from equation[5] $\log k_{ortho} = -0.727 + 1.61\sigma_I + 1.37\sigma°_R + 1.38E_s{}^B$. [h] The 2-$CO_2CH_3$ derivative was omitted. [i] The $\Delta\log k^1$ values for 2-SO_2CH_3, 2-CO_2CH_3, 2-$COCH_3$ and 2,6-$(NO_2)_2$ derivatives were calculated from equation in note [f]. [j] The $\Delta\log k^2$ values for 2-SO_2CH_3, 2-CO_2CH_3, 2-$COCH_3$ and 2,6-$(NO_2)_2$ derivatives were calculated from equation in note [g]. [k] The 2-CO_2CH_3 derivative was excluded. [l] The 4-SO_2CH_3 and 4-NH_2 derivatives were omitted. [m] The 4-SO_2CH_3 and 4-CF_3 derivatives were not included. There are no ν_{CO} values for 4-SO_2CH_3 and 4-CF_3 derivatives available in literature. [n] The $\log k^1$ values in water at 25 °C for 4-CF_3 and 4-SO_2CH_3 derivative were calculated from equation[5] $\log k_{m,p} = -0.377 + 1.11\sigma°$. [o] The $\log k^2$ values in aqueous 0.5 M Bu_4NBr at 25 °C for 4-CF_3 and 4-SO_2CH_3 derivatives were calculated from equation[5] $\log k_{m,p} = -0.754 + 1.45\sigma°$. [p] The 3-$NH_2$ derivative was excluded. [q] The 3-Br, 3-CF_3 and 3-$N(CH_3)_2$ derivatives were not included. The ν_{CO} values for 3-Br, 3-CF_3 and 3-$N(CH_3)_2$ derivatives are not available. [r] The $\log k^1$ values in water at 25 °C for 3-Br, 3-CF_3 and 3-$N(CH_3)_2$ derivatives were calculated from equation[5] $\log k_{m,p} = -0.377 + 1.11\sigma°$ (see note [n]). [s] The $\log k^2$ values in aqueous 0.5 M Bu_4NBr at 25 °C for 3-Br, 3-CF_3 and 3-$N(CH_3)_2$ derivatives were calculated from equation[5] $\log k_{m,p} = -0.754 + 1.45\sigma°$ (see note [o]). [t] The $\log k^1$ values for alkaline hydrolysis of esters $C_6H_5CO_2CH_2CH_2Br$ and $C_6H_5CO_2CH_2CHCl_2$ in water were calculated from equation[11] $\log k = -1.272\sigma_I + 0.98\ E_s{}^B$. [u] The $\log k^2$ value for alkaline hydrolysis of ester $C_6H_5CO_2CH_2CH_2Br$ in aqueous 0.5 M Bu_4NBr was calculated from equation[11] $\log k = -1.613\sigma_I + 1.17E_s{}^B$.

$$R = 0.983,\ s = 0.297,\ n/n_0 = 6/6$$

$$(\delta^{17}\mathrm{O})_{\mathrm{ortho}} = (345.5 \pm 1.3) + (0.457 \pm 0.130)\Delta\nu_{\mathrm{CO}} + + (7.96 \pm 3.66)\sigma°_{\mathrm{R}} - (5.67 \pm 2.25)E_{\mathrm{s}}^{\mathrm{B}} \qquad (23)$$

$$R = 0.827,\ s = 0.885,\ n/n_0 = 6/6$$

$$(\delta^{17}\mathrm{O})_{\mathrm{ortho}} = (345.5 \pm 0.6) + (5.94 \pm 0.67)\Delta\log k + + (3.88 \pm 1.38)\sigma°_{\mathrm{R}} - (10.8 \pm 1.4)E_{\mathrm{s}}^{\mathrm{B}} \qquad (24)$$

$$R = 0.965,\ s = 0.447,\ n/n_0 = 7/7$$

In the case of substituted phenyl benzoates containing –*R* substituents, we found Eqs (*25*) and (*26*) (Table IV).

$$(\delta^{17}\mathrm{O})_{\mathrm{ortho}} = (346.3 \pm 0.4) - (2.47 \pm 0.50)\Delta\delta_{\mathrm{CO}} \qquad (25)$$

$$R = 0.894,\ s = 0.791,\ n/n_0 = 7/7$$

$$(\delta^{17}\mathrm{O})_{\mathrm{ortho}} = (345.7 \pm 0.9) + (5.60 \pm 0.60)\Delta\log k - - (22.5 \pm 3.5)\sigma°_{\mathrm{R}} - (5.56 \pm 0.80)E_{\mathrm{s}}^{\mathrm{B}} \qquad (26)$$

$$R = 0.978,\ s = 0.364,\ n/n_0 = 7/8$$

For alkyl benzoates, Eqs (*27*)–(*29*) were obtained (Table IV).

$$(\delta^{17}\mathrm{O})_{\mathrm{Alk}} = (336.0 \pm 0.9) - (4.55 \pm 0.67)\Delta\delta_{\mathrm{CO}} \qquad (27)$$

$$R = 0.913,\ s = 1.49,\ n/n_0 = 10/10$$

$$(\delta^{17}\mathrm{O})_{\mathrm{Alk}} = (340.0 \pm 0.4) + (0.421 \pm 0.048)\Delta\nu_{\mathrm{CO}} \tag{28}$$

$$R = 0.945,\ s = 1.20,\ n/n_0 = 10/10$$

$$(\delta^{17}\mathrm{O})_{\mathrm{Alk}} = (339.9 \pm 1.0) + (7.21 \pm 0.76)\Delta\log k + (8.99 \pm 2.92)E_{\mathrm{s}}^{\mathrm{B}} \tag{29}$$

$$R = 0.964,\ s = 0.974,\ n/n_0 = 10/10$$

The negative values of the parameter $a_1 = \rho_\mathrm{I}(^{17}\mathrm{O})/\rho_\mathrm{I}(\delta_{\mathrm{CO}})$ (see Supplementary material) in correlation of the $\delta(^{17}\mathrm{O})$ values with the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{\mathrm{CO}}$, show that in *ortho*-, *meta*- and *para*-substituted phenyl esters of benzoic acid, $C_6H_5CO_2C_6H_4$-X, as well as substituted alkyl benzoates, $C_6H_5CO_2R$, the influence of the substituent-induced inductive effect on the $\delta(^{17}\mathrm{O})$ values is opposite to that in ^{13}C NMR chemical shifts, $\Delta\delta_{\mathrm{CO}}$ (Table IV). Earlier[12] when studying the ^{13}C NMR chemical shifts in $C_6H_5CO_2C_6H_4$-X we found the inductive effect of the electron-attracting *ortho*, *meta* and *para*, as well as alkyl substituents to increase in the electron density at the carbonyl carbon while the electron-donating +*R* substituents deshielded the carbonyl carbon. The influence of –*R* and +*R* substituents on the $\delta(^{17}\mathrm{O})$ values (Table III) was reverse to that found in ^{13}C NMR chemical shifts, $\Delta\delta_{\mathrm{CO}}$.

When the carbonyl oxygen chemical shifts, $\delta(^{17}\mathrm{O})$, were correlated with the corresponding substituent-induced carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{\mathrm{CO}}$, the a_1 values for *ortho*, *para* and *meta* derivatives were $a_1 = \rho_\mathrm{I}(^{17}\mathrm{O})/\rho_\mathrm{I}(\delta_{\mathrm{CO}}) = -4.00$, -2.85 and -2.52, respectively. Approximately the same values for the parameter $a_1 = \rho_\mathrm{I}(^{17}\mathrm{O})/\rho_\mathrm{I}(\delta_{\mathrm{CO}}) = -3.62$, -3.10 and -2.20 we found in the previous work[14] for phenyl esters of *ortho*-, *para*- and *meta*-substituted benzoic acids, X-$C_6H_4CO_2C_6H_5$.

The positive values of the parameter a_1 in Table IV prove that the substituent-induced $\delta(^{17}\mathrm{O})$ values, the $\Delta\log k$ values of the alkaline hydrolysis and the IR carbonyl stretching frequencies, (ν_{CO}), grow with increase of the inductive effects of substituent included.

CONCLUSIONS

The ^{17}O NMR spectra for 44 *ortho*-, *meta*- and *para*-substituted phenyl esters $C_6H_5CO_2C_6H_4$-X, and alkyl esters, $C_6H_5CO_2R$ of benzoic acid containing substituents in phenoxy OC_6H_4-X and alkoxy OR moieties were recorded. The ^{17}O NMR chemical shifts, $\delta(^{17}O)$, of the carbonyl oxygen for *para* and *meta* derivatives showed a good correlation with the $\sigma°$ constants as the dual substituent parameter treatment using the Taft inductive, σ_I, and resonance, $\sigma°_R$, substituent constants. This reveals the absence of through conjugation and coplanarity between the ester carboxyl group plane and the aromatic plane in phenoxy part. The chemical shifts, $\delta(^{17}O)$, for *ortho* derivatives correlated well with the Charton equation containing the inductive, σ_I, resonance, $\sigma°_R$, and the steric (E_s^B) substituent constants in case the correlation was carried out separately for esters with the electron-donating +*R* substituents and –*R* substituents. The positive ρ_I and ρ_R values proved that electron-attracting *ortho*, *meta* and *para*, as well as alkyl substituents caused the deshielding effect (downfield shift) of the carbonyl and single-bonded ^{17}O signal. The electron-donating +*R* and +*I* substituents resulted in shielding effect (upfield shift). In *ortho* derivatives with +*R* substituents the carbonyl oxygen and single-bonded oxygen were found to be deshielded due to the –*I* inductive and steric effects and shielded by the +*R* resonance effect. The contribution of the *ortho* resonance term to the single-bonded oxygen chemical shifts was ca. five times stronger than that to the carbonyl oxygen. In the carbonyl oxygen chemical shifts, $\delta(^{17}O)$, the susceptibility to the inductive effect of *ortho*, *meta* and *para* substitutents from the phenyl side was found to be ca. twice weaker than that from the benzoyl side. In substituted alkyl benzoates, $C_6H_5CO_2R$, for carbonyl oxygen and single-bonded oxygen chemical shifts, $\delta(^{17}O)$, the positive inductive ($\rho_I > 0$) and negative steric effects ($\delta_{Alk}E_s^B < 0$) were detected. The carbonyl oxygen chemical shifts, $\delta(^{17}O)$, for *ortho*-substituted benzoates, $C_6H_5CO_2C_6H_4$-X, correlated well with the corresponding substituent-induced carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, IR carbonyl stretching frequencies, $\Delta\nu_{CO}$, and the rates of the alkaline hydrolysis, $\Delta\log k$, in case the additional resonance and steric terms were involved and the data treatment was carried out separately for esters containing +*R* substituents and –*R* substituents.

SUPPLEMENTARY MATERIAL

The following supplementary material is available:

Synthesis of compounds. The preparation procedure and analyses of substituted phenyl benzoates and alkyl benzoate; the ^1H and ^{13}C NMR spectra for 2-(Methylsulfonyl)phenyl benzoate, 2-Acetylphenyl benzoate, 2-(Trifluoromethyl)phenyl benzoate, 2-Bromophenyl benzoate, 2,6-Dimethylphenyl benzoate, 2,6-Dinitrophenyl benzoate, 3-Chlorophenyl benzoate, 3-Bromophenyl benzoate, 3-(Trifluoromethyl)phenyl benzoate, 3-(Dimethylamino)phenyl benzoate, 4-(Methylsulfonyl)phenyl benzoate, 4-(Trifluoromethyl)phenyl benzoate, 2,2,2-Trichloroethyl benzoate, 2-Bromoethyl benzoate.

Data processing. Equations for correlation of NMR chemical shifts, $\delta(^{17}O)$, with substituent constants (Eqs (*1*)–(*5*)) and for correlation of the carbonyl oxygen ^{17}O NMR chemical shifts, $\delta(^{17}O)$, with the carbonyl carbon ^{13}C NMR chemical shifts, $\Delta\delta_{CO}$, the carbonyl IR stretching frequencies, $\Delta\nu_{CO}$ and the $\Delta\log k$ values of the alkaline hydrolysis using Eqs (*6*)–(*9*).

This work was supported by the grant No. 8162 of the Estonian Science Foundation.

REFERENCES

1. Nummert V., Piirsalu M., Vahur S., Travnikova O., Koppel I. A.: *Collect. Czech. Chem. Commun.* **2009**, *74*, 29.
2. Nummert V., Piirsalu M., Koppel I. A.: *J. Phys. Org. Chem.* **2010**, *23*, 497.
3. Nummert V., Piirsalu M.: *J. Chem. Soc., Perkin Trans. 2* **2000**, 583.
4. Nummert V., Piirsalu M.: *Collect. Czech. Chem. Commun.* **2002**, *67*, 1833.
5. Nummert V., Piirsalu M., Mäemets V., Koppel I.: *J. Phys. Org. Chem.* **2005**, *18*, 1138.
6. Nummert V., Piirsalu M., Mäemets V., Koppel I.: *Collect. Czech. Chem. Commun.* **2006**, *71*, 107.
7. Nummert V., Piirsalu M., Koppel I. A.: *J. Phys. Org. Chem.* **2007**, *20*, 778.
8. Palm V. A., Püssa T. O., Nummert V. M., Talvik I. V.: *Reakts. Sposobnost Organ. Soedin. (Tartu)* **1973**, *10*, 243; *Chem. Abstr.* **1973**, *79*, 114921.
9. Püssa T. O., Nummert (Maremäe) V. M., Palm V. A.: *Reakts. Sposobnost Organ. Soedin. (Tartu)* **1972**, *9*, 871; *Chem. Abstr.* **1973**, *78*, 140894.
10. Nummert V., Piirsalu M.: *J. Phys. Org. Chem.* **2002**, *15*, 353.
11. Nummert V., Piirsalu M., Koppel I. A.: *Collect. Czech. Chem. Commun.* **2006**, *71*, 1557.
12. Nummert V., Piirsalu M., Mäemets V., Vahur S., Koppel I. A.: *J. Phys. Org. Chem.* **2009**, *22*, 1155.
13. Nummert V., Travnikova O., Vahur S., Leito I., Piirsalu M., Mäemets V., Koppel I., Koppel I. A.: *J. Phys. Org. Chem.* **2006**, *19*, 654.
14. Nummert V., Mäemets, V., Piirsalu M., Koppel I. A.: *J. Phys. Org. Chem.* **2011**, *24*, 539.
15. Boykin D. W. (Ed.): *^{17}O NMR Spectroscopy in Organic Chemistry*. CRC Press, Boca Raton, Ann Arbor, Boston 1990.
16. Duddeck H., Tóth G., Simon A.: *Nuclear Magnetic Resonance (NMR) Data: Chemical Shifts for Oxygen-17* (R. R. Gupta and M. D. Lechner, Eds), III/35E. Springer-Verlag, Berlin, Heidelberg, New York 2002.
17. Cheng C. P., Lin S. C., Shaw G.-S.: *J. Magn. Reson.* **1986**, *69*, 58.
18. Gibson J. L., Hart L. S.: *J. Chem. Soc., Perkin Trans. 2* **1991**, 1343.
19. Orsini F., Ricca G. S.: *Org. Magn. Reson.* **1984**, *22*, 653.
20. Boykin D. W., Deadwyler G. H., Baumstark A. L.: *Magn. Reson. Chem.* **1988**, *26*, 19.
21. Mark H., Baker T., Noe E. A.: *J. Am. Chem. Soc.* **1989**, *111*, 6551.
22. Jios J. L., Duddeck H.: *Z. Naturforsch., B: Chem. Sci.* **2000**, *55*, 189.

23. Perumal S., Vasuki G., Vijayabaskar V., Selvaraj S., Boykin D. W.: *Magn. Reson. Chem.* **1998**, *36*, 720.
24. Neuvonen H., Neuvonen K., Pasanen P.: *J. Org. Chem.* **2004**, *69*, 3794.
25. Neuvonen H., Neuvonen K., Koch A., Kleinpeter E., Pasanen P.: *J. Org. Chem.* **2002**, *67*, 6995.
26. Dell'Erba C., Sancassan F., Leandri G., Novi M., Pertillo G., Mele A.: *Gazz. Chim. Ital.* **1989**, *119*, 643.
27. Lee C. K., Yu J. S., Lee H.-J.: *J. Heterocycl. Chem.* **2002**, *37*, 1207.
28. Exner O., Dahn H., Péchy P.: *Magn. Reson. Chem.* **1992**, *30*, 381.
29. Maccagno M., Mele A., Musio R., Petrillo G., Sancassan F., Sciacovelli O., Spinelli D.: *ARKIVOC* **2009**, 212.
30. Balakrishnan P., Baumstark A. L., Boykin D. W.: *Org. Magn. Reson.* **1984**, *22*, 753.
31. Zhuo J.-C.: *Molecules* **1999**, *4*, 320.
32. Balakrishnan P., Baumstark A. L., Boykin D. W.: *Tetrahedron Lett.* **1984**, *25*, 169.
33. Baumstark A. L., Balakrishnan P., Dotrong M., McCloskey C. J., Oakley M. G., Boykin D. W.: *J. Am. Chem. Soc.* **1987**, *109*, 1059.
34. Boykin D. W., Chandrasekaran S., Baumstark A. L.: *Magn. Reson. Chem.* **1993**, *31*, 489.
35. Sugawara T., Kawada Y., Katoh M., Iwamura H.: *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3391.
36. Orendt A. M., Biekofsky R. R., Pomilio A. B., Contreras R. H., Facelli J. C.: *J. Phys. Chem.* **1991**, *95*, 6179.
37. Katoh M., Sugawara T., Kawada Y., Iwamura H.: *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3475.
38. Kolehmainen E., Knuutinen J.: *Magn. Reson. Chem.* **1988**, *26*, 1112.
39. Kalabin G. A., Kushnarev D. F., Valeyev R. B., Trofimov B. A., Fedotov M. A.: *Org. Magn. Reson.* **1982**, *18*, 1.
40. Jios J. L., Duddeck H., Romanelli G. P., Autino J. C.: *Magn. Reson. Chem.* **2003**, *41*, 739.
41. Liepinč E. E., Zicmane I. A., Lukevics E., Dubinskaja E. I., Voronkov M. G.: *Zh. Obshch. Khim.* **1983**, *53*, 1092.
42. Crandall J. K., Centeno M. A.: *J. Org. Chem.* **1979**, *44*, 1183.
43. Liepinč E., Zicmane I., Lukevics E.: *J. Organomet. Chem.* **1986**, *306*, 167.
44. Alam T. M.: *Magn. Reson. Chem.* **1998**, *36*, 132.
45. Alam T. M., Click C. A.: *Spectrosc. Lett.* **1998**, *31*, 587.
46. Liepinč E., Zicmane I., Lukevics E.: *J. Organomet. Chem.* **1986**, *306*, 327.
47. Delseth C., Kintzinger J.-P.: *Helv. Chim. Acta* **1978**, *61*, 1327.
48. Béraldin M.-T., Vauthier E., Fliszár S.: *Can. J. Chem.* **1982**, *60*, 106.
49. Delseth C., Kintzinger J.-P.: *Helv. Chim. Acta* **1976**, *59*, 466.
50. Charton M.: *J. Am. Chem. Soc.* **1969**, *91*, 624.
51. Nummert V., Piirsalu M.: *Org. Reactiv. (Tartu)* **1995**, *29*, 109; *Chem. Abstr.* **1995**, *124*, 145051.
52. Püssa T. O., Nummert (Maremäe) V. M., Palm V. A.: *Reakts. Sposobnost Organ. Soedin. (Tartu)* **1972**, *9*, 697; *Chem. Abstr.* **1973**, *78*, 147026.
53. Nummert V. M., Piirsalu M. V.: *Org. Reactiv. (Tartu)* **1975**, *11*, 899; *Chem. Abstr.* **1976**, *84*, 58393.
54. Nummert V. M., Bogdanov A.: *Org. Reactiv. (Tartu)* **1989**, *26*, 231.
55. Nummert V., Eek M., Piirsalu M.: *Org. Reactiv. (Tartu)* **1981**, *18*, 363; *Chem. Abstr.* **1983**, *98*, 178451.
56. Weygand C.: *Weygand-Hilgetag: Organish-Chemische Experimentierkunst*, 4th ed. (G. Hilgetag and A. Martini, Eds). Johann Ambrosius Barth, Leipzig 1970.

57. Krayushkin M. M., Levchenko K. S., Yarovenko V. N., Zavarzin I. V., Barachevsky V. A., Puankov Y. A., Valova T. M., Kobeleva O. I.: *ARKIVOC* **2009**, 269.
58. Bernoulli A. L., St. Goar A.: *Helv. Chim. Acta* **1926**, *9*, 730.
59. Heilbron I., Bunbury H. M. (Eds): *Dictionary of Organic Compounds*, Vol. 1. Eyre & Spottiswoode, London 1946.
60. Finnegan R. A., Mattice J. J.: *Tetrahedron* **1965**, *21*, 1015.
61. Kirsch J. F., Clewell, W., Simon A.: *J. Org. Chem.* **1968**, *33*, 127.
62. Akahori Y.: *Chem. Pharm. Bull.* **1965**, *13*, 368.
63. Palm V. A. (Ed.): *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*, 5(2), pp. 164–165. Publishing House of VINITI, Moscow 1979.
64. Exner O.: *Correlation Analysis in Chemistry* (N. B. Chapman and J. Shorter, Eds), pp. 439–540. Plenum Press, New York, London 1978.
65. Taft R. W., Jr., Lewis I. C.: *J. Am. Chem. Soc.* **1958**, *80*, 2436.
66. Taft R. W., Jr., Ehrenson S., Lewis I. C., Glick R. E.: *J. Am. Chem. Soc.* **1959**, *81*, 5352.
67. Nummert V. M., Piirsalu M. V.: *Org. Reactiv. (Tartu)* **1975**, *11*, 921; *Chem. Abstr.* **1973**, *79*, 114921.
68. Aslam M. H., Burden A. G., Chapman N. B., Shorter J., Charton M.: *J. Chem. Soc., Perkin Trans. 2* **1981**, 500.
69. Charton M.: *Steric Effects in Drug Design* (M. Charton and I. Motoc, Eds), pp. 107–118. Academie-Verlag, Berlin 1983.
70. Charton M.: *J. Am. Chem. Soc.* **1975**, *97*, 1552.
71. Püssa T. O., Palm V. A.: *Reakts. Sposobnost Organ. Soedin. (Tartu)* **1972**, *9*, 1209; *Chem. Abstr.* **1973**, *79*, 104511.
72. St. Amour T. E., Burgar M. I., Valentine B., Fiat D.: *J. Am. Chem. Soc.* **1981**, *103*, 1128.
73. Ditchfield R., Del Bene J. E., Pople J. A.: *J. Am. Chem. Soc.* **1972**, *94*, 703.
74. Dahn H., Carrupt P.-A.: *Magn. Reson. Chem.* **1997**, *35*, 577.
75. Dahn H., Péchy P., Toan V. V.: *Magn. Reson. Chem.* **1997**, *35*, 589.
76. Dahn H.: *J. Chem. Educ.* **2000**, *77*, 905.
77. Le Fèvre R. J. W., Sundaram A.: *J. Chem. Soc.* **1962**, 3904.
78. Exner O., Fidlerová Z., Jehlička V.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 2019.
79. Adams J. M., Morsi S. E.: *Acta Crystallogr., Sect. B* **1976**, *32*, 1345.
80. Cinacchi G., Prampolini G.: *J. Phys. Chem. A* **2005**, *109*, 6290.
81. Wrzalik R., Merkel K., Kocot A.: *J. Mol. Model.* **2003**, *9*, 248.
82. Bogatyreva I. K., Avakyan V. G., Khodzhaeva V. L.: *Russ. Chem. Bull.* **1995**, *44*, 443.
83. Abdullin S. N., Furer V. L.: *Zh. Prikl. Spektrosk.* **1988**, *48*, 592.
84. Vizitiu D., Lazar C., Radke J. P., Hartley C. S., Glaser M. A., Lemieux R. P.: *Chem. Mater.* **2001**, *13*, 1692.
85. Li S., Chesnut D. B.: *Magn. Reson. Chem.* **1985**, *23*, 625.
86. Li S., Chesnut D. B.: *Magn. Reson. Chem.* **1986**, *24*, 93.
87. Guy R. G., Lau R., Rahman A. U., Swinbourne F. J.: *Spectrochim. Acta, Part A* **1997**, *53*, 361.
88. Muchall H. M.: *J. Phys. Chem. A* **2008**, *112*, 9118.
89. Kolehmainen E., Laihia K., Kauppinen R., Rasala D., Puchala A.: *J. Phys. Org. Chem.* **1995**, *8*, 577.