

¹³C NMR substituent induced chemical shifts in the side-chain carbons of α,β -unsaturated sulphones

C SRINIVASAN*, P K GANESAN, A SHUNMUGASUNDARAM and N ARUMUGAM

School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

MS received 8 November 1985

Abstract. The ¹³C NMR chemical shifts of α,β -unsaturated sulphones of the types E-2-aryl-1-phenyl-sulphonylethylenes (series I) and E-1-arylsulphonyl-2-phenylethylenes (series II) have been measured in CDCl₃ solution. The chemical shifts of the side-chain and a few ring carbons have been correlated with various single and multiparameter linear free energy relationships. Analysis of the ¹³C NMR spectral data by a dual substituent parameter equation shows that the resonance effect is the dominant factor at C- α in series I and C- β in series II. The inductive effect is predominant at C- β in series I with a reverse substituent effect at this carbon atom. The reverse inductive contribution is explained in terms of π -polarisation mechanism.

Keywords. ¹³C NMR chemical shifts; substituent effect; α,β -unsaturated sulphones; reverse substituent effect.

1. Introduction

The study of correlations between the Hammett substituent constants and ¹³C NMR substituent induced chemical shifts (SCS) of side-chain carbon atoms of aromatic systems and the use of SCS to monitor the transmission of electronic effects in molecular structures, in general, and to understand the mode of transmission of long-range substituent effects in extended π -electron systems, in particular, are topics of current interest (Inamoto *et al* 1974; Dawson and Reynolds 1975; Solčániová *et al* 1976, 1982; Shapiro 1977; Bromilow *et al* 1981; Srinivasan *et al* 1985). In recent years SCS of C- α and C- β of ethenyl group in several conjugated systems (Happer 1976; Solčániová *et al* 1976, 1982; Bromilow *et al* 1977, 1981; Srinivasan *et al* 1985) have been correlated by the dual substituent parameter (DSP) extension of the Hammett approach and this has revealed new features of a very important mechanism for the transmission of substituent effects i.e. π -polarisation (Bromilow *et al* 1981; Brownlee and Craik 1981). It is, therefore, of interest to investigate whether this new phenomenon exists in other systems, notably in α,β -unsaturated sulphones. In this study, the ¹³C NMR spectra of E-2-aryl-1-phenylsulphonylethylenes (series I) and E-1-arylsulphonyl-2-phenylethylenes (series II) have been recorded and the SCS analysed by the simpler single substituent parameter and DSP treatments. The results of the analysis have been compared with those of chalcones.

* To whom all correspondence should be addressed.

2. Experimental

All the α,β -unsaturated sulphones used in this study were prepared by literature methods (Baliah and Seshapathi Rao 1959; Srinivasan *et al* 1983). Their purity was checked by m.p. measurements and TLC analyses. The observed coupling constants ($J = 15$ Hz) for ethylenic protons in the ^1H NMR spectra of all the α,β -unsaturated sulphones indicate that they exist in an E-configuration. The ^{13}C NMR spectra were run on a Varian XL-100-A₁₂ spectrometer, equipped with a Varian 620 L computer operating in the fourier transform mode at 25.2 MHz under noise-modulated proton-decoupled conditions with 2 kHz band width at 10 W for normal spectra and with upfield irradiation by 200 Hz at 8 W for off-resonance spectra. For the spectra 10,000 time-domain data points were used. The peak positions printed out in Hz units were converted into chemical shifts in ppm. Spectra were measured in dilute solution ($\sim 5\%$) in CDCl_3 . All shifts reported are referenced to TMS and estimated to be accurate to ± 0.05 ppm. The correlation analyses were performed with a Micro 2200 Diskette Recorder (Hindustan Computers).

Table 1 (a). ^{13}C NMR chemical shifts* of E-2-aryl-1-phenylsulphonylethylenes (series I).

| Substituent | C-3 | C-2 | C-1 | C- β | C- α | C-1' | C-2' | C-3' | C-4' |
|---------------------------|--------|--------|--------|------------|-------------|--------|--------|--------|--------|
| Series I | | | | | | | | | |
| H | 130.30 | 131.35 | 135.01 | 145.14 | 130.23 | 143.53 | 131.79 | 132.14 | 136.18 |
| <i>p</i> -OMe | 117.29 | 130.15 | 127.64 | 145.01 | 127.26 | 143.94 | 132.03 | 133.16 | 135.91 |
| <i>p</i> -Me | 130.27 | 131.37 | 132.42 | 145.22 | 129.01 | 144.53 | 132.08 | 132.55 | 136.04 |
| <i>p</i> -i-pr | 129.78 | 131.35 | 132.85 | 145.16 | 129.02 | 145.34 | 131.64 | 132.20 | 135.98 |
| <i>p</i> -F | 119.24 | 133.33 | 131.64 | 143.92 | — | — | 130.43 | 132.13 | 136.43 |
| <i>p</i> -Cl | 130.38 | 132.04 | 133.63 | 143.68 | 130.81 | 142.99 | 132.16 | 132.59 | 136.26 |
| <i>p</i> -Br | 130.28 | 132.04 | — | 143.79 | 130.75 | — | 132.53 | — | 136.13 |
| <i>m</i> -Cl | 129.53 | 130.52 | 137.12 | 143.35 | 133.09 | — | 131.64 | 132.16 | 136.26 |
| <i>m</i> -NO ₂ | 128.07 | 130.59 | 136.87 | 142.15 | 133.03 | 142.02 | 132.26 | 132.26 | 136.56 |
| <i>p</i> -NO ₂ | 127.02 | 130.63 | 141.15 | 141.98 | 133.05 | 142.42 | 132.02 | 132.28 | 136.62 |

* Chemical shifts are in ppm relative to TMS.

Table 1 (b). ^{13}C NMR chemical shifts* of E-1-arylsulphonyl-2-phenylethylenes (series II).

| Substituent | C-3' | C-2' | C-1' | C- α | C- β | C-1 | C-2 | C-3 | C-4 |
|---------------------------|--------|---------------------|--------|-------------|------------|--------|--------|---------------------|--------|
| Series II | | | | | | | | | |
| H | 131.25 | 132.14 | 143.53 | 130.23 | 145.14 | 135.01 | 131.79 | 130.30 | 134.05 |
| <i>p</i> -OMe | 117.31 | 132.53 | 131.92 | 130.78 | 144.03 | — | 131.73 | 131.17 | — |
| <i>p</i> -Me | 131.27 | 132.74 | 140.93 | 130.88 | 144.62 | 135.48 | 131.85 | 130.52 | 133.80 |
| <i>p</i> -Cl | 131.29 | 132.17 | 145.53 | 129.55 | 145.57 | 134.83 | 131.74 | 131.29 | 133.93 |
| <i>p</i> -Br | 132.86 | 131.84 ^b | 145.74 | 129.57 | 145.80 | 135.28 | 131.32 | 131.32 ^b | 134.04 |
| <i>p</i> -NO ₂ | 127.38 | 132.05 | 149.06 | 130.88 | 147.75 | 134.89 | 131.73 | 131.82 | 134.61 |

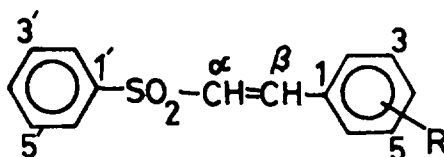
* Chemical shifts are in ppm relative to TMS; ^b there are some uncertainties in the assignment since the compound is sparingly soluble in the solvent.

3. Results and discussion

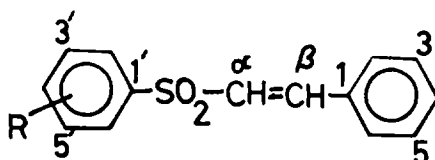
In the present study, the ^{13}C NMR chemical shifts of α - and β -carbons and the ring carbons of series I and II are given in tables 1a and b. Assignments of these carbons were made on the basis of the chemical shifts exhibited by the signals, the off-resonance decoupling technique and the relative signal intensity. All the ring carbons were identified by assuming the rule of additivity. The chemical shifts of the carbon atoms of the substituted ring were compared with the corresponding chalcones (Solčániová *et al* 1976), styrenes (Dhami and Stothers 1965; Hamer *et al* 1973) and phenyl methyl sulphones (Buchanan *et al* 1974). The signals due to C- α and C- β were readily identified by their splitting patterns and low intensities. These two carbons appear as overlapping multiplets due to long range coupling in the off-resonance proton-decoupled spectrum. The chemical shifts (in ppm relative to TMS) for C- α fall in the region 127.3–133.1 and 129.6–130.9 in series I and II, respectively, and for C- β fall in the region 142.0–145.2 and 144.0–147.8 in series I and II, respectively. The low field shift of C- α and C- β as compared to styrenes (116–126 ppm and 133–138 ppm, respectively) (Dhami and Stothers 1965; Hammer *et al* 1973) is presumably due to the greater electron-withdrawing ability of the phenylsulphonyl group attached to the neighbouring carbon. A similar trend in chemical shifts has been reported in the chalcones (Solčániová *et al* 1976), furan and thiophene chalcone analogues (Masumarra and Ballistreri 1980).

In series I, the chemical shift of C- α is more susceptible to the polar effects of substituents ($\Delta\delta \sim 6$ ppm), than that of C- β ($\Delta\delta \sim 3$ ppm). In series II, the effect is the opposite, i.e., the chemical shift of C- β is more sensitive ($\Delta\delta \sim 4$ ppm) than that of C- α ($\Delta\delta \sim 1$ ppm).

The SCS data of C- α and C- β in series I and II were correlated with the Hammett single parameter equation, employing σ or σ^+ or σ^+/σ^- constants, and the results of correlations with the best correlation coefficient for each carbon are set forth in table 2. While a fair correlation is obtained in series I for the SCS for C- α , correlation of the C- β SCS with substituent constants is poor. The correlation of SCS of C- β in series II is good. The correlation of chemical shifts of C- α of series II has not been attempted due to the poor spread of SCS ($\Delta\delta \sim 1.33$) which is comparable to that reported for the



Series I



Series II

Table 2. Results of the statistical treatment on ^{13}C NMR chemical shifts with σ or σ^+ or σ^+/σ^- using the single parameter equation.

| Series | Carbon chemical shifts | scale | ρ | r | s | n |
|--------|------------------------|---------------------|-------------------|-------|-------|-----|
| I | C- α | σ^+/σ^- | 4.66 ± 0.652 | 0.988 | 0.461 | 9 |
| | C- β | σ | -3.26 ± 0.691 | 0.968 | 0.323 | 10 |
| | C-1 | σ^+/σ^- | 6.22 ± 1.62 | 0.960 | 1.15 | 9 |
| II | C- β | σ^+/σ^- | 1.89 ± 0.320 | 0.992 | 0.173 | 6 |
| | C-1' | σ^+ | 10.6 ± 4.89 | 0.950 | 2.06 | 6 |

r = Correlation co-efficient; s = standard deviation; n = number of data points taken for consideration.

corresponding C- α in chalcones ($\Delta\delta \sim 1.14$). The results of correlations for C-1 (series I), and C-1' (series II) carbons are also included in table 2. The correlations for other carbons are poor.

Since the correlations with the single parameter equation are not excellent, the correlation of SCS of C- β in series I in particular being very poor, the SCS have been treated by the DSP equations (1) and (2).

$$\text{SCS} = \rho_I \sigma_I + \rho_R \sigma_R, \quad (1)$$

$$\text{SCS} = fF + rR. \quad (2)$$

The DSP method 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. By DSP treatment using (1), the correlations were done for each of the four resonance scales, viz, σ_R^0 , $\sigma_R^{(BA)}$, σ_R^+ and σ_R^- and the results for the one with the lowest standard error are taken for consideration. The values of σ_I and σ_R used in the present analysis are those given by Ehrenson *et al* (1973) and F and R are those given by Swain and Lupton (1968). The results of the DSP equations are presented in table 3 for both the series I and II. Generally, electron-withdrawing substituents cause a downfield shift by decreasing the extent of shielding and electron-releasing substituents an upfield shift by increasing the shielding. Consequently, DSP treatment is expected to give a positive value of ρ_I and ρ_R . This is indeed the case for C- α carbon in series I. The chemical shifts of C- α carbon exhibit a normal substituent effect, the resonance effect being the predominant factor ($\rho_I = 6.621$; $\rho_R = 11.402$). Our recent DSP analysis of ^1H NMR SCS of H- α indicates that the resonance contribution to the chemical shift predominates over the field effect (Srinivasan *et al* 1983). The chemical shifts of C- β in series II also exhibit a normal substituent effect but the magnitudes of ρ_I and ρ_R are lower than those of C- α in series I ($\rho_I = 3.029$; $\rho_R = 4.247$). It is interesting to note that the resonance contribution is more than that of the inductive effect for C- β in series II, which is remarkably similar to the dominant resonance effect of the β -protons of series II as revealed by the DSP treatment of SCS of the β -protons (Srinivasan *et al* 1983). Corresponding correlations with F and R parameters also show comparable values for the coefficients, f and r . Analysis of several similar systems like substituted chalcones (Solčaniová *et al* 1976,

Table 3. DSP analysis of SCS data of carbon atoms for *p*-substituted compounds.

| Series | Carbon Chemical shifts | Scale ^a | Equation | R | SE | n | CL (%) |
|--------|------------------------|------------------------|---|-------|-------|---|--------|
| I | C- α | σ_I, σ_R^0 | SCS = 6.621 σ_I + 11.402 σ_R^0 ± 0.387 ± 0.583 | 0.997 | 0.269 | 7 | 99.9 |
| | | F, R | SCS = 3.718 F + 10.226 R ± 0.624 ± 1.291 | 0.989 | 0.607 | 6 | 99.5 |
| | C- β | σ_I, σ_R^0 | SCS = -3.756 σ_I - 2.571 σ_R^0 ± 0.215 ± 0.315 | 0.993 | 0.157 | 8 | 99.9 |
| | | F, R | SCS = -2.368 F - 1.977 R ± 0.144 ± 0.294 | 0.994 | 0.151 | 7 | 99.9 |
| II | C- β | σ_I, σ_R^0 | SCS = 3.029 σ_I + 4.247 σ_R^0 ± 0.121 ± 0.162 | 0.999 | 0.073 | 6 | 99.9 |
| | | F, R | SCS = 1.716 F + 3.820 R ± 0.130 ± 0.270 | 0.997 | 0.127 | 6 | 99.9 |

R = multiple regression correlation coefficient; SE = standard error of the estimate; CL = confidence levels based on F-test.

^a In the DSP analysis the correlations were done for each of the four resonance scales ($\sigma_R^0, \sigma_R^{(BA)}, \sigma_R^+, \sigma_R^-$), and the results for the one with the lowest standard error are shown.

1982), N-benzylidenebenzylamines (Arrowsmith *et al* 1978), N-methyl-4-styrylpyridinium iodides (Srinivasan *et al* 1985) and the others (Hamer *et al* 1973; Happer *et al* 1977; Bromilow *et al* 1981; Butt and Topsom 1982) also show a normal substituent effect at these carbons.

The notable feature of the study is that C- β in series I gives negative values for ρ_I and ρ_R indicating a reverse substituent effect.

As seen from the results of the DSP equation in table 3 for series I, the inductive effect contributes more to the chemical shifts of C- β than the resonance effect. The DSP method of analysis of SCS values in a series of several unsaturated systems of the type $X-C_6H_4-CH=CH-$, show that the C- β leads to almost a constant ρ_I value of ~ -3.8 (see table 4). The near constancy and the negative ρ_I value in these cases have been attributed to a π -polarisation mechanism postulated by Brownlee (Brownlee and Craik 1981; Bromilow *et al* 1981). The π -polarisation mechanism occurs through space interaction of the substituent dipole and the ethylenic π -electrons. According to this concept, polarisation of the conjugated styryl system, as a whole, does not play a significant part in the determination of ρ_I value for the C- β position. The present investigation on ^{13}C NMR spectra in series I which is analogous to the systems $X-C_6H_4-CH=CH-$, gives $\rho_I = -3.8$ on DSP analysis by (1). Consequently, we attribute this reverse substituent effect to the 'localised polarisation' involving the separate polarisation of ethylene, the phenyl π -system and the phenylsulphonyl group. It is independent of the nature of the α -substituent in the unsaturated system corroborating Brownlee's concept.

It is highly interesting to note that the plot of chemical shifts of C- β of sulphones (series I) gives an excellent correlation with C- β of the corresponding chalcones ($r = 0.998$; *s.d.* = 0.090; $n = 9$), with a slope of exactly unity, confirming the operation of similar type of transmission of electronic effects in the two unsaturated systems.

Table 4. DSP analysis of ^{13}C NMR SCS data of C- α and C- β in a number of systems.

| System | Carbon | ρ_I | ρ_R | Scale | Reference |
|---|----------|----------|----------|--------------------------|---|
| $p\text{-X-C}_6\text{H}_4\text{-CH}^{\beta}=\text{CH}^{\alpha}\text{-C}(=\text{O})\text{-C}_6\text{H}_5$ | β | -4.0 | -1.8 | $\sigma_R^{(\text{BA})}$ | Sořániová <i>et al</i> 1976; Bromilow <i>et al</i> 1981 |
| $p\text{-X-C}_6\text{H}_4\text{-CH}^{\beta}=\text{N}^{\alpha}\text{-CH}_2\text{-C}_6\text{H}_5$ | β | -3.6 | -0.7 | σ_R^0 | Bromilow <i>et al</i> 1981 |
| $p\text{-X-C}_6\text{H}_4\text{-CH}^{\beta}=\text{CH}^{\alpha}\text{-C}_5\text{H}_4\text{N}^+\text{MeI}^-$ | β | -3.7 | -1.8 | $\sigma_R^{(\text{BA})}$ | Srinivasan <i>et al</i> (1985) |
| $p\text{-X-C}_6\text{H}_4\text{-CH}^{\delta}=\text{CH}^{\nu}\text{-CH}^{\beta}=\text{CH}^{\alpha}\text{-COOMe}$ | δ | -4.0 | -1.6 | $\sigma_R^{(\text{BA})}$ | data from Banerji <i>et al</i> (1984) and calculated by the authors |
| $p\text{-X-C}_6\text{H}_4\text{-CH}^{\beta}=\text{C}^{\alpha}(\text{COCH}_3)_2$ | β | -3.4 | -1.01 | σ_R^+ | Sořániová <i>et al</i> 1982 |
| $p\text{-X-C}_6\text{H}_4\text{-CH}^{\beta}=\text{CH}^{\alpha}\text{-SO}_2\text{C}_6\text{H}_5$ | β | -3.8 | -2.6 | σ_R^0 | Present work |

4. Conclusion

The following conclusions emerge from the foregoing discussions on ^{13}C NMR study of α,β -unsaturated sulphones: (i) The resonance effect is the dominant factor at C- α in series I and C- β in series II. (ii) The inductive effect is predominant at C- β in series I and a reverse substituent effect operates at this carbon atom which can be explained in terms of a π -polarisation mechanism, (iii) A comparison of the ^{13}C SCS of chalcones with sulphones supports the π -polarisation mechanism.

Acknowledgement

PKG thanks the UGC, New Delhi and the Principal and the Management, Aditanar College, Tiruchendur, for the award of a Fellowship under a Faculty Improvement Programme. The authors thank RSIC, IIT, Madras for ^{13}C NMR spectra.

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