^{17}O vs ^{13}C NMR chemical shifts as effective indicators of π-electron-density distribution in hindered methyl benzoates

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Dedicated to Prof. Nicolò Vivona on his 70th birthday

Abstract

^{17}O NMR Substituent Chemical Shift (*SCS*) values on the carbonyl and methoxy oxygens in methyl 2,6-dimethyl-4-X-benzoates **2'** have been measured in acetonitrile-d_3 and compared with those of the 2,6-unsubstituted methyl 4-X-benzoates **2**, the former exhibiting very little sensitivity to the effect of 4-substituents and not appearing to be related to π-electron density changes in such sterically hindered systems.

Conversely ^{13}C NMR *SCS* values of the methoxy carbon of the ester function in either **2** and **2'**, although modest in size, exhibit a very good dual substituent parameter (*DSP*) correlation with the polar and resonance effect of 4-substituents and are therefore effective indicators of local π-electron densities.

Moreover, ^{13}C NMR *SCS* values of the methoxy carbon of **2'** exhibit an excellent linear correlation with those of 2,6-unsubstituted benzoates **2**. Once more this agrees with our previous conclusion that the resonance interaction between the aromatic ring and the ester group is essentially related to a π-polarization effect, not involving charge-transfer between the two moieties and therefore not sensitive to steric hindrance to their coplanarity.

Keywords: ^{17}O and ^{13}C NMR spectroscopy, alkyl benzoates, substituent effect

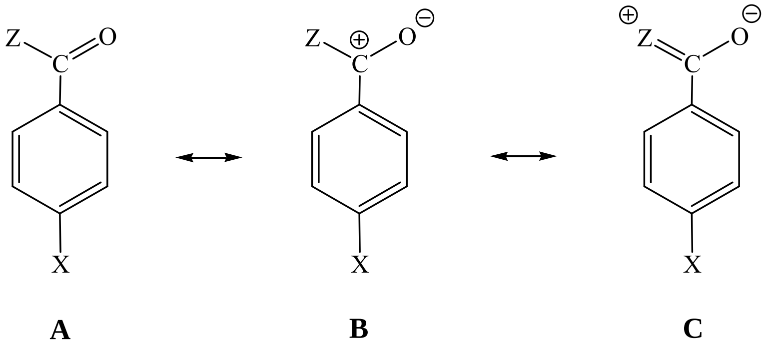
Introduction

Craik, Brownlee and coworkers, in their pioneering and extensive study on ^{13}C NMR chemical shifts in 1,4-disubstituted benzenes,[1] pointed out that in closely related series of compounds chemical-shift changes at a probe carbon induced by remote substituents can be related to π-electron-density variations, as most unwanted effects cancel out. On this basis, they stressed that the Substituent Chemical Shift ($SCS = \delta_{4\text{-}X} - \delta_{4\text{-}H}$) values on the carbonyl carbon of, *e.g.,* 4-X-substituted benzaldehydes, acetophenones, ethyl benzoates and benzamides can be dissected into a polar and a resonance component [dual substituent parameter (*DSP*) model][2] according to the equation

$$SCS = \rho_I\sigma_I + \rho_R\sigma_R$$

where σ_I and σ_R are previously determined constants mirroring the polar and resonance effect of the substituents while ρ_I and ρ_R estimate the sensitivity of the probe carbon to the two effects. The σ_R values can be chosen between four different sets of constants, named σ_R^+, σ_R^{BA}, σ_R^0, σ_R^-, and the goodness of fit is judged from the error-function $f = SD/RMS$, where *SD* represents the standard deviation of the fit and *RMS* is the root mean square of the experimental data.

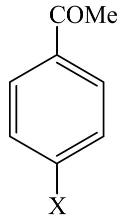
They found[1] that for all of the aromatic carbonyl compounds examined ρ_I is negative, mirroring a "reverse" polar effect of 4-substituents, *i.e.*, the electron withdrawing effect of a 4-substituent shields the carbonyl carbon and viceversa. This was explained on the basis of a polarization of the functional group π-system induced by the substituent dipole. More intriguingly, ρ_R was found to be positive ("normal" resonance effect) for the carbonyl carbon of benzaldehydes and acetophenones, but negative ("reverse" resonance effect) for that of ethyl benzoates and benzamides. Thus, e.g., electron-donor 4-substituents shield the carbonyl carbon of benzaldehydes and acetophenones but deshield that of ethyl benzoates and benzamides. This was interpreted[1b] on the basis of the importance of resonance structure **C** in the description of the latter compounds (Scheme 1). It was therefore argued that the main electronic interaction of an electron-donating *para* substituent produces, in benzaldehydes and acetophenones (A↔B), a "normal" effect at the carbonyl carbon as it is really a conjugating site, while it causes in ethyl



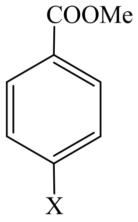
Scheme 1

benzoates and benzamides (A↔C) a "reverse" effect as the carbonyl carbon is now a non-conjugating site.

Starting from 1984, the dichotomy in the resonance interaction between carbonyl-based or other groups and benzene or thiophene moieties was further stressed by several studies of our group and a different rationale was given.[3] In particular, we have found[3c] that in CDCl$_3$ the carbonyl carbon chemical shifts of 2,6-dimethyl-4-X-acetophenones **1'**



1



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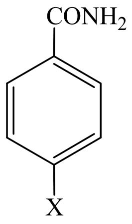

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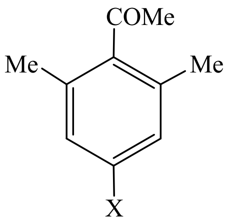
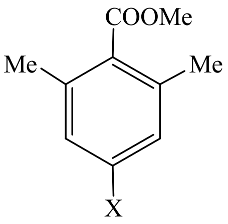
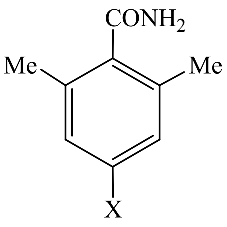


1'



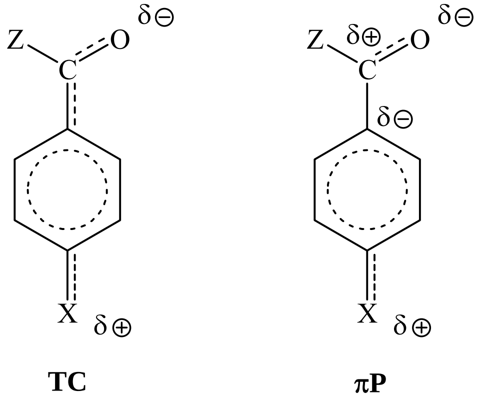
2'



3'

expectedly do not correlate with those of the corresponding 2,6-unsubstituted 4-X-acetophenone **1** (n = 8, r = 0.623), but the carbonyl carbon chemical shifts of methyl 2,6-dimethyl-4-X-benzoates **2'** *do correlate* with those of the corresponding 2,6-unsubstituted derivatives **2** (n = 8, r = 0.988) in spite of the quasi-planar structure[4a-c,e] of **2** and the large deviation from coplanarity[4c-e] between the carbonyl and the benzene ring in **2'**. Linear correlations were observed[3c] also between the carbonyl carbon chemical shifts of benzoates **2** and the hindered acetophenones **1'** (n = 8, r = 0.972) and, in DMSO-d_6, between benzamides **3'** and **3** (n = 7, r = 0.967),[3f] although in 2,6-dimethylbenzamides[5b] the torsion angle between the main functional group and the ring is much larger than in 2,6-unsubstituted ones.[5]

The different rationale we have given[2] is based on a dissection of the resonance interaction between the aromatic ring and the carbonyl-based functionalities into two components (see Scheme 2), (i) a through-conjugation (**TC**) component, with an effective charge-transfer between the ring and the carbonyl and (ii) a polarization of the π-system (**πP**) of the probe group induced by the charge-density variation that the conjugative interaction between the 4-X substituent and the aromatic ring determines on C(1). The former dominates in aromatic aldehydes and ketones, while the latter plays a major role in aromatic esters and amides so that, e.g., electron-donor 4-substituents induce a positive charge on the carbonyl carbon, thus producing a reverse resonance effect. This appears to be a consequence of the through-conjugation between the methoxy or amino group and the carbonyl *within* the functional group, prevailing in the competition with the through-conjugation between the ring and the carbonyl.



Scheme 2

Moreover we have found[6] that the one-bond ^{13}C-^{13}C coupling constants between the carbonyl carbon and C(1) in the hindered benzoates **2'** do correlate with those of the corresponding **2** (n = 9, r = 0.991). Therefore our conclusion that the interaction between 4-X-substituent and the methoxycarbonyl group is similar in nature in the two series of benzoates is supported by two independent observables, such as chemical shifts and one-bond coupling constants, and does not rely only on the factors influencing chemical-shift values. Further independent support to the importance of the **πP** vs the **TC** mechanism of resonance interactions in methyl benzoate comes from the low rotational barrier about the phenyl-carbonyl bond (4.92 kcal mol^{-1}), as compared with those of benzaldehyde and acetophenone (7.6÷7.9 and 5.4 kcal mol^{-1} respectively).[7]

Also ^{17}O NMR chemical shifts are investigated as possible probes of molecular properties.[8] In this line, we have studied ^{17}O chemical shifts in acetophenones **1** and **1'** and found[8e] that the small *SCS* values on the carbonyl oxygen of **1'** exhibit only a modest correlation with σ_p (n = 9, r = 0.961), while the larger *SCS* values of **1** exhibit an excellent correlation with σ_p^+ (n = 12, r = 0.999). We concluded that ^{17}O *SCS* values are good indicators of local π-electron-density variations only in the series **1**, while in **1'** they appear to be governed by a blend of several effects.

Boykin and Coworkers, in their extensive studies on ^{17}O NMR chemical shifts,[8a] have reported ^{17}O data for isotopically enriched methyl 4-X-benzoates **2** (X = OMe, Me, H, Cl, F, CF_3, CN, NO_2) in acetone.[8b] The *DSP* treatment of the *SCS* values gave always the best fit with the σ_R^+ scale. The steric effects on ^{17}O chemical shifts were studied both in rigid molecules and in *ortho*-substituted methyl benzoates bearing substituents with minimal electronic effects (see later).[4c] Exner, Dahn and Pechy[8d] submitted the carbonyl oxygen *SCS* values of many methyl 4-X-benzoates to Hammett-type, *DSP* and Principal Component Analysis (*PCA*). Monoparametric treatments were found to exhibit high statistical significance, comparable to that of more refined analyses and a particularly good correlation was obtained with σ_p^+.

We are now reporting on ^{17}O NMR chemical shifts of the methoxycarbonyl function in methyl 2,6-dimethyl-4-X-benzoates **2'** in acetonitrile-d_3. For homogeneity sake we have redetermined in identical conditions the ^{17}O chemical shifts for the corresponding 2,6-unsubstituted-4-X-benzoates **2.** The ^{13}C NMR chemical shifts of the methoxy carbon in the two series of benzoates are also determined. The choice of substituents is in close agreement with previous suggestions,[1,2] covering all kinds of substituent effects and avoiding clusters of points in *DSP* correlations.

Results and Discussion

^{17}O chemical shift values of methyl 4-X-benzoates **2** are reported in Table 1 and are in line with those previously reported.[8b,d]

Table 1. ^{17}O NMR chemical shifts of methyl 4-X-benzoates **2**^{a}

X	$\delta(\text{C=}\underline{\text{O}})^b$	$\Delta\nu_{1/2}{}^c$	*SCS*	$\delta(\underline{\text{O}}\text{Me})^b$	$\Delta\nu_{1/2}{}^c$	*SCS*
NH_2	319.8	230	–16.2	121.7	305	–4.3
OMe	327.0	280	–9.0	121.0	320	–5.0
Me	334.3	275	–1.7	125.0	330	–1.0
H	336.0	155	0.0	126.0	150	0.0
F	335.0	230	–1.0	126.0	245	0.0
Br	336.6	215	0.6	125.6	240	–0.4
COMe	342.0	300	6.0	128.4	280	2.4
NO_2	343.9	200	7.9	128.5	310	2.5

[a] Natural abundance in CD_3CN at 40 °C. [b] From external H_2O. [c] Line width (Hz) at half-height.

As previously reported by Boykin and Coworkers,[8b] the ^{17}O chemical shifts of the carbonyl oxygen of **2** (i) correlate with the methoxy oxygen chemical shifts ($r = 0.943$; $n = 8$; slope = 2.68 ± 0.39) and, better, with C(1) chemical shifts ($r = 0.975$; $n = 8$; slope = 1.43 ± 0.13), and (ii) give a good *DSP* correlation when using the σ_R^+ resonance scale (see Table 2), showing positive ρ_I and ρ_R values and a ρ_R/ρ_I ratio close to one. This further confirms that the inductive and the resonance components of the *SCS* values are both normal and both important. The ^{17}O chemical shifts of the methoxy carbon of **2** exhibit a much more restricted range and a poorer *DSP* correlation.

Table 2. *DSP* analysis of the ^{17}O NMR chemical shifts of the methoxycarbonyl group in methyl 4-X-benzoates **2**

	C=O	OMe
Range (ppm)	24.1	6.8
Best resonance scale in *DSP* analysis	σ_R^+	σ_R^+
	(σ_R^+)[a]	(σ_R^+)[a]
ρ_I	9.97 ± 1.10	2.89 ± 1.05
	(10.02 ± 0.51)[a]	(4.96 ± 0.22)[a]
ρ_R	10.95 ± 0.43	3.67 ± 0.41
	(9.01 ± 0.49)[a]	(3.58 ± 0.21)[a]
ρ_R/ρ_I	1.10	1.27
	(0.90)[a]	(0.72)[a]
n	8	8
	(8)[a]	(8)[a]
f	0.10	0.36
	(0.12)[a]	(0.11)[a]

[a] From ref. 8b, isotopically enriched compounds in acetone at 40 °C.

^{17}O chemical shift values of methyl 4-X-benzoates **2** are reported in Table 3. The carbonyl oxygen in methyl 2,6-dimethylbenzoate is 37.5 ppm less shielded than in methyl benzoate itself. This difference can be compared to the 50 ppm deshielding previously observed on going from **1** (X = H) to **1’** (X = H).[8e]

Table 3. ^{17}O NMR chemical shifts of methyl 2,6-dimethyl-4-X-benzoates **2’**[a]

X	δ(C=O)[b]	$\Delta\nu_{1/2}$[c]	*SCS*	δ(OMe)	$\Delta\nu_{1/2}$[c]	*SCS*
NH_2	365.0	290	–8.5	144.0	320	–1.1
OMe	373.0	320	–0.5	143.0	345	–2.1
Me	372.0	270	–1.5	146.0	290	0.9
H	373.5	320	0.0	145.1	245	0.0
F	373.0	275	–0.5	146.0	255	0.9
Br	374.0	290	0.5	146.0	355	0.9
NO_2	374.0	300	0.5	146.0	300	0.9

[a,b,c] See Table 1.

Both the carbonyl and methoxy ^{17}O chemical shifts of the ester function of methyl 2,6-dimethyl-4-X-benzoates **2’** appear to exhibit a very low, if any, sensitivity to 4-substituents. However the polar effect which we have found to be remarkable in the 2,6-unsubstituted compounds must be still operative here, and it is hardly conceivable that the resonance effect can exactly compensate the polar one for all of the examined **2'**. Therefore, *SCS* values do not appear to be good indicators of local π-electron-density variations in this series of compounds.

Several factors can contribute to this outcome. On going from **2** to **2'** the methoxycarbonyl oxygens change their position with respect to the aromatic ring. Moreover, the torsion angle ω between the ester function and the ring can vary with the 4-substituent and this could cause a different shielding effect by the ring current and a different solvation effect. A further possible explanation can rely on the reported sensitivity of chemical shifts to the steric compression of p-orbitals,[8c] as oxygens are more external than carbons in the ester functional group and their p-orbitals could undergo steric compression by the *ortho* methyls. Boykin and Coworkers[4c] tend to consider this effect only in rigid systems, as in **2'** steric compression can be alleviated by increasing the torsion angle *ω*. However, some steric compression could be still effective in **2'**, as the X-ray crystal structure of **2'** (X = OMe), in spite of a large (64°) value of *ω*, still exhibits rather close contacts between the oxygen atoms of the methoxycarbonyl function and the *ortho* methyl groups.[4d] Also the extent of this compression effect could vary with the 4-substituent.

As ^{17}O chemical shifts of compounds **2'** are not reliable indicators of π-electron distribution, we have turned our attention to the methoxy carbon, measuring its chemical shifts in both the benzoates **2** and **2'.** The methoxy carbon is obviously protected by methoxy protons against direct steric interactions and is farther from the 2,6-methyl groups and from the ring current as a consequence of the eclipsed orientation of the O-Me with respect to the C=O bond. The methoxy carbon chemical shifts of benzoates **2** and **2'** are collected in Table 4. *SCS* values are small, but the great accuracy of ^{13}C chemical shift measurements can allow to evidence possible correlations.

Table 4. ^{13}C chemical shifts and corresponding *SCS* values[a] for the methoxy carbon of the ester function in benzoates **2** and **2'**

	2		**2'**	
	$\delta(O\underline{C}H_3)^b$	*SCS*($O\underline{C}H_3$)	$\delta(O\underline{C}H_3)^b$	*SCS*($O\underline{C}H_3$)
NMe_2	51.39	–0.68		
NH_2	51.56	–0.51	51.42	–0.38
OMe	51.79	–0.28	51.64	–0.16
Me	51.91	–0.16	51.69	–0.11
H	52.07	0.00	51.80	0.00
F	52.16	0.09	51.90	0.10
Br	52.25	0.18	51.95	0.15
CF_3	52.48	0.41		
COMe	52.41	0.34	52.06	0.26
NO_2	52.77	0.70	52.38	0.58

[a] 0.2 M in $CDCl_3$ at room temperature. [b] From TMS.

The *DSP* analyses give the results collected in Table 5. The correlation is excellent for either series, showing that the analyzed chemical shifts are really governed by the electronic effects in either benzoates **2** or **2'**. For either series the best fit is given by the σ_R^{BA} rather than by the σ_R^+ scale, indicating a not strong resonance interaction with the 4-substituent. The positive ρ_I and ρ_R values show that both the polar and the resonance effects are normal in either series. These findings are, however, in agreement with either the **TC** or the **πP** scheme of transmission of resonance effects of 4-substituents (see above).

More interestingly, the calculated ρ_I and ρ_R values, although moderately reduced in the hindered benzoates **2'**, exhibit a similar ratio in the two series, thus showing a similar blend of polar and resonance effects. As a consequence, the methoxy carbon chemical shifts of the hindered benzoates **2'** give an excellent linear correlation (r = 0.998) with those of the 2,6-unsubstituted **2**. This can be explained only on the basis of the importance of the **πP** scheme, as through-conjugation should be deeply affected by the marked torsion angle between the carbonyl and the ring plane in the hindered benzoates **2'**. The calculated slope of 0.77 ± 0.02 indicate a significantly lower substituent effect in **2'** than in **2**.

Table 5. Results of the *DSP* analysis of the methoxy carbon *SCS* in benzoates **2** and **2'**.

	2	**2'**
Best resonance scale	σ_R^{BA}	σ_R^{BA}
ρ_I	0.84 ± 0.03	0.70 ± 0.03
ρ_R	0.81 ± 0.02	0.58 ± 0.02
ρ_R/ρ_I	0.96	0.83
n	10	8
f	0.09	0.09

In order to check if the *SCS* values at the methoxy *carbon* of the ester group can be effective indicators of π-electron-density changes at the methoxy *oxygen* a correlation between ^{17}O and ^{13}C chemical shift of the unhindered esters **2** was attempted. However, the data provide only an approximately linear correlation with r = 0.896. The value of the correlation coefficient could be biased by the different accuracy in chemical shift determination of the two nuclei but is mainly determined by some difference in the nature of the electronic effects experienced by the two atoms, as indicated by the different resonance scales, σ^+_R and σ^+_{BA}, used for *DSP* analysis of ^{17}O and ^{13}C chemical shifts, respectively.

Conclusions

The analysis of ^{17}O *SCS* values of 2,6-dimethyl-4-X-benzoates **2'** shows that they are not good indicators of π-electron-density variations induced by 4-substituents in such sterically hindered systems. Conversely, chemical shift variations at the methoxy carbon exhibit a good correlation with the electronic effect of 4-substituents, as well as the previously studied variations of the chemical shift of the carbonyl carbon[3c] and of the one-bond C(α)-C(1) coupling constant.[6]

The outcome that all of these three indicators for the hindered benzoates **2’** give very good linear correlations with those of the relevant 2,6-unsubstituted benzoates **2** is indeed remarkable, also because chemical shifts and coupling constants are governed by different mechanisms. This strongly supports our conclusion that the resonance effect of 4-X substituents on the methoxycarbonyl function is governed by the π-polarization mechanism without appreciable charge-transfer between the two moieties, as the latter would be affected by 2,6-dimethyl substitution.

Experimental Section

Benzoates **2** and **2’** have been fully characterized elsewhere.[3c]
^{13}C spectra were acquired at 50.3 MHz, 0.2 M in $CDCl_3$, at room temperature. The chemical shift scale was referenced to TMS. The following acquisition parameters were used: 45° pulse angle, spectral width 13000 Hz, acquisition time 1.26 s, digital resolution 0.8 Hz.
^{17}O spectra were obtained at 27.12 MHz, on a spectrometer equipped with a 10 mm probe, from solutions 0.2 M in CD_3CN at 40 °C. Chemical shifts were referred to H_2O used as external standard. The following acquisition parameters were used: 90° pulse, spectral width 25000 Hz, acquisition time 79 ms, digital resolution 12.7 Hz. Acoustic ringing artefacts were minimized by using suitable pulse sequences.

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