On the Nature of Resonance Interactions in Substituted Benzenes. Part 3.[1] A ^{13}C Nuclear Magnetic Resonance Study of Substituent Effects in 4-Substituted Benzamides and Methyl Benzoates in Dimethyl Sulphoxide

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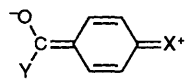
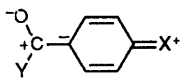
The substituent effect on the carbonyl-carbon chemical shift in 4-X-benzamides **2** and in 2,6-dimethyl-4-X-benzamides **2'** has been studied in $(CD_3)_2SO$. Comparison of the results with those obtained from the corresponding methyl 4-X-benzoates **1** and **1'** in the same solvent and their analysis by both the dual-substituent parameter (DSP) and Exner–Budesinsky's methods suggest that in the less hindered benzamides **2** the carbamoyl-carbon chemical shift is not significantly affected by through-conjugation with the *para*-substituent, π-polarization appearing to be the prevalent resonance effect.

There is continuing interest in the analysis of ^{13}C chemical shifts in unsaturated molecules as possible probes of electron-density distribution.[1–4] Considerable support to these efforts comes from the observation[3a] that in homogeneous series of compounds the chemical shifts of a probe carbon are linearly related to its *ab-initio*-calculated π-electron densities, although some limitations of this method have been stressed.[5] Our recent work on the effect of 4-substituents on the carbonyl-carbon chemical shift of 4-X- and 2,6-dimethyl-4-X-acetophenones,[4d] methyl 4-X- and 2,6-dimethyl-4-X-benzoates **1** and **1'**,[4d] as well as of aryl 4-X-benzoates[1] in $CDCl_3$ suggests that the so-called resonance effect ($-R$ effect) of a COY group has to be regarded as a blend of conjugation and π-polarization: such two components would correspond, in the case of an electron-donating X subsituent, to structures **A** and **B** respectively, the former causing a shielding of the carbonyl carbon ('normal' resonance effect), the latter giving an opposite result ('reverse' resonance effect). The balance between the two components



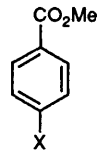
A



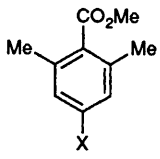
B

was found to be influenced by the nature of Y, favouring conjugation when Y = Me or OR with R = 2,4,6-trinitrophenyl, but π-polarization when Y = OR with R = alkyl, phenyl, 4-nitrophenyl and 2,4-dinitrophenyl; we suggested that in the latter cases the marked conjugation within the COO moiety plays a major role in limiting conjugation between the same group and the ring.[1]

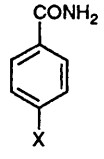
In this connection it has seemed worth studying the effect of 4-substituents† on the carbonyl-carbon chemical shift of benzamides **2**, which was previously[3a,b] interpreted by regarding the $-R$ effect of the $CONH_2$ group as an essentially conjugative interaction with the ring. Herein, the data for compounds **2** in $(CD_3)_2SO$ (remeasured for the sake of consistency) have been compared with those obtained from 2,6-dimethylbenzamides **2'** and benzoates **1** and **1'** in the same solvent. The choice of $(CD_3)_2SO$ as solvent has been enforced by the low solubility of both benzamides **2** and **2'** in the more commonly used solvent $CDCl_3$.



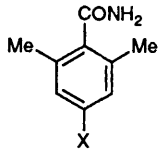
1a–j



1'b–g, i, j



2a–g, i, j



2'b–g, j

a; X = NMe_2. **b**; X = NH_2. **c**; X = OMe. **d**; X = Me. **e**; X = H. **f**; X = F. **g**; X = Br. **h**; X = CF_3. **i**; X = Ac. **j**; X = NO_2.

Results and Discussion

Tables 1 and 2 report the chemical-shift variations brought about by 4-X-substituents on the carbonyl-carbon [hereinafter referred to as C(α)] and on C(1), respectively, in the studied compounds. The chemical shifts of the parent substrates (δ—H) are also reported. All the obtained C(α) chemical shifts of the benzamides **2** are *ca.* 0.5 ppm lower than literature values,[3a,b] so that the relevant SCS values are not significantly affected.

Inspection of the δ—H values of Table 1 reveals that, as previously found[4d] in $CDCl_3$, 2,6-dimethyl substitution deshields the C(α) of methyl benzoate to a moderate extent (3.3 ppm), if compared with the corresponding effect (*ca.* 10 ppm)‡ on acetophenone: as methyl 2,6-dimethylbenzoate is expected[6]

† The set of substituents was chosen, according to earlier suggestions,[3a,5c] to avoid alignment or clustering of points when the resonance parameters of the X substituents are plotted against the corresponding polar ones.

‡ In an independent experiment we have found that the C(α) chemical shifts of 2,6-dimethylacetophenone and acetophenone [0.3 mol dm^{-3} in $(CD_3)_2SO$] are δ_C 207.63 and 197.80, respectively.

Table 1 Substituent chemical shift (SCS) (δ) values[a] on the carbonyl-carbon of the CO_2Me and $CONH_2$ groups in benzoates **1** and **1′** and in benzamides **2** and **2′** [0.3 mol dm^{-3} in $(CD_3)_2SO$]

	Compound			
X	**1**	**1′**	**2**	**2′**
NMe_2	0.14		0.06	
NH_2	0.12	0.02	0.23	0.80
OMe	−0.32	−0.16	−0.41	0.08
Me	−0.02	0.10	−0.07	0.22
H	0.00	0.00	0.00	0.00
F	−0.90	−0.70	−1.02	−0.70
Br	−0.67	−0.79	−0.93	−0.94
CF_3	−1.01			
Ac	−0.61	−0.53	−0.73	
NO_2	−1.45	−1.40	−1.61	−1.69
δ—H[b]	166.18	169.48	167.80	171.01

[a] Negative figures correspond to shielding effects. [b] Chemical shifts (δ relative to Me_4Si) for the parent systems (X = H).

Table 2 SCS (δ) values[a] for C(1) in benzoates **1** and **1′** and in benzamides **2** and **2′** [0.3 mol dm^{-3} in $(CD_3)_2SO$]

	Compound			
	1	**1′**	**2**	**2′**
NMe_2	−13.84		−13.23	
NH_2	−13.86	−13.74	−13.13	−11.75
OMe	−7.75	−7.73	−7.67	−7.10
Me	−2.68	−2.90	−2.69	−2.67
H	0.00	0.00	0.00	0.00
F	−3.38	−3.61	−3.41	−3.47
Br	−0.83	−0.81	−0.82	−0.75
CF_3	3.77			
Ac	3.59	4.00	3.91	
NO_2	5.36	5.82	5.86	6.09
δ—H[b]	129.62	133.75	134.17	138.84

[a, b] See corresponding footnotes of Table 1.

Table 3 Results of the analysis of the carbonyl-carbon SCS values for compounds **1**, **1′**, **2** and **2′** in $(CD_3)_2SO$ according to the equation $SCS = \rho_I\sigma_I + \rho_R\sigma_R^{BA}$

	Compound			
	1	**1′**	**2**	**2′**
ρ_I	−2.05	−1.92	−2.35	−2.45
ρ_R	−0.38	−0.43	−0.40	−1.24
ρ_R/ρ_I	0.19	0.22	0.17	0.51
n[a]	10	8	9	7
f	0.11	0.11	0.14	0.07

[a] Number of experimental points.

to exhibit a marked torsion angle between the methoxycarbonyl group and the ring, this result suggests[4d] that in $(CD_3)_2SO$ also, conjugative interactions are not important even in the quasi-planar methyl benzoate.[7] Interestingly, 2,6-dimethyl substitution also deshields the C(α) of benzamide to a moderate extent (3.2 ppm): this result alone could suggest a close similarity between benzamide and methyl benzoate and then little importance of conjugative interactions between the $CONH_2$ group and the ring also in benzamide itself. This finding has to be interpreted with some caution because, unlike the quasi-planar structure of methyl benzoate, the torsion angle between the $CONH_2$ and the ring is reported to be sizeable (*ca.* 25° in the crystal structure) for benzamide **2e** itself.[8] Such a torsion angle is expected to be much larger in the 2,6-dimethyl derivative **2′e**.[6a,*]

In our opinion a better understanding of the analogies between benzamides and benzoates can arise from the comparison of the substituent effects on the C(α) and C(1) chemical shifts in the studied series of compounds. In this connection, the observed C(1) SCS values (Table 2) always appear to be essentially governed by a strong 'normal' resonance effect [by which, *e.g.*, electron-donating groups shield C(1)]. Accordingly, excellent linear correlations of the C(1) SCS values with the σ_p^+ constants are found, whose high positive slopes are not significantly different in the four series of compounds (**1**: ρ 8.36 ± 0.52, *r* 0.985; **1′**: ρ 9.18 ± 0.67, *r* 0.984; **2**: ρ 8.14 ± 0.58, *r* 0.983; **2′**: ρ 8.16 ± 0.69, *r* 0.983). Conversely, the figures obtained for C(α) (Table 1) exhibit a less evident pattern and therefore require a more detailed analysis.

As a first step we have observed that a plot of the C(α) chemical shifts of esters **1′** *vs.* those of the corresponding esters **1** shows a satisfactory linear correlation (*r* 0.976) with a slope (0.95 ± 0.08) close to unity. These results, similar to those previously obtained[4d] in $CDCl_3$, suggest that also in $(CD_3)_2SO$ the carbonyl-carbon chemical shifts of esters **1** and **1′** are determined by the same blend of substituent effects, and moreover that the latter are quantitatively similar in the two series of compounds. From the corresponding plot of the C(α) chemical shifts of amides **2′** *vs.* those of the parent amides **2**, (*r* 0.967; slope 1.22 ± 0.13), the substituent effects appear to be less similar in nature in the two series of benzamides and slightly larger in the 2,6-dimethylamides **2′** than in parent compounds **2**. The observed linear trend could be indicative[4d] of an unremarkable reduction of conjugative interactions between the carbamoyl group and the ring as a result of 2,6-dimethyl substitution, notwithstanding the expected large variation in the torsion angle between compounds **2** and **2′** (see above).

In order to check the significance of the above mentioned differences between benzoates and benzamides, and to get a more detailed picture of the substituent effects involved, we have dissected the C(α) SCS values of the studied compounds into their polar and resonance components according to equation (1).[3a,9]

$$SCS = \rho_I\sigma_I + \rho_R\sigma_R \quad (1)$$

The results of such treatment are collected in Table 3. For any series of compounds examined the agreement factor (*f*-value)[9] is comparable to those obtained for similar DSP analyses,[3a,b,4d] showing that the SCS values herein are really determined by the electronic effects of the 4-substituents. Inspection of the results in Table 3 furthermore reveals that: (i) good fits are obtained for all the series by using the same σ_R^{BA} substituent parameters,† thus allowing a more direct comparison of the calculated coefficients ρ_I and ρ_R; (ii) much in line with all the previous studies on 1,4-disubstituted benzenes,[1,3a–c,4d] the ρ_I-values obtained are always negative, showing a 'reverse' polar effect of 4-substituents (by which, *e.g.*, electron-withdrawing groups shield the carbonyl carbon), whose origin was thoroughly discussed elsewhere;[3a,b] (iii) as

* An X-ray diffraction study (A. Mugnoli, F. Sancassan, M. Novi and G. Petrillo, manuscript in preparation) of the crystal structure of compound **2′c** brought to evidence a 56° rotation angle between the $CONH_2$ and aryl moieties.

† No significant improvement has been observed by using other resonance scales.

Table 4 Results of the analysis of the carbonyl-carbon SCS values of compounds **1**, **1′**, **2**, and **2′** in $(CD_3)_2SO$ according to the equation $SCS = \alpha + \beta B^p + \gamma C^p$

	Compound			
	1	**1′**	**2**	**2′**
β	−2.11 ± 0.14	−2.05 ± 0.14	−2.33 ± 0.23	−2.54 ± 0.19
γ	0.06 ± 0.05[a]	0.07 ± 0.06[a]	0.06 ± 0.09[a]	−0.42 ± 0.09
n^b	10	8	9	7
f	0.10	0.10	0.15	0.10
α	0.02 ± 0.06	0.07 ± 0.06	−0.02 ± 0.10	−0.01 ± 0.09

[a] Values not different from zero. [b] Number of experimental points.

previously observed[4d] for esters **1** and **1′** in $CDCl_3$, ρ_R is herein always negative, evidencing a reverse character of the resonance effect and hence a larger contribution of the π-polarization component with respect to the conjugative one; moreover, it seems interesting to stress that in compounds **1** and **2** the balance between the two components appears quite similar to that in the hindered esters **1′**; (iv) the closer similarity of the ρ_R- and ρ_R/ρ_I-values between esters **1** and **1′** than between amides **2** and **2′** appears to correlate with the differences observed between the linear correlations of the C(α) chemical shifts for benzoates and benzamides.

Although the results outlined in (iii) appear to rule out a marked effect of conjugative interactions in the less hindered compounds **1** and **2**, the overall picture emerging from the results of the DSP analysis is not yet completely clear. In fact, the larger reverse effects exhibited by compounds **2′** as compared with esters **1′** suggest a greater polarizability of the hindered $CONH_2$ with respect to the CO_2Me group; if such enhanced polarizability should hold also for the unhindered carbamoyl moiety, the observed similarity in the ρ_R- and ρ_R/ρ_I-values of compounds **1** and **2** could be the result of a compensating parallel increase in the conjugative component of the resonance effect in amides **2**; according to this hypothesis, the more negative ρ_R exhibited by the hindered amides **2′** with respect to the less hindered amides **2** could be ascribed to steric hindrance, in compounds **2′**, of the conjugative interactions operative in compounds **2**. However, these conclusions would conflict with the aforementioned linear correlation between the C(α) chemical shifts of the amides **2′** and **2**. Thus, further analysis on the subtle interplay of substituent effects in the studied compounds seems desirable.

Recently, Exner and Budesinsky[2f] have proposed a new two-parameter treatment based on equation (2), where B^p and C^p are substituent constants obtained by principal-component analysis of ^{13}C NMR data, the former correlating with σ_m-values and the latter being roughly proportional to σ_R^+-parameters.

$$SCS = \alpha + \beta B^p + \gamma C^p \quad (2)$$

While β has been found to be negative for all the disubstituted benzenes examined,[1,2e,f] the γ parameter has appeared to vary more significantly, both in absolute value and sign: in particular, positive values (slightly larger than unity for 4-X-benzaldehydes and 4-X-acetophenones)[2f] have been interpreted on the basis of a direct conjugation between the 4-X substituent and the probe group, while negative values (found for 4-X-benzonitriles and, to a lesser extent, for 4-X-phenylacetylenes and *N,N*-dimethyl-4-X-benzamides)[2f] have been related to the π-polarization of the probe group itself; alkyl 4-X-benzoates exhibited γ-values close to zero,[2e,f] but no interpretation for this has been offered as yet. Upon application of such analysis to the C(α) SCS values of compounds **1**, **1′**, **2** and **2′**, the results reported in Table 4 were obtained; the data for amides **2** are similar to those previously quoted.[2f] The goodness-of-fit, as judged by the relevant standard deviations as well as by the *f*- and α-values, is satisfactory. While the always negative β-values line up with previous analyses,[1,2f] the results obtained for the γ parameter deserve some discussion. The significantly negative γ-value exhibited by hindered amides **2′** confirms the marked influence of π-polarization in determining the SCS values in this series of compounds. Conversely, the results obtained for unhindered esters **1**, hindered esters **1′**, and unhindered amides **2**, for which the γ-values are close to zero, show that the relevant SCS values are essentially governed by the B^p parameters. It follows that for compounds **1**, **1′** and **2** the resonance component of the substituent effect, as measured by $\rho_R\sigma_R$ in the DSP analysis, is nearly completely included in the βB^p term of the Exner–Budesinsky treatment as already observed in similar cases.[1] As the B^p parameters are in turn proportional to σ_m, the results herein allow us definitely to rule out the idea that conjugative interactions between the substituents and the probe group could be prevalent in determining the SCS values of compound **1**, **1′** and **2** in $(CD_3)_2SO$.

In our opinion, the observed similarity in both β- and γ-values for compounds **1**, **1′** and **2** definitely points to a similarly negligible contribution of the conjugative component to the resonance effects of the methoxycarbonyl and carbamoyl groups. The last intriguing aspect is therefore that the π-polarization component of the $CONH_2$ group appears to be abnormally low in amides **2**, if compared with that shown for the hindered amides **2′**. Any rationalization of the results herein should take account also of different specific solvation effects[10] on the various probe groups in the four series examined. Nevertheless, we believe that the analysis herein allows us to classify the carbamoyl moiety among those COY probes where the marked internal conjugation plays a major role in limiting that between the group itself and the aromatic ring.

Experimental

^1H NMR spectra were recorded in $(CD_3)_2SO$ on a Varian FT-80 spectrometer operating at 80 MHz, and chemical shifts are given relative to internal $SiMe_4$ standard.

Syntheses.—Methyl benzoates **1** and **1′** have been described elsewhere.[4d] Commercial samples of amides **2c–j** were purified by crystallization to match literature physical constants.

4-(Dimethylamino)benzamide **2a** was prepared in 65% yield by alkaline hydrolysis of the corresponding nitrile.[4d] The crude solid was purified by silica gel chromatography (AcOEt as eluant) and was crystallized from aq. EtOH; m.p. 209–210 °C (lit.,[11] 203 °C).

4-Amino- **2b** and 4-*amino*-2,6-*dimethylbenzamide* **2′b** were obtained in almost quantitative yield by hydrogenation of the corresponding nitro derivatives **2j** and **2′j** over 10% Pd/C in EtOH. The amide **2b** had m.p. 182–184 °C (from EtOH) (lit.,[12a] 182.9 °C). The *amide* **2′b** had m.p. 175–176 °C (from EtOH) (Found: C, 65.7; H, 7.4; N, 17.1. $C_9H_{12}N_2O$ requires C, 65.8; H, 7.3; N, 17.1%); δ_H 7.39 and 7.15 (2 H, each br s), 6.18 (2 H, s), 4.93 (2 H, br s) and 2.10 (6 H, s).

4-Methoxy-2,6-dimethyl- **2′c**, 2,4,6-trimethyl- **2′d** and 2,6-dimethyl-benzamide **2′e** were prepared in almost quantitative yield by ammonolysis of the corresponding acyl chlorides, easily obtained from the carboxylic acid following standard procedure.[13] The reaction was performed by bubbling gaseous NH_3 through a stirred, anhydrous benzene solution of the acyl chloride. The solvent was then removed under reduced pressure. The amide **2′c** had m.p. 166–167 °C (from AcOEt) (lit.,[14] 188–189 °C) (Found: C, 67.1; H, 7.3; N, 7.7. Calc. for $C_{10}H_{13}NO_2$: C, 67.0; H, 7.3; N, 7.8%); δ_H 7.57 and 7.34 (2 H, each br s), 6.58

(2 H, s), 3.70 (3 H, s), and 2.22 (6 H, s). The amide **2'd** had m.p. 190–191 °C (from EtOH) (lit.,[12b] 187–188 °C); δ_H 7.59 and 7.34 (2 H, each br s), 6.81 (2 H, s) and 2.20 (9 H, s). The amide **2'e** had m.p. 139 °C (from water) (lit.,[12c] 139 °C); δ_H 7.43 and 7.11 (2 H, each br s), 7.08 (3 H, m) and 2.24 (6 H, s).

4-*Fluoro*-2,6-*dimethyl*- **2'f**, 4-*bromo*-2,6-*dimethyl*- **2'g** and 2,6-dimethyl-4-nitro-benzamide **2'j** were prepared by acid hydrolysis (80% H_2SO_4; 100 °C; 24 h in a sealed glass tube) of the corresponding nitriles.[4d] The crude solids were purified by silica gel chromatography (AcOEt as eluant). The *amide* **2'f** (28%) had m.p. 158–159 °C (from water) (Found: C, 64.5; H, 5.9; N, 8.3. $C_9H_{10}FNO$ requires C, 64.7; H, 6.0; N, 8.4%); δ_H 7.73 and 7.49 (2 H, each br s), 6.86 (2 H, d, J_{HF} 10.0 Hz) and 2.25 (6 H, s). The *amide* **2'g** (58%) had m.p. 196–197 °C (from AcOEt) (Found: C, 47.4; H, 4.4; N, 6.1. $C_9H_{10}BrNO$ requires C, 47.4; H, 4.4; N, 6.1%); δ_H 7.72 and 7.49 (2 H, each br s), 7.25 (2 H, s) and 2.23 (6 H, s). The amide **2'j** (65%) had m.p. 221–223 °C (from acetone) (lit.,[15] 221–223 °C); δ_H 7.94 (3 H, s), 7.74 (1 H, br s) and 2.37 (6 H, s).

^{13}C *NMR Measurements*.—Solutions of compounds **1**, **1'**, **2** and **2'**, 0.3 mol dm^{-3} in dry $(CD_3)_2SO$, were prepared in 10 mm sample tubes. As expected[3e] on the basis of the high solvating properties of this solvent, a study conducted on the ester **1b** showed that neither a decrease in concentration nor the presence of moisture have an appreciable effect on chemical-shift values. Spectra were obtained at 25 °C on a Varian FT-80 spectrometer at 20 MHz, 8K data points being collected over a spectral width of 4.5 kHz for 4-acetyl derivatives and 4 KHz for the other compounds, giving a digital resolution of 0.06 and 0.05 ppm, respectively. All chemical shifts were measured relative to Me_4Si in proton-noise decoupling experiments. Assignments were assisted by the proton-coupled spectra.

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