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THE t-BUTYL GROUP AS SENSOR GROUP OF THE ORTHO EFFECT

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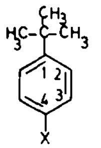
Abstract—The ^{13}C chemical shift difference between the Me group C atoms and the quaternary C atom of the t-Bu group in 58 *p*-, *m*- and *o*-substituted t-butyl-benzenes has been measured and analysed in terms of inductive, mesomeric and proximity effects. It is shown that the *ortho effect* is too complex to justify a unified explanation by a correlation treatment.

INTRODUCTION

The discussion on linear free energy relationships[1] has brought forward a vast amount of parameter sets. Besides the original Hammett σ_m and σ_p constants[2] an ever increasing number of new substituent constants are being introduced leading finally to dual parameter fits like the F/M system by Dewar[3] or the *F*/*R* system by Swain and Lupton.[4,5] For the so called *ortho effect* no common solution has been found.[6] There are many different ortho σ sets and again dual parameter treatments.[7] In this work we want to show that the *ortho effect* can be too complex to justify the search for a correlation set which explains the behaviour of all *ortho* substituents. Our results are based on new data with some considerable advantages: enough data points are provided within the *para*, *meta* and the *ortho* series and problematic substituents have not been eliminated. Furthermore all three series of compounds have been studied with the same method.

Choice of the system. Linear free energy relationships try to predict the reactivity of organic compounds which in most cases means the reactivity on a C atom center. Therefore ^{13}C NMR spectroscopy seems to be a reasonable probe taking into account the shortcomings of all physical ground state methods. In order to get more insight into the *ortho* effect we have chosen a monitor group with large steric requirements and have thus measured the ^{13}C chemical shifts in a series of 23 *para* t-butyl-benzenes **1**, 19 *meta* t-butyl-benzenes **2** and 16 *ortho* t-butyl-benzenes **3**.



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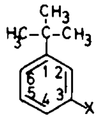

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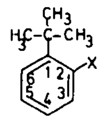

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As a measure of the substituent effect we have taken the chemical shift *difference* between the quaternary C atom and the Me group C atoms of the t-Bu groups for two reasons: A given substituent can affect the chemical shifts of these C atoms in different directions[8] and, experimentally, the chemical shift difference is better reproducable since concentration and solvent effects are at least attenuated.

RESULTS AND DISCUSSION

1. *Hammett type correlations.* The chemical shift difference within the t-Bu groups of the compounds measured are given in Table 1. All values are normalized to the parent compound t-butyl-benzene 1 1, hence positive values indicate a larger chemical shift difference than in t-butyl-benzene. ($\Delta\delta$ 3.21 ppm).

A correlation of the data in column 1 of Table 1 with σ_p and the data in column 2 with σ_m yields the following results:

$$\Delta\delta_{para} = 1.77\sigma_p - 0.18 \quad (n = 23, \sigma = 0.40\,\text{ppm}, r = 0.932)^\dagger$$

$$\Delta\delta_{meta} = 0.895\sigma_m + 0.11 \quad (n = 19, \sigma = 0.16\,\text{ppm}, r = 0.858).$$

We regard these fair correlations as sufficient to prove that the chemical shift difference within the t-Bu group can be taken as a measure of the electronic effects of a substituent. It should be pointed out, however, that a correlation with σ_p or σ_m seems rather to be a problem of selecting the proper σ_p and σ_m values, especially if one has a large number of experimental points available. The σ_p and σ_m values used for the correlations in this work were taken from McDaniel and Brown[9] as compiled by Exner.[10] By selecting σ_p values out of different Hammett parameter sets as given by Exner or by omitting certain substituents significantly better correlations can be achieved. This, however, is not the aim of this work.

With the Swain Lupton approach[4] we obtain the following results:

$$\Delta\delta_{para} = 0.82F + 0.21R \quad (n = 18, \sigma = 0.33\,\text{ppm}, r = 0.949)$$

$$\Delta\delta_{meta} = 0.68F + 0.18R \quad (n = 17, \sigma = 0.14\,\text{ppm}, r = 0.908).$$

The resonance contribution as defined by Swain and Lupton is 54% for the *para* compounds, that for the *meta* compounds 10%.

By taking the chemical shift of the quaternary C atom or of the Me group C atoms directly a good correlation can be achieved only for the quaternary C atom of the *para* series. Zuckermann[8] used the extended Hammett equa-

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† n = number of data points, σ = standard deviation, r = correlation coefficient. Different number of points in the correlations reported are due to the limited availability of the various substituent constants.

Table 1. ^{13}C chemical shift difference $\Delta\delta$ within the t-Bu group of substituted t-butylbenzenes[a]

Substituent	1	2	3	$1-2^{b)}$	$3-1^{c)}$
a $N \equiv N^+BF_4^-$	3.67				
b NO_2	1.14	0.8	1.78	0.34	0.64
c $C \equiv N$	1.09				
d COOH	0.85	0.33	1.31	0.52	0.46
e $COCH_3$	0.77	0.38	0.92	0.39	0.15
f $COOCH_2CH_3$	0.69	0.3	1.30	0.39	0.61
g $N(CH_3)_3^+\ J^-$	0.54	1.04		-0.5	
h $C \equiv CH$	0.45				
i J	0.17	0.34	3.52	-0.17	3.35
j $COO^{-\ e)}$	0.17	0.01	1.1	0.16	0.93
k Br	0.05	0.38	3.6	-0.33	3.55
l H	0.0	0.0	0.0	0.0	0.0
m CL	-0.04	0.84	3.17	-0.88	3.21
n C_6H_5	-0.08	0.16		-0.24	
o $OCOCH_3$	-0.19	0.3	1.0	-0.49	1.19
p F	-0.37	0.39		-0.76	
q CH_3	-0.38	-0.08	1.67	-0.30	2.05
r $t.C_4H_9$	-0.5	0.11	-0.45	-0.61	0.05
s OH	-0.69	0.17	1.64	-0.86	2.33
t OCH_3	-0.75	0.17	1.77	-0.92	2.52
u NH_2	-0.93	-0.09	1.38	-0.84	2.31
v $N(CH_3)_2$	-1.03	0.26	1.25	-1.29	2.28
w $O^{-\ f)}$	-2.17	-1.02	1.43	-1.15	3.6

a) given in ppm normalized to t.Butylbenzene 1l, measured in $CDCl_3$
b) difference between the para and meta compounds, compare text.
c) difference between the ortho and para compounds, compare text.
d) in CD_3OD
e) in D_2O
f) in DMSO-d_6

tion on a limited number of *para* compounds and found an inverse dependence on σ_I and σ_R for the Me groups as compared to the quaternary C atom. In view of a recent communication on the slope of the regression line between ^{13}C chemical shifts and substituent constants[11] we want to point out that the t-Bu group seems to be indeed another case, where this inverse relationship holds. These findings justify furthermore taking the chemical shift difference between both C atoms as a probe for the bond polarization. If one accepts, therefore, that the chemical shift difference within the t-Bu group does reflect substituent effects one can try to examine the following first order approximations:

(1a) $\Delta\delta_{para} \approx$ inductive + resonance effects
(1b) $\Delta\delta_{meta} \approx$ inductive effects
(1c) $\Delta\delta_{ortho} \approx$ inductive + resonance + proximity effects.

Hence, the difference between the *para* and *meta* series should at best reflect the resonance contribution. A correlation of this difference as listed in column 4 of Table 1 with σ_R values yields the following equation:

$$\Delta\delta_{para} - \Delta\delta_{meta} = 2.14\sigma_R - 0.05 \quad (n = 18, \sigma = 0.21\ \text{ppm}, r = 0.915).$$

Accordingly, the *meta* values do correlate with σ_I:

$$\Delta\delta_{meta} = 0.99\sigma_I - 0.002 \quad (n = 18, \sigma = 0.14\ \text{ppm}, r = 0.886).$$

2. *The* orthò effect. Any attempts to correlate the data in column 3 of Table 1 with different sets of σ_{ortho} constants[6] failed drastically. Dual parameter fits as the *F*/*R* system by Swain and Lupton or the use of the extended Hammett equation in the manner of Charton failed as well (multiple correlation factor $r = 0.65$, $n = 15$). Since most of the reactivity data in available *ortho* series correlate with the extended Hammett equation Charton concluded that steric effects play only a minor role for ortho substituted compounds. Because of the impossibility to correlate our $\Delta\delta_{ortho}$ values to any of the existing *ortho* parameter sets we assume that proximity effects are important in our case. The proximity effect sensed by the t-Bu group may be at best extracted by taking the difference between the values of the *ortho* and *para* series as suggested by Eqn 1c. These data are listed in column 5 of Table 1. They do not correlate with Tafts E_s values.

The *ortho effects* reported here are most likely not general but dependent on the method used for their detection, in our case ^{13}C spectroscopy. Hence, steric effects and local anisotropies are expected to be important. Use of these data, however, for predicting reactivities is limited.

If we group the data listed in column 5 of Table 1 we find substituents with an *ortho* deviation less than 1 ppm (NO_2, COOH, $COCH_3$, COOR, COO^-), some with a deviation between 1 and 3 ppm ($OCOCH_3$, CH_3, OH, OCH_3, NH_2, $N(CH_3)_2$) and four with values even more than 3 ppm (Cl, Br, J, O^-). The most outstanding value is that of the t-Bu group in **3r**.[12] For steric reasons one would have expected a large *ortho effect*. The fact, that $\Delta\delta_{ortho}$ has no difference at all from the corresponding *para* compound results from a downfield shift of both the quaternary and the Me group C atoms by about 3.5 ppm. Downfield shifts in ^{13}C-NMR in case of steric overcrowding are being discussed by several groups,[13,14] however, a theory of this effect has not been given. The substituents with *ortho* deviations higher than 3 ppm have three free electron pairs. Local anisotropies are expected to be mainly responsible for this effect. With the exception of **3q** all substituents of the second group have at least one free electron pair at the atom next to the benzene ring. Their steric requirements seem to be of the same order apart from the dimethylaminogroup. The value for this group is somewhat less than for the amino group, likely for the same reasons already discussed for the t-Bu group in **3r**. The ^{13}C spectrum of **3q** has been discussed by Pearson.[15] The polar effects of the substituents with a deviation less than 1 ppm are all similar. It is difficult to attempt a further factorization without overinterpreting the data.

It is interesting, however, to comment on the chemical shifts of the other side chain C atoms. In **3d**, **e**, **f** and **i** CO groups are attached directly to the benzene ring. Downfield shifts of up to 10 ppm are obtained if one compares the corresponding values in the *ortho* with the *para* or *meta* series. These downfield shifts can be explained by assuming less overlap between the π electrons of the CO group with the benzene π system in the sterically hindered *ortho* compounds. A detailed investigation of this effect has recently been published by Leibfritz.[16] No significant deviation from the corresponding *para* and *meta* compounds can be observed in **3n** or **t**, since the C atoms here are only in β position with respect to the benzene ring. A rather large downfield shift is observed for the *ortho* dimethylamino-group this being a further example of downfield ^{13}C shifts in case of steric overcrowding.[12-15]

3. *Aromatic carbon atoms*. The aromatic C atoms of the *para* series have been fully assigned using the standard substituent parameters for aromatic systems.[17] The data are in complete agreement with the eight compounds already reported by Zuckermann[8] and are given in Table 2.

The chemical shifts of the C atom 1 (*para* with respect to the substituent) correlate very well with the Swain Lupton parameters ($n = 18$, $\sigma = 1.77$ ppm, $r = 0.966$) predicting a resonance contribution of 70%. Similar findings have been reported for other aromatic systems.[18] From the data in Table 2 one can calculate the chemical shifts of the *meta* series. The experimental shifts are in good agreement with the calculated ones. However, in the *meta* series many signals are isochronous or very close to-

Table 2. ^{13}C chemical shifts of *para* substituted t-butylbenzenes **1**[a]

1		C-1	C-2	C-3	C-4	C_q	C_{Me}	others
a	$N\equiv N^+BF_4^-$	168.8	130.3	133.9	112.3	37.9	31.0	
b	NO_2	158.9	126.3	123 3	146.1	35.4	31.0	
c	$C\equiv N$	156.7	126.2	132.0	109.5	35.3	31.0	119.0
d	COOH	157.6	125.5	130.2	126.9	35.2	31.1	172.7
e	$COCH_3$	156.8	125.5	128.3	134.9	35.1	31.1	197.4, 26.4
f	$COOCH_2CH_3$	156.4	125.3	129.5	127.9	35.1	31.2	166.6, 60.7, 14.4
g	$N(CH_3)_3^+J^-$	153.9	127.7	119.9	144.7	34.9	31.1	58.3
h	$C\equiv CH$	152.2	125.3	132.0	119.3	34.8	31.2	83.9, 76.4
i	J	150.8	127.5	137.1	90.6	34.5	31.1	
j	COO^- [c]	154.6	125.6	129.9	134.4	35.0	31.6	175.5
k	Br	150.0	127.1	131.0	119.2	34.4	31.2	
l	H	151.0	125.2	128.1	125.4	34.6	31.4	
m	Cl	149.6	126.8	128.2	131.3	34.5	31.3	
n	C_6H_5	150.3	125.7	127.0	138.4	34.5	31.4	141.2, 128.7, 127.0, 126.8
o	$OCOCH_3$	148.6	126.3	120.0	148.6	34.5	31.4	169.3, 21.0
p	F [d]	146.8 (3)	126.8 (8)	114.7 (21)	161.0 (243)	34.4	31.5	
q	CH_3	148.2	125.1	128.8	134.7	34.3	31.5	20.8
r	$t.C_4H_9$	147.8	124.8	124.8	147.8	34.1	31.4	
s	OH	143.7	126.5	115.0	153.0	34.1	31.6	
t	OCH_3	143.3	126.2	113.5	157.5	34.0	31.6	55.0
u	NH_2	141.2	125.9	114.9	144.0	33.8	31.6	
v	$N(CH_3)_2$	139.5	125.8	112.8	148.7	33.8	31.6	40.8
w	O^- [e]	130.5	125.1	118.2	168.3	33.2	32.2	

[a] measured in $CDCl_3$ vs TMS

[b] in CD_3OD

[c] in D_2O vs $(CH_3)_3SiCD_2CD_2COONa$ (TSP), values were calculated with $\delta_{TSP} - \delta_{TMS} = 1.7$ ppm

[d] numbers in parentheses are $J_{^{19}F^{13}C}$ in Hz

[e] in DMSO-d_6

Table 3. ^{13}C chemical shifts of *meta* substituted t-butyl-benzenes 2[a]

2	C-1	C-3	C-2, C-4, C-5, C-6[b)]	C_q	C_{Me}	others
b NO_2	153.1	148.2	131.4, 128.8, 120.3, 120.0	34.8	30.8	
d COOH	151.7	129.4	130.9, 128.3, 127.6, 127.2	34.8	31.3	173.0
e $COCH_3$	151.8	137.2	130.1, 128.3 125.7, 124.9	34.8	31.2	198,3, 26.5
f $COOCH_2CH_3$	151.3	130.1	129.7, 127.9, 126.6, 126.3	34.6	31.1	166.8, 60.7, 14.2
g $N(CH_3)_3^+J^-$	154.7	147.1	130.3, 127.6, 117.0, 116.2	35.5	31.3	57.9
i J	153.7	94.6	134.6(2), 129.8, 124.6	34.7	31.2	
j COO^- c)	151.4	136.7	128.6, 128.3, 127.0, 126.7	34.8	31.6	175.7
k Br	153.5	122.5	129.6, 128.6(2) 123.9	34.8	31.2	
m Cl	154.6	134.6	125.7, 124.2 (3)	35.0	30.9	
n C_6H_5	151.7	142.1	128.7(2), 124.4(2)[d)]	34.9	31.5	141.2, 128.5, 127.1 127.4
o $OCOCH_3$	153.0	150.8	128.9, 122.7, 118.6(2)	34.8	31.3	169.3, 21.0
p F[f)]	154.0	163.0	129.4, 120.9, 112.9, 111.8	34.8	31.2	
	(7)	(244)	(8) (2) (6) (5)	(2)		
q CH_3	151.1	137.4	127.9, 126.1(2), 122.3	34.5	31.4	21.7
r $t.C_4H_9$	150.6	150.6	127.6, 122.4(2)122.2	34.8	31.5	
s OH	153.5	155.2	129.3, 118.0, 112.8, 112.6	34.7	31.3	
t OCH_3	153.0	159.6	129.0, 117.9, 112.1, 110.2	34.8	31.4	55.1
u NH_2	152.4	146.3	128.9, 115.6, 112.4(2)	34.5	31.3	
v $N(CH_3)_2$	152.3	149.8	128.8, 115.7, 115.6, 110.9	34.9	31.4	41.5
w O^- g)	150.7	171.3	128.1, 116.5, 116.3, 105.4	34.0	31.8	

a) measured in $CDCl_3$ vs TMS

b) not assigned, compare text. Numbers in parentheses indicate isochronous signals.

c) in D_2O vs $(CH_3)_3SiCD_2CD_2COONa$ (TSP), values were calculated with $\delta_{TSP}-\delta_{TMS}$ = 1.7 ppm

d) distinction to substituent signals tentative

f) numbers in parentheses are $J_{^{19}F^{13}C}$ in Hz

g) in DMSO-d_6

Table 4. ^{13}C chemical shifts of *ortho* substituted t-butyl-benzenes 3[a]

3	C-1	C-2	C-3, C-4, C-5, C-6[b)]	C_q	C_{Me}	others
b NO_2	151.5	141.3	130.7, 128.6, 126.9, 123.9	35.7	30.7	
d COOH	148.2	132.0	130.4, 129.0, 127.1, 125.5	36.0	31.5	178.0
e $COCH_3$	146.7	142.0	129.0, 127.1, 125.8, 125.2	35.8	31.7	207.6, 32.4
f $COOCH_2CH_3$	148.0	133.8	129.7, 129.0, 127.0, 125.4	36.1	31.6	171.7, 61.0 14.1
i J	150.3	95.0	143.7, 127.9, 127.4(2)	36.7	30.0	
j COO^- c)	145.2	141.0	127.9, 127.7, 127.4, 126.2	36.0	31.7	182.0
k Br	147.8	122.7	135.8, 127.9, 127.4, 127.2	36.6	29.8	
m Cl	146.5	133.8	131.9, 127.6, 127.1, 126.6	36.1	29.7	
o $OCOCH_3$	142.3	141.0	127.2, 126.9, 125.8, 124.1	34.5	30.3	169.5, 21.6
q CH_3	147.7	135.9	132.6, 125.7(2), 125.6	35.7	30.8	23.2
r $t.C_4H_9$	148.8	148.8	129.5(2)125.5(2)	37.6	34.9	
s OH	136.3	154.2	127.0(2), 120.7, 116.4	34.5	29.7	
t OCH_3	138.5	158.7	127.0, 126.6, 120.4, 111.8	34.8	29.8	54.9
u NH_2	133.6	144.6	126.9, 126.4, 118.6, 117.8	34.2	29.6	
v $N(CH_3)_2$	147.3	155.1	126.9, 125.6, 125.1, 126.7	35.5	31.0	47.1
w O^- d)	136.6	169.6	126.2, 124.6, 120.3, 107.9	34.4	29.8	

a) measured in $CDCl_3$ vs TMS

b) not assigned, compare text. Numbers in parentheses indicate isochronous signals.

c) in D_2O vs $(CH_3)_3SiCD_2CD_2COONa$ (TSP), values were calculated with δ_{TSP}- δ_{TMS} = 1.7 ppm

d) in DMSO-d_6

gether. The error in the calculation by substituent increments is too large to allow rigid assignment in all cases. We prefer, therefore, to give these data unassigned in the form of Table 3, especially since it is not the aim of this work to comment further on ^{13}C chemical shifts of aromatic C atoms. In the *ortho* series the error of the chemical shift calculation is larger and in most of the compounds C atoms 3, 4, 5 and 6 resonate very close together.

CONCLUSIONS

In this work it is shown that the *ortho effect* sensed by a physical ground state method such as nuclear magnetic resonance is highly dependent on special effects inherent in the method used for its detection. By taking a pilot group with large steric requirements strong deviations from para and meta compounds can indeed be observed. The sign and magnitude of these deviations, however, do not reflect pure polar or pure steric effects of a given substituent but are a complex mixture of very different changes. Any correlation with single or dual substituent parameters are therefore bound to fail.

EXPERIMENTAL

Compounds **1d, l, q, s, 2s** and **3s** were from commercial sources. For samples of **1b, u, 2u** and **3u** I thank Dr. W. Grahn, for a sample of **1r** Prof. H. G. Aurich and for a sample of **3q** Dr. H. Pearson. All other compounds were synthesized according to reported literature procedures.

Computations were carried out on a Varian V-73 Computer System with an adapted version of the multiple correlation program of Swain and Lupton.[4]

^{13}C-*Measurements.* The spectra were taken on a Varian CFT-20 spectrometer equipped with a 16k computer system and a 10 mm probe at 38°. Whenever possible all solns were 1 M in $CDCl_3$. In some cases, however, due to limited solubility or the small amount of material available the solns were more diluted. The chemical shifts in Tables 2–4 are therefore reported to one decimal place. For the compilation of the chemical shift difference in Table 1 two decimal places were used.

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