Substituent effects on carbon-13 NMR chemical shifts of side chain carbonyl carbons of 4-substituted 1-naphthamides

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Abstract. Substituent induced ^{13}C NMR chemical shifts of side chain carbonyl carbons of several 4-substituted 1-naphthamides have been measured in DMSO-d_6 solvent. Analysis of the substituent induced chemical shifts by the DSP equation gave the regression equation. Both p_I and p_R values were negative. The negative sign on p_I term indicates the operation of a reverse substituent effect and that π-polarisation is the important mechanism for the transmission of substituent effects by inductive effect. The *peri*-hydrogen interaction in naphthamides forces the amide group out of the plane of the naphthalene ring.

Keywords. Naphthamides; substituent chemical shifts; reverse substituent effect; π-polarisation.

1. Introduction

In recent years much attention has been paid to correlate the substituent induced ^{13}C NMR chemical shifts of aromatic compounds with the Hammett substituent constants. The effect of substituents in the ring on the chemical shifts of side chain carbon is of obvious interest, especially in those cases where the side chain carbon is capable of conjugating with the ring. Correlation of ^{13}C NMR chemical shifts of π-bonded groups conjugated with substituted aryl rings have appeared for several classes of compounds such as styrenes (Dhami and Stothers 1965; Hamer *et al* 1973), phenylacetylenes (Dawson and Reynolds 1975), 1-aryl-propenes and propynes (Izawa *et al* 1973), benzylidene anilines (Inamoto *et al* 1974), benzonitriles (Bromilo and Brownlee 1975), and α,β-unsaturated sulphones (Srinivasan *et al* 1986). The ^{13}C NMR chemical shifts of carbonyl groups conjugated with aryl rings have generally been observed to be 'insensitive' to substituent effects (Mathias 1966; Dhami and Stothers 1965, 1967) and only limited reports of their linear free energy relationships have appeared. Benzoic acids exhibit carbonyl carbon ^{13}C chemical shifts of range 2·4 ppm (Niwa and Yamazaki 1974). A series of N-phenacylpyridinium bromides (Harch *et al* 1977) with substituents in the pyridine ring exhibit greater sensitivity for the carbonyl resonance.

The substituent induced chemical shifts (SCS) of sp^2 and sp carbons directly bonded to the ring have been observed to show 'reverse substituent effects' (Bromilow *et al* 1977, 1981; Brownlee and Craik 1981; Srinivasan *et al* 1986), i.e., electron-attracting substituents apparently increase the electron density on the

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carbon concerned whereas electron-releasing substituents decrease it. This phenomenon has been attributed to the polarisation of the π-system of the side chain. Almost all studies in this area have involved carbon bonded to oxygen, nitrogen or other carbon atoms (Butt and Topsom 1980, 1982; Solcaniova *et al* 1976, 1980). In this study, ^{13}C NMR chemical shifts of carbonyl carbons of several 4-substituted 1-naphthamides have been measured and the SCS have been analysed by the DSP equation. The results of the analysis have been compared with those of the benzamides.

2. Experimental

Substituted 1-naphthoic acids were prepared by the hypobromite oxidation of the corresponding acetonaphthones (Ananthakrishna Nadar and Gnanasekaran 1978). The acids were converted into amides by the acid chloride method. Carbon-13 NMR spectra were run on Nicolet NT-300 spectrophotometer at 75·45 MHz using 5 mm sample tubes. The solvent is DMSO-d_6 and 16 K data points were used for all the samples. The chemical shifts were measured relative to internal TMS standard and are accurate within 0·02 ppm.

3. Results and discussion

The carbonyl carbon of aromatic amide group resonates near 170 ppm. These are well removed from other carbons in the spectrum and these absorptions are all of low intensity due to minimal nuclear overhauser enhancement and to their relatively long relaxation times. So these carbons can be unequivocally assigned. The side chain carbonyl carbon chemical shifts of several 4-substituted 1-naphthamides are presented in table 1 along with the relevant data for para-substituted benzamides.

Examination of data in table 1 shows that substituents have a relatively small influence on ^{13}C chemical shifts ($\Delta\delta = 1\cdot6$ ppm). All substituents cause upfield shift of the carbonyl carbon resonance compared to unsubstituted compound. The observed upfield shift for electron-attracting substituents is contrary to the

Table 1. Carbon-13 NMR chemical shifts of carbonyl carbons of naphthamides and benzamides.

| Substituent | 4-Substituted 1-naphthamides | | | | | | | |
	OCH$_3$	CH$_3$	H	F	Cl	Br	I	NO$_2$
δ (ppm)	170·60	170·82	170·89	169·80	169·88	169·94	170·01	169·28
$\Delta\delta$ (ppm)	−0·29	−0·07	0·00	−1·09	−1·01	−0·95	−0·88	−1·61

para-substituted benzamides

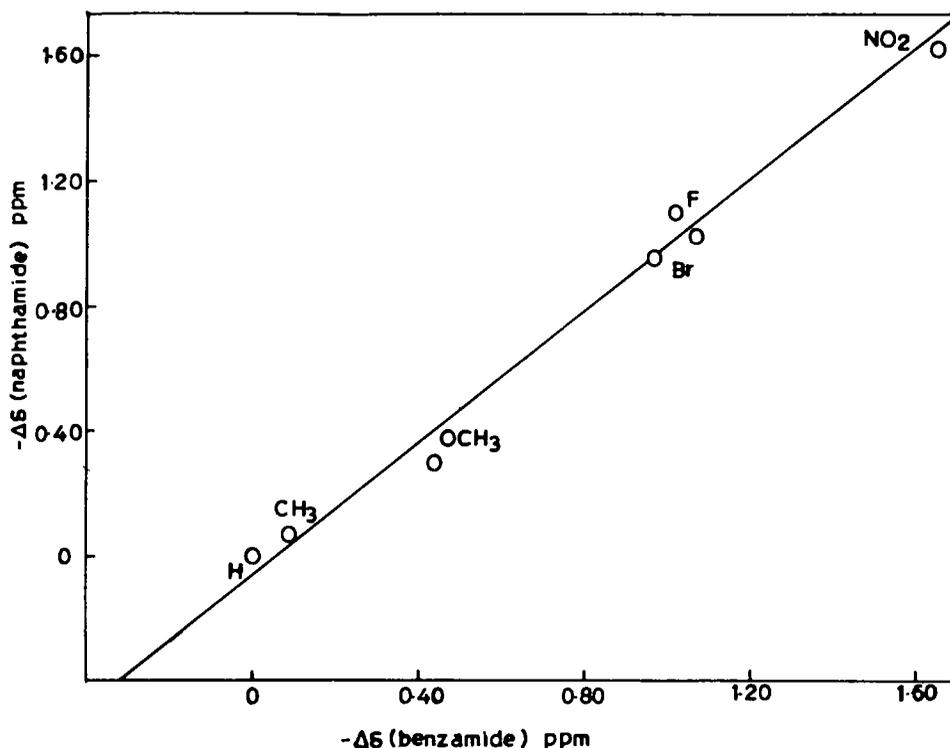| Substituent	OCH$_3$	CH$_3$	H	F	Cl	Br	NO$_2$
δ (ppm)	167·85	168·20	168·29	167·27	167·22	167·32	166·64
$\Delta\delta$ (ppm)	−0·44	−0·09	0·00	−1·02	−1·07	−0·97	−1·65

Figure 1. Plot of SCS of 4-substituted 1-naphthamides versus para-substituted benzamides. $\Delta\delta$ (ppm) values for benzamides are from Bromilow *et al* (1981).

expectation that they should withdraw electron density, decrease the shielding and cause a down-field shift. The plot of SCS of 4-substituted 1-naphthamides versus SCS of para-substituted benzamides is linear (figure 1) with a slope of 1·00 ($r = 0·994$; s.d. $= 0·07$). This indicates that the mechanism for transmission of electronic effects of the substituents in these two series is similar.

The SCS were analysed by the single parameter equation and the correlations obtained were poor. Since single parameter equation has failed, the SCS have been analysed by the DSP equation in the form

$$\text{SCS} = \rho_I \sigma_I + \rho_R \sigma_R. \tag{1}$$

The DSP methods (Ehrenson 1964) provides the relative magnitudes of various modes of transmission of substituent effects like ρ_I and ρ_R values, which are not obtainable from single parameter treatment. The DSP analysis gave the following regression equation

$$\text{SCS} = -2·25\sigma_I - 0·51\sigma_R^{(BA)}$$

$$\pm 0·15 \quad \pm 0·15 \quad (n = 8; \ R = 0·990) \tag{2}$$

As seen from the results of the regression analysis, the inductive effect contributes more to the chemical shifts of the carbonyl carbons than the resonance effect. The ρ_I term is negative and its magnitude is quite comparable to that of para-substituted

benzamides ($\rho_I = -2\cdot4$). The negative sign on ρ_I term indicates the operation of reverse SCS effect. This is due to the fact that π-polarisation of the carbon-oxygen bond is the major contribution to the inductive component of ^{13}C SCS values (Bromilow *et al* 1981). This type of polarisation is the 'localised polarisation' involving the separate polarisation of the side-chain as shown in chart 1.
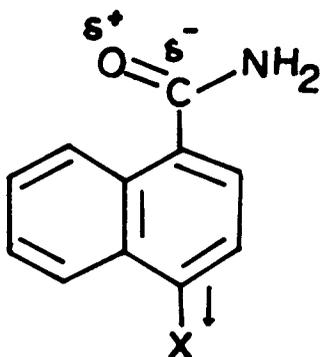

Chart 1.

In chart 1, if X is an inductive electron-attracting substituent, a dipole on X or near C–X is set up, the interaction of this dipole through space of the molecular cavity results in the polarisation shown. The net result is that the inductive electron-attracting substituent increases the electron density at the carbonyl carbon and hence increases the shielding to cause upfield shift.

Bromilow *et al* (1981) have shown that for series of the general form X–C_6H_4–COZ, the inductive effect of X on SCS of the side chain carbonyl carbon is largely determined by localised π-polarisation of C=O π-electrons and is independent of the adjacent Z group. On the other hand, the resonance effect of X on SCS varies from one series to another, and is determined by both the inductive and resonance effects of the Z group. When Z is a strong resonance donor (Z=NH_2), ρ_R is negative, and when Z is neutral (Z=H) or inductive donor (Z=CH_3), ρ_R is positive. The observed negative ρ_R value for the present system is in accordance with the observations reported by Bromilow *et al* (1981).

The carbonyl carbon resonance of 2-naphthamide (168·15 ppm) is very close to that of benzamide (168·29 ppm). Compared to benzamide and 2-naphthamide the carbonyl carbon resonance of 1-naphthamide (170·89 ppm) occurs at down field. This may be due to the *peri*-hydrogen interaction in 1-naphthamide. The *peri*-hydrogen forces the amide group out of the naphthalene ring and thereby reduces the conjugation with the aromatic ring. This decrease in conjugation increases the deshielding of the carbonyl carbon and hence downfield resonance occurs.

It is reasonable to assume that the conjugative interaction between the carbonyl group and the aromatic ring will be maximum, if the dihedral angle, θ, between the aromatic ring and the carbonyl group is zero. This interaction is minimum if $\theta = 90°$ (chart 2).
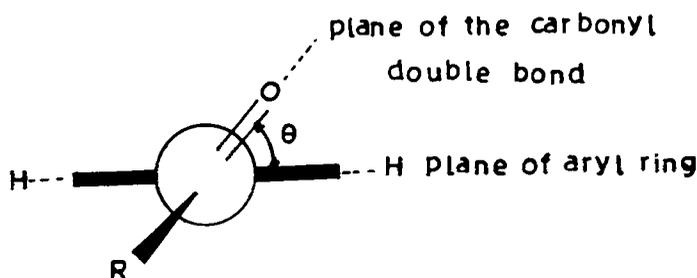
Chart 2.

Table 2. Dihedral angle in 4-substituted 1-naphthamides.

Substituent	OCH₃	CH₃	H	F	Cl	Br	NO₂
$\theta°$	21·8	21·2	21·1	20·8	21·4	21·2	21·3

The chemical shifts of carbonyl carbon in benzene derivatives can be taken as that typical for a planar system where θ is zero. A relationship between the interplanar angle θ and the carbonyl carbon chemical shift has been proposed based on model compounds with complete ($\theta = 0°$) and minimum ($\theta = 90°$) orbital overlap (Dhami and Stothers 1964). The observed carbonyl carbon resonance δ_o^x, the interplanar angle θ and the chemical shift δ_b^x for benzene analogues are related by the following expression:

$$\cos^2 \theta = [(\delta_b^x + 20) - \delta_o^x]/20. \tag{3}$$

Substituting the δ_b^x (Bromilow *et al* 1981) and δ_o^x values (present data) in (3), θ values are evaluated for 1-naphthamide and several 4-substituted 1-naphthamides (table 2). In all the naphthamides, the amide group is out of the plane of the naphthalene ring to an extent of 21°.

Acknowledgements

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