SUPPLEMENTARY MATERIAL

$^{17}$O NMR study of ortho and alkyl substituent effects in substituted phenyl and alkyl esters of benzoic acid

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1. EXPERIMENTAL

a. Synthesis of compounds

The preparation procedure and characteristics for the most ortho-, meta-, and para-substituted phenyl esters of benzoic acids, $C_6H_5CO_2C_6H_4X$, and alkyl esters of benzoic acid, $C_6H_5CO_2R$, have been previously described.$^9,51-55$

The phenyl benzoates, $C_6H_5CO_2C_6H_4X$, (X = 2-SO$_2$CH$_3$, 2-COCH$_3$, 2-CF$_3$, 3-Cl, 4-SO$_2$CH$_3$, 4-CF$_3$) were prepared by the addition of benzyol chloride to the corresponding substituted phenol in pyridine with stirring at 0 ºC (the Einhorn method)$^{56}$. The crude esters were recrystallized from aqueous ethanol. 2-(Methylsulfonyl)phenyl benzoate: yield 42 %, m.p. 172-173 ºC. 2-Acetylphenyl benzoate: yield 66 %, m.p. 84-86 ºC, Reference$^57$, m.p. 87-88 ºC. 2-(Trifluoromethyl)phenyl benzoate: yield 56 %, m.p. 39-40 ºC, Reference$^5$, b.p. 125-126 ºC. 3-Chlorophenyl benzoate: yield 73 %, m.p. 70-71 ºC, Reference$^58$, 70 ºC. 4-(Methylsulfonyl)phenyl benzoate: yield 61 %, m.p. 155-156 ºC. 4-(Trifluoromethyl)phenyl benzoate: yield 67 %, m.p. 113-114 ºC. The phenyl benzoates, $C_6H_5CO_2C_6H_4X$, (X = 3-Br, 3-N(CH$_3$)$_2$, 3-CF$_3$, 2-Br) and 2,6-dimethylphenyl benzoate, were prepared by addition the benzyol chloride to the mixture of the corresponding substituted phenol in aqueous 10 % sodium hydroxide (the Schotten-Baumann method). 3-Bromophenyl benzoate: yield 54 %, m.p. 85-86 ºC, Reference$^{27}$, m.p. 83-85 ºC. 3-(Dimethylamino)phenyl benzoate: yield 55 %, m.p. 92-93 ºC, Reference$^{59}$, m.p. 94 ºC. 3-(Trifluoromethyl)phenyl benzoate: yield 43 %, b.p. 118-120 ºC/1.9 mbar. 2-Bromophenyl benzoate: yield 24 %, b.p. 148-149 ºC/1.8 mbar. 2,6-Dimethylphenyl benzoate: yield 49 %, m.p. 41-42 ºC, Reference$^{60}$, m.p. 42-42.8 ºC. 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 ºC.$^{61}$ 2,6-Dinitrophenyl benzoate: yield 54 %, m.p. 116-117 ºC, Reference$^{62}$, m.p. 112 ºC. 2,2,2-Trichloroethyl benzoate$^{12}$ was purified by distillation, b.p. 108 ºC/2.2 mbar.
b. $^1$H and $^{13}$C NMR spectra of phenyl benzoates

Purity of synthesized phenyl benzoates, C$_6$H$_5$CO$_2$C$_6$H$_4$X (X = 2-SO$_2$CH$_3$, 2-COCH$_3$, 2-CF$_3$, 2-Br, 2,6-(CH$_3$)$_2$, 2,6-(NO$_2$)$_2$, 3-Cl, 3-N(CH$_3$)$_2$, 3-CF$_3$, 4-SO$_2$CH$_3$, 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.

2-(Methylsulfonyl)phenyl benzoate

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1H NMR: 8.24 m, 2H (H-2,6); 7.55 t, 2H (H-3,5) $^3J_{av}$ = 7.6; 7.65-7.78 m, 2H (H-4,12); 8.10 m, 1H (H-10); 7.44-7.51 m, 2H (H-11,13), 3.16 s, 3H (H-14).
$^{13}$C NMR: 129.00 (C-1); 130.47 (C-2,6); 128.90 (C-3,5); 134.13 (C-4); 164.37 (C-7); 148.99 (C-8); 133.12 (C-9); 130.07 (C-10); 126.50 (C-11); 135.03 (C-12); 124.80 (C-13); 44.01 (C-14).
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2-Acetylphenyl benzoate

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1H NMR: 8.21 m, 2H (H-2,6); 7.46-7.68 m, 4H (H-3,4,5,12); 7.85 dd, 1H (H-10), $^2J$ = 7.8, $^4J$ = 1.8; 7.34 dt, 1H (H-11), $^3J_{av}$ = 7.6, $^4J$ = 1.3; 7.22 dd, 1H (H-13) 2.53 s, 3H (H-15). $^{13}$C NMR: 129.33 (C-1); 130.28 (C-2,6); 128.69 (C-3,5); 133.78 (C-4); 165.10 (C-7); 149.38 (C-8); 131.38 (C-9); 130.23 (C-10); 126.14 (C-11); 133.33 (C-12); 123.90 (C-13); 197.40 (C-14); 29.70 (C-15).
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2-(Trifluoromethyl)phenyl benzoate
1H NMR: 7.2-7.7 m, 7H (H-3,4,5,10,11,12,13); 8.21 m, 2H (H-2,6). 13C NMR: 129.10 (C-1); 130.46 (C-2,6); 128.76 (C-3,5); 133.93 (C-4); 164.52 (C-7); 148.70 q (C-8), 3 J_{C-F} = 2.0; 123.20 q (C-9), 4 J_{C-F} = 31.2; 127.00 q (C-10), 3 J_{C-F} = 5.0; 125.92 (C-11); 133.05 (C-12); 124.55 (C-13); 123.30 q (C-14), 1 J_{C-F} = 273.0.

2-Bromophenyl benzoate

1H NMR: 8.23 m, 2H (H-2,6); 7.47 m, 2H (H-3,5); 7.56-7.64 m, 2H (H-4, 10); 7.10 ddd, 1H (H-11), 2 J = 7.9, 3 J = 7.0, 4 J = 2.0; 7.31 ddd, 1H (H-12), 2 J = 8.0, 3 J = 7.0, 4 J = 1.5; 7.25 ddd, 1H (H-13), 2 J = 8.0, 3 J = 2.0, 4 J = 0.5. 13C NMR: 129.10 (C-1); 130.33 (C-2,6,10); 128.61 (C-3,5); 133.36 (C-4); 164.13 (C-7); 148.53 (C-8); 116.27 (C-9); 133.75 (C-10); 127.26 (C-11); 128.43 (C-12); 123.92 (C-13).

2,6-Dimethylphenyl benzoate

1H NMR: 8.25 m, 2H (H-2,6); 7.50 m, 2H (H-3,5); 7.62 m, 1H (H-4), 3 J = 7.3; 7.09 br s, 2H (H-10, 12) 7.08 br s, 1H (H-11). 13C NMR: 129.59 (C-1); 130.18 (C-2,6); 128.65 (C-3,5,10,12); 133.51 (C-4); 164.31 (C-7); 148.54 (C-8); 130.43 (C-9,13); 125.90 (C-11); 16.34 (C-14).

2,6-Dinitrophenyl benzoate
\[ \text{O}_2\text{N} \]

\[ \text{O}_2\text{N} \]

\[ \text{O}_2\text{N} \]

\[ \text{O}_2\text{N} \]

1H NMR: 7.50-7.74 m, 4H (H-3,4,5,11); 8.17 m, 2H (H-2,6); 8.34 d, 2H (H-10,12), \( ^3J = 8.2 \). 13C NMR: 127.39 (C-1); 129.94 (C-2,6); 128.91 (C-3,5); 134.77 (C-4); 163.21 (C-7); 139.03 (C-8); 144.03 (C-9,13); 130.86 (C-10,12); 126.61 (C-11).

3-Chlorophenyl benzoate

\[ \text{O}_2\text{N} \]

\[ \text{O}_2\text{N} \]

1H NMR: 8.18 m, 2H (H-2,6); 7.50 m, 2H (H-3,5); 7.64 m, 1H (H-4); 7.22-7.29 m, 2H (H-9,11); 7.35 m, 1H (H-12); 7.13 ddd, 1H (H-13), \( ^3J = 7.9 \), \( ^4J = 1.5 \), \( ^4J = 2.1 \). 13C NMR: 129.32 (C-1); 130.24 (C-2,6); 128.67 (C-3,5); 133.79 (C-4); 164.71 (C-7); 151.63 (C-8); 122.46 (C-9); 134.85 (C-10); 126.16 (C-11); 130.24 (C-12); 120.15.

3-Bromophenyl benzoate

\[ \text{O}_2\text{N} \]

\[ \text{O}_2\text{N} \]

1H NMR: 8.17 m, 2H (H-2,6); 7.49 m, 2H (H-3,5); 7.63 m, 1H (H-4) \( ^3J = 7.3 \); 7.37-7.42 m, 2H (H-9,11); 7.28 t, 1H (H-12), \( ^3J_{av} = 8.2 \); 7.16 ddd, 1H (H-13), \( ^3J = 8.1 \), \( ^4J = 1.5 \), \( ^4J = 2.0 \). 13C NMR: 129.27 (C-1); 130.22 (C-2,6); 128.65 (C-3,5); 133.78 (C-4); 164.66 (C-7); 151.64 (C-8); 125.29 (C-9); 122.46 (C-10); 129.05 (C-11); 130.48 (C-12); 120.61 (C-13).

3-(Trifluoromethyl)phenyl benzoate

\[ \text{O}_2\text{N} \]

\[ \text{O}_2\text{N} \]

1H NMR: 8.18 m, 2H (H-2,6); 7.37-7.51 m, 6H (H-3,5,9,11,12,13); 7.62 m, 1H (H-4) \( ^3J = 7.3 \).
$^1$H NMR: 8.20 m, 2H (H-2,6); 7.50-7.63 m, 4H (H-3,5,9,13); 7.73 m, 1H (H-4), $^3$$J = 7.3$; 6.51-6.64 m, 3H (H-9,11,13); 7.26 t, 1H (H-12), $^3$$J_{av} = 8.0$; 6.94 s, 6H (H-14).

$^{13}$C NMR: 130.36 (C-1); 131.21 (C-2,6); 130.04 (C-3,5); 135.25 (C-4); 165.72 (C-7); 156.29 (C-8); 124.09 (C-9,13); 130.22 (C-10,12); 139.88 (C-11); 44.92 (C-14).

4-(Trifluoromethyl)phenyl benzoate

$^1$H NMR: 8.20 m, 2H (H-2,6); 7.51 m, 2H (H-3,5); 7.61-7.71 m, 3H (H-4,10,12); 7.34 d, 2H (H-9,13), $^3$$J = 8.5$.

$^{13}$C NMR: 129.28 (C-1); 130.35 (C-2,6); 128.77 (C-3,5); 133.97 (C-4); 164.66 (C-7); 153.76 (C-8), $^3$$J_{F-C} =1.5$; 122.32 (C-9,13);126.91 (C-10,12), $^3$$J_{F-C} =3.7$; 128.34 (C-11), $^2$$J_{F-C} =32.8$; 124.07 (C-14), $^1$$J_{F-C} =272.2$. 

2,2,2-Trichloroethyl benzoate
H NMR: 8.12 m, 2H (H-2,6); 7.44 m, 2H (H-3,5); 7.58 m, 1H (H-4); 4.95 s, 2H (H-8). \( ^{13} \)C NMR: 128.72 (C-1); 130.00 (C-2,6); 128.54 (C-3,5); 133.69 (C-4); 164.68 (C-7); 74.36 (C-8); 95.12 (C-9).

2-Bromoethyl benzoate (Aldrich)

H NMR: 8.05 m, 2H (H-2,6); 7.41 m, 2H (H-3,5); 7.54 m, 1H (H-4); 4.58 t, 2H (H-8), \( \delta \)J = 6.1; 3.60 t, 2H (H-9), \( \delta \)J = 6.1. \( ^{13} \)C NMR: 129.75 (C-1); 129.70 (C-2,6); 128.40 (C-3,5); 133.17 (C-4); 165.87 (C-7); 64.19 (C-8); 28.83 (C-9).

2. DATA PROCESSING

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, \( \text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4-\text{X} \), given in Table I were treated according to the Taft and Charton equations using the Taft's \( \sigma ^{\circ} \)63,64, inductive \( \sigma _{I} \)64,65, and the resonance \( \sigma _{R}^{\circ} \)(\( \sigma _{R}^{\circ} = \sigma _{p}^{\circ} - \sigma _{I} \))64,66 substituent constants:

\[
\delta ^{17} \text{O}_{\text{para(meta)}} = \delta ^{17} \text{O}_H + (\rho _{\text{para(meta)}}) \sigma ^{\circ} \tag{1}
\]

\[
\delta ^{17} \text{O}_{\text{para(meta)}} = \delta ^{17} \text{O}_H + (\rho _{\text{para(meta)}}) \sigma _I + (\rho _{\text{para(meta)}}) \sigma _{R}^{\circ} \tag{2}
\]

In the case of ortho derivatives the significance of the inductive, resonance and steric effects to the substituent-induced chemical shift, \( \delta ^{17} \text{O} \), was estimated using the following Charton equations50 (3) and (4):

\[
\delta ^{17} \text{O}_{\text{ortho}} = \delta ^{17} \text{O}_H + (\rho _{\text{ortho}}) \sigma _I + (\rho _{\text{ortho}}) \sigma _{R}^{\circ} + \delta _{\text{ortho}} \tag{3}
\]

\[
\delta ^{17} \text{O}_{\text{ortho}} = \delta ^{17} \text{O}_H + (\rho _{\text{ortho}}) \sigma _I + (\rho _{\text{ortho}}) \sigma _{R}^{\circ} + \delta _{\text{ortho}} \tag{4}
\]

Eqs (11) and (12) were used separately for ortho-substituted derivatives containing the ortho electron-donating +R substituents (X = H, OCH₃, CH₃, (CH₃)₂, C(CH₃)₃, F, Cl, Br)
and derivatives with the ortho electron-withdrawing –R substituents (X = H, NO₂, CN, CF₃, SO₂CH₃, CO₂CH₃, CH₂O, 2,6-(NO₂)$_2$).

To compare of the substituent effects on the carbonyl oxygen chemical shifts, $\delta^{17}$O, for ortho-, para-, and meta-substituted phenyl and alkyl esters of benzoic acid (C₆H₅CO₂C₆H₄-X, C₆H₅CO₂R) with those in the corresponding carbonyl carbon $^{13}$C NMR chemical shifts, $\delta_{CO}$, the infrared stretching frequencies of the carbonyl group, $\nu_{CO}$, and the $\Delta$ log $k$ values of the alkaline hydrolysis following relationships were used:

$$
\delta^{17}$O$^{\text{ortho}} = \delta^{17}$O$^X + a_1(\text{ortho})((\Delta\delta_{CO})X (\Delta\nu_{CO})X (\Delta \log k)_X) + a_2(\text{ortho})n^R + a_3(\text{ortho})E^B_s
$$

(6)

$$
\delta^{17}$O$^{\text{para}} = \delta^{17}$O$^X + a_1(\text{para})((\Delta\delta_{CO})X (\Delta\nu_{CO})X (\Delta \log k)_X) + a_2(\text{para})n^R
$$

(7)

$$
\delta^{17}$O$^{\text{meta}} = \delta^{17}$O$^X + a_1(\text{meta})((\Delta\delta_{CO})X (\Delta\nu_{CO})X (\Delta \log k)_X) + a_2(\text{meta})n^R
$$

(8)

$$
\delta^{17}$O$^{\text{alk}} = \delta^{17}$O$^\text{CH}_3 + a_1(\text{alk})((\Delta\delta_{CO})R (\Delta\nu_{CO})R (\Delta \log k)_R) + a_2E^B_s
$$

(9)

In Eqs (6)-(9) ($\Delta\delta_{CO})X = (\delta_{CO})X - (\delta_{CO})^X, (\Delta\nu_{CO})X = (\nu_{CO})X - (\nu_{CO})^X$, and $\Delta \log k_X = \log k^X - \log k_X$. In correlations with Eqs (6)-(9) the carbonyl carbon $^{13}$C NMR chemical shifts, $\delta_{CO}$, given in Reference 12, the IR stretching frequencies of the carbonyl group, $\nu_{CO}$, in Reference 13 and the $\log k$ values for alkaline hydrolysis in water and aqueous 0.5 M Bu₄NBr for phenyl benzoates, C₆H₅CO₂C₆H₄-X, and alkylbenzoates, C₆H₅CO₂R, in Reference 5,10,11,51,52 were used.

The slope $a_1$ in Eqs (6)-(9) is the ratio of the inductive effects in the $^{17}$O NMR chemical shifts and in the corresponding process compared. In Eqs (6)-(9) $a_1 = \rho_1^{(17)}O/\rho_1(\delta_{CO}), \rho_1(\delta^{17}O)/\rho_1(\nu_{CO}), \rho_1(\delta^{17}O)/\rho_1(\nu\text{AH}), a_2 = \rho_R(\delta^{17}O) - a_1\rho_R(\delta_{CO}), \rho_R(\delta^{17}O) - a_1\rho_R(\nu_{CO}), \rho_R(\delta^{17}O) - a_1\rho_R(\nu\text{AH})$ and $a_3 = \delta_S(\delta^{17}O) - a_1\delta_S(\delta_{CO}), \delta_S(\delta^{17}O) - a_1\delta_S(\nu_{CO}), \delta_S(\delta^{17}O) - a_1\delta_S(\nu\text{AH})$. In relations shown the carbonyl carbon $^{13}$C chemical shifts is denoted by ($\delta_{CO}$), the IR carbonyl stretching frequencies by ($\nu_{CO}$), the alkaline hydrolysis is denoted by (AH), and the susceptibility to the steric factor by $\delta_S$.

The results of correlations of the carbonyl and the single-bonded oxygen $^{17}$O NMR chemical shifts, $\delta^{17}$O, for para-, meta-, and ortho-substituted phenyl esters of benzoic acid, C₆H₅CO₂C₆H₄-X, and alkyl benzoates, C₆H₅CO₂R, with Eqs (6)-(9) are shown in Table IV.