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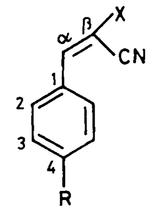
Further Application of Dual Substituent Parameter and Dual Substituent Parameter–Non-linear Resonance Methods in Modelling ^{13}C Substituent Chemical Shifts in β-Substituted Styrenes

Sumana Datta and Asish De*
Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India
Sankar Prasad Bhattacharyya and (in part) Chitrani Medhi
'Theory Group', Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India
Ajit Kumar Chakravarty
Department of Medicinal Chemistry, Indian Institute of Chemical Biology, Jadavpur, Calcutta 700 032, India
John S. A. Brunskill, Solomon Fadoujou, and Kenneth Fish
Department of Applied Chemistry, UWIST, P.O. Box 13, Cardiff CF1 3XF

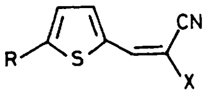
Dual substituent parameter and dual substituent parameter–non-linear resonances analysis have been successfully applied to model the long-range substituent effect on ^{13}C substituent chemical shifts (SCS) in eight series of β-substituted styrenes, each carrying a nitrile group in the β-position. Different blends of polar and mesomeric effects at various sites were successfully accounted for.

Hammett-type correlation[1] of substituent-induced ^{13}C chemical shifts (^{13}C SCS) of the vinylic side-chain carbon atoms in ring-substituted styrenes by Reynolds[2] was one of the early successful attempts in quantifying substitutent-induced electronic effects in conjugated aromatic systems. In a series of elegant studies,[3–6] this group was able to elucidate the respective modes of transmission of polar and mesomeric effects in these systems and delineate the precise nature of the polar effect.[4] The essence of these studies is the validity of Tafts' Dual Substituent Parameter[7] (DSP) approach in this type of system and the assertion that two parameters are both *necessary* and *sufficient* to model long-range substituent effects on chemical shifts in substituted aromatic compunds.[5,6]

Since the publication of Reynold's early work, several groups,[8–10] including ourselves,[11–13] have extended these studies to β-substituted styrenes, including their heteroaryl analogues, where the conjugation is further extended by one carbon atom. Apart from the standard single substituent (SSP) and DSP treatments, the ^{13}C SCS data in these systems have been subjected to analysis by multivariate statistics.[14–16] Jones[9] has also utilised the n.m.r. data to assign the stereochemistry of these compounds. We have been interested in the substituent effects in systems (**1**) and (**2**) where the vinyl side-chain carries a nitrile group in the β-position and we investigated these effects both on the reactivity of these compounds through kinetic studies[17,18] of nucleophilic addition to the vinylic double bond as well as correlation of ^{13}C SCS data.[11–13] Our investigations on 2-cyano-3-(*para*-substituted phenyl)-prop-2-enamides[12] (**1**; X = $CONH_2$), 2-cyano-3-(5-substituted thienyl)prop-2-enamides[12] (**2**; X = $CONH_2$), and 5-substituted 2-thenylidenemalononitriles[11,13] (**2**; X = CN), using multiple linear regression analysis showed that the substituent effects on all the side-chain carbon atoms as well as on the carbon atom *ipso* to the side-chain are indicative of unequal blends of polar and mesomeric effects and can be accounted for by the Dual Substituent Parameter (DSP) and Dual Substituent Parameter–Non-linear Resonance (DSP–NLR) approaches.[19] The principal polar effect in these systems was observed to be the field-induced π-polarisation,[4] comprising both direct [(**6**), (**7**)]† and extended [(**8**), (**9**)] polarisation of the π-electrons of



(**1**)



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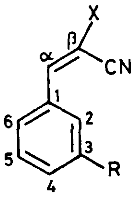

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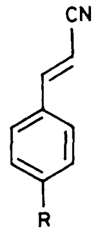

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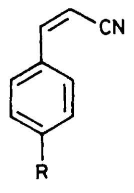

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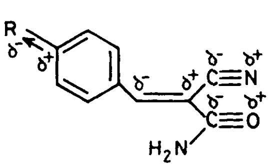
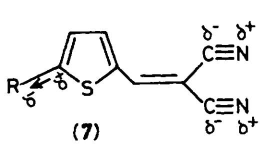
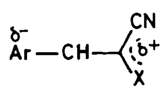


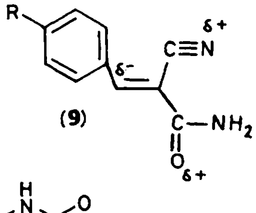
(**6**)



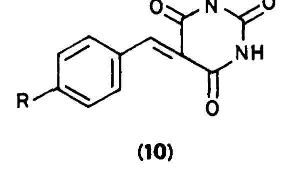
(**7**)



(**8**)



(**9**)



(**10**)

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† In the absence of a reliable correlation of SCS C-α (**2**; X = CN)[13] by simple DSP treatment we could not pronounce on the direct polarisation of Cα–Cβ double bond. (However, see later).

the side-chain. The most intriguing feature of our study in the series (**1**; X = $CONH_2$) was, however, the finding that the α- and β-carbon atoms of the side-chain needed two widely different resonance scales, approaching σ_{R^-} and σ_{R^+}, respectively, for correlation of their SCS, forcing the rather unusual conclusion that the two adjacent sites in the same series manifested an exalted resonance response of the opposite type. It thus became necessary to find out whether this feature is equally present in other related systems or if it is unique for the series we had examined. The publication of our results was prompted by a paper,[16] incorporating ^{13}C SCS studies on a number of compounds, some of which had already featured in our earlier publications. That these authors seemed to have drawn a widely different conclusion from ourselves, even though they examined the same series of compounds, is manifest from their conjecture that the SCS examined 'can be better rationalised and predicted by direct comparison of experimental shifts than by correlation with substituent parameters'. These authors seem to favour examining these compounds with the aid of multivariate statistics, which can furnish certain types of statistical information but which cannot provide the same kind of information provided by DSP analysis and is far from proving the inadequacy of the latter. The authors' suggestion about the lack of proper statistical support of the DSP analysis is unfounded since our published results have been corroborated by rigorous statistical tests *e.g.* correlation coefficient, standard deviation of the estimated parameter, Taft's *f* value (standard deviation divided by root mean square), and *F* test of variance. We present our results which, we believe, have established the usefulness of the DSP and DSP–NLR approach in analysing the ^{13}C SCS in the type of systems we have examined.

Results and Discussion

In order to make it comprehensive, we included in our investigation, in addition to the compounds examined earlier, *para*-substituted benzylidenemalononitriles (**1**; X = CN), ethyl 2-cyano-3-(*para*-substituted phenyl)prop-2-enoates (**1**; X = CO_2Et), *meta*-substituted benzylidenemalononitriles (**3**; X = CN), ethyl 2-cyano-3-(*meta*-substituted phenyl)prop-2-enoates (**3**; X = CO_2Et), and 2-cyano-3-(*meta*-substituted phenyl)prop-2-enamides (**3**; X = $CONH_2$). Apart from these, we have also included in our study the ^{13}C SCS of *trans*- (**4**) and *cis*-cinnamonitriles (**5**) carrying substituents in the *para*-position in the benzene ring, reported earlier by Butt and Topsom.[20,21] These authors have reported the DSP analysis of these SCS but have not subjected them to DSP–NLR analysis. Similarly we have reinvestigated the ^{13}C SCS of the thiophene series (**2**; X = CN), whose DSP analysis we have reported earlier,[13] this time using the DSP–NLR analysis. None of our studies feature *ortho*-substituted compounds, as they do in some publications,[16] since the large steric effect exerted by the *ortho*-substituent would make it impossible to get a true picture of the contribution of polar and mesomeric effects.

We have used equations (*a*)[5] and (*b*)[19] for DSP and DSP–NLR analysis. As σ_R scales in the equation (*a*), we have used σ_{R°

$$SCS = \rho_F\sigma_F + \rho_R\sigma_R \qquad (a)$$

$$SCS = \rho_F\sigma_F + \rho_R\sigma_{R^\circ}/(1 - \varepsilon\sigma_{R^\circ}) \qquad (b)$$

(Reynolds),[22] σ_{R^+} (Taft),[5] and σ_{R^+} (Charton)[23] values. It was implied in the criticism of Bottino *et al.*[16] that the substituent constants used in multiple regression analysis, as independent variables (a) may not be relevant, (b) may not be error free, and (c) may be linearly related among themselves. The σ_F and σ_{R° values derived by Reynolds[22] represent pure field and resonance effects, which have been derived with accuracy and since it is precisely these effects whose relative proportions we intend to find out at different carbon atoms in the compounds under investigation, they are relevant to our problem. In every correlation of SCS with σ_F and σ_R values, we checked if there is any linear relationship between the independent variables themselves and in not a single instance was such a relationship observed. In each series the number of substituents examined satisfied the minimum basis set of requirements[5] except in the thiophene series where the difficulty of accessibility constrained us to a comparatively limited number of substituents.

4-Substituted Benzylidenemalononitriles (**1**; X = CN).—A discrepancy has been noted[8] among the values of ^{13}C SCS of this series, reported by various groups. Table 1 lists the SCS values of C-1 and four side-chain carbon atoms of eleven compounds of this series whose ^{13}C n.m.r. spectra we have recorded (in [$^2H_6$]DMSO). Previous studies on these compounds included SSP and DSP analysis of the SCS of side-chain carbon atoms. We observed that the SCS of C-1 also undergoes excellent correlation with σ_F[22] and σ_{R°[22] as field and resonance parameters respectively. The regression equation can be written as (*c*).

Table 1. ^{13}C SCS[a] in 4-substituted benzylidenemalononitriles (**1**; X = CN)

Substituent	C-1	C-α	C-β	CN_Z	CN_E
H	131.2	161.4	81.5	113.1	114.1
Me	−2.6	−0.3	−1.6	0.2	0.2
Bu^t	−2.6	−0.6	−1.6	0.0	0.0
OMe	−7.2	−1.3	−4.8	0.6	0.5
NMe_2	−12.6	−3.1	−12.8	1.9	1.8
F	−3.4	−1.6	−0.6	−0.2	−0.2
Cl	−1.2	−1.5	0.7	−0.2	−0.2
Br	−0.9	−1.3	0.7	−0.2	−0.1
CF_3	3.5	−1.6	3.3	−0.6	−0.5
NO_2	5.3	−2.4	4.2	−0.9	−0.7
CN	3.7	−2.0	3.7	−0.8	−0.6

[a] Relative to the parent compound.

Table 2. Results of the DSP–NLR analysis of the ^{13}C SCS values in 4-substituted benzylidenemalononitriles (**1**; X = CN)*

Site	ρ_F	ρ_R	λ[a]	Intercept	ε[b]	*r*[c]	S.d.[d]	*f*[e]	*F*[f]
C-1	4.52	17.96	3.97	−0.01	−0.49	0.999	0.60	0.04	2 313
C-β	5.37	7.13	1.33	−0.01	−1.23	0.998	0.09	0.07	1 040
CN_Z	−1.14	−0.90	0.79	0.00	−1.32	0.994	0.03	0.11	305
CN_E	−0.94	−0.77	0.82	0.00	−1.36	0.993	0.02	0.12	263

[a] Ratio of $\rho_R:\rho_F$. [b] Electron demand. [c] Multiple correlation coefficient. [d] Standard deviation. [e] Taft's *f* value.[5] [f] *F* test for variance.

* Originally we had included the SCS C-α in these analyses. It was, however, rightly pointed out by a referee that in spite of the good correlation (*r* 0.979, s.d. 0.06, *f* 0.12, *F* 55, ε −1.70) a very low value of ρ_R (0.17) for SCS C-α makes it difficult to attach any particular significance to the value of the electron demand parameter.

$$\mathrm{SCS} = 4.25\,\sigma_F + 18.88\,\sigma_{R^\circ} - 0.04\ (r\,0.998,\ F\,924,\ \mathrm{s.d.}\ 0.17,\ f\,0.11) \qquad (c)$$

An unequal blend of polar and mesomeric effect with the dominance of the latter as reflected in the value of 4.44 for $\lambda(\rho_R/\rho_F)$ indicates the inadequacy of the SSP treatment in such cases. A comparison with the SCS C-1 in the parent styrene[2] using a common ten-point data set shows that the SCS at this carbon atom show analogous behaviour which is indicative of the same model of transmission of substituent-induced electronic effects in the two systems. The regression equation can be written as (*d*) with *r* 0.996. If the point due to NMe_2 is omitted,

$$\mathrm{SCS\ C\text{-}1\ (\mathbf{1};\ X = CN) = 0.935\ SCS\ C\text{-}1\ (styrene) + 0.018} \qquad (d)$$

there is some improvement in the correlation and *r* becomes 0.998.

SCS Values of C-1 and the four side-chain carbon atoms were then subjected to DSP–NLR[19] analysis and the results are summarised in Table 2. The improvement in the quality of correlation of SCS C-1 is obvious from the comparison of the values of the correlation coefficient, standard deviation, Taft's *f* value, and the *F* test of variance. The other sites also show equally excellent goodness of fits. While the value of the electron-demand parameter ε for SCS C-1 indicates that the electron demand for the group $-CH{=}C(CN)_2$ is the same for that of the group $-CH{=}C(CN)CONH_2$, both groups behaving approximately the same as a CO_2Et group, the ε value of SCS C-α in the series (**1**; X = CN) indicates that the σ_R scale needed for correlating SCS C-α in 4-substituted benzylidenemalononitriles and 2-cyano-3-(*para*-substituted phenyl)prop-2-enamides are different. Unlike the latter series, the SCS C-α in the former do not show an exalted resonance response of the type opposite to that shown by its adjacent carbon atoms. This fact also shows that contrary to the expressed opinion,[16] comparison of chemical shifts between two similar series is not sufficient to bring out all the finer details of the substituent-induced electronic effects. The value of ε (−1.23) at C-β show that the two nitrile functions have approximately additive effect (ε for CN is −0.60).

Table 3. ^{13}C SCS[a] in ethyl 2-cyano-3-(*para*-substituted phenyl)prop-2-enoates (**1**; X = CO_2Et)

Sub-stituent	C-1	C-α	C-β	CN	CO
H	131.4	155.0	102.7	115.5	161.8
Me	−2.8	−0.2	−1.6	0.2	0.1
OMe	−7.6	−1.0	−3.2	0.4	0.4
NMe_2	−13.0	−1.4	−10.6	1.0	1.7
F	−3.1	−1.3	−0.6	−0.1	−0.1
Cl	−1.3	−1.5	0.5	−0.3	−0.3
Br	−0.9	−1.3	0.6	−0.2	−0.2
CF_3	3.7	−1.7	3.0	−0.5	−0.6
NO_2	5.8	−2.3	3.8	−0.6	−0.7
CN	4.1	−2.0	3.3	−0.6	−0.7

[a] Relative to the parent compound.

The ρ_F values in Table 2 shows that the main polar effect exerted by the substituent R on the side-chain is field-induced π-polarisation with direct polarisation of the α–β double bond and the CN group (**6**) and the extended polarisation of type (**8**) evident from the large ρ_F value of 5.37 for C-β, which is larger than the corresponding value of 4.91[12] in the series (**1**; X = $CONH_2$). This increased value is probably due to a lesser degree of twist[24] (11 compared with 15°) between the phenyl and the dicyanovinyl moieties. The comparatively large value of ρ_F for C-α (−3.41) also suggests the existence of the second extended polarisation of type (**9**). The sign of the ρ_F values for C-α and the two nitrile carbon atoms also indicate the existence of reverse substituent effects at these sites. The dominance of the mesomeric effects at C-1 and C-β is also evident from the results.

Ethyl 2-*Cyano*-3-(para-*substituted phenyl*)*prop*-2-*enoates* (**1**; X = CO_2Et).—SCS Values of ten members of the series are given in Table 3. Results of DSP treatment of these values with σ_F as polar substituent parameters and all three resonance scales σ_{R° (Reynolds), σ_{R^+} (Taft), and σ_{R^+} (Charton) as resonance parameters are summarised in Table 4. It appears that the resonance scale suitable for C-1 is σ_{R° while that for the side-chain carbon atoms is σ_{R^+}. The relative importance of the polar and mesomeric effects at different sites appears to follow the same trend as the other two series, (**1**; X = CN) and (**1**; X = $CONH_2$). As for those two series SCS C-1 and SCS C-β show analogous behaviour with the SCS at these two sites of the parent styrene[2] with the correlation coefficients 0.996 and 0.939, respectively; when the point due to NMe_2 is omitted from the common ten-point data set there is significant improvement in the quality of the correlation with *r* 0.998 and 0.985, respectively. A similar trend was earlier observed[12] in the series (**1**; X = $CONH_2$). The real power of the DSP–NLR approach is evident from the results summarised in Table 5 which show an all-around improvement in the quality of correlation of all the SCS that have been examined. While the trend of the relative importance of polar and mesomeric effects at different sites and the different kinds of field-induced π-polarisation show a parallelism with other related series which we have examined, a comparatively smaller value of ρ_F at C-β presumably suggests a greater degree of twist between the benzene ring and the $-CH{=}C(CN)CO_2Et$ moiety. From the sign of ε at C-α we find

Table 4. DSP Analysis of ^{13}SCS in ethyl 2-cyano-3-(*para*-substituted phenyl)prop-2-enoates

Site	Model[a]	ρ_F	ρ_R	λ	Intercept	*r*	S.d.	*f*	*F*
C-1	A	5.02	21.73	4.33	−0.01	0.994	0.61	0.10	305
C-1	C	5.84	11.56	1.98	−0.63	0.988	0.27	0.16	144
C-α	A	−3.30	0.82	−0.25	−0.01	0.901	0.10	0.21	29
C-α	B	−3.55	0.49	−0.14	0.00	0.972	0.05	0.11	59
C-α	C	−3.28	0.59	−0.18	0.00	0.929	0.08	0.18	22
C-β	A	4.92	14.36	2.92	−0.01	0.945	0.41	0.33	29
C-β	C	4.82	8.43	1.64	−0.14	0.992	0.16	0.12	221
CN	A	−0.89	−1.53	1.72	0.00	0.968	0.04	0.25	52
CN	B	−0.52	−0.51	0.98	0.01	0.919	0.96	0.42	19
CN	C	−0.87	−0.89	1.02	0.00	0.996	0.01	0.09	442
CO	A	−1.06	−2.20	2.08	0.00	0.927	0.08	0.37	21
CO	C	−1.06	−1.32	1.25	0.00	0.986	0.04	0.16	122

[a] Models A—C use σ_{R° (Reynolds), σ_{R^+} (Taft), and σ_{R^+} (Charton) as resonance parameters, respectively.

Table 5. DSP–NLR Analysis of ^{13}C SCS of ethyl 2-cyano-3-(*para*-substituted phenyl)prop-2-enoates (**1**; X = CO_2Et)*

Site	ρ_F	ρ_R	λ	Intercept	ε	*r*	S.d.	*f*	*F*
C-1	5.21	17.33	3.33	−0.01	−0.47	0.999	0.08	0.05	1 561
C-β	3.47	4.54	1.31	−0.02	−1.35	0.983	0.24	0.19	280
CN	−0.89	−0.82	0.92	0.00	−1.00	0.994	0.02	0.11	249
CO	−0.79	−0.47	0.59	0.00	−1.50	0.989	0.03	0.15	161

* SCS C-α is excluded for the same reason as in the series (**1**; X = CN). See footnote in Table 2.

Table 6. DSP–NLR Analysis of ^{13}C SCS in 4-substituted *cis*-cinnamonitriles

Site	ρ_F	ρ_R	λ	Intercept	ε	*r*	S.d.	*f*	*F*
C-1	4.35	18.33	4.21	0.00	−0.25	0.999	0.08	0.04	2 758
C-α	−3.63	−0.41	0.11	0.00	−0.10	0.989	0.05	0.11	589
C-β	5.37	7.61	1.42	−0.01	−0.80	0.998	0.07	0.06	864
CN	−1.45	−1.44	0.99	0.00	−0.96	0.998	0.02	0.07	93

Table 7. DSP–NLR Analysis of ^{13}C SCS in 4-substituted *trans*-cinnamonitriles

Site	ρ_F	ρ_R	λ	Intercept	ε	*r*	S.d.	*f*	*F*
C-1	4.73	19.68	4.16	0.00	−0.10	0.999	0.06	0.03	1 396
C-α	−3.21	−1.29	0.40	−0.05	0.00	0.991	0.04	0.10	196
C-β	5.81	7.72	1.33	−0.01	−0.72	0.998	0.07	0.06	760
CN	−1.21	−1.60	1.32	0.00	−0.90	0.997	0.02	0.07	589

Table 8. DSP–NLR Analysis of ^{13}C SCS of 5-substituted 2-thenylidenemalononitriles

Site	ρ_F	ρ_R	λ	Intercept	ε	*r*	S.d.	*f*	*F*
C-2	4.74	8.63	1.82	−0.01	−1.80	0.993	0.27	0.11	103
C-α	−0.83	0.57	−0.69	0.03	−2.50	0.996	0.08	0.08	298
C-β	6.61	16.08	2.43	0.00	−0.55	0.998	0.09	0.06	452
CN_Z	−0.89	−2.22	2.49	0.00	−0.60	0.996	0.02	0.09	175
CN_E	−1.34	−1.90	1.42	0.00	−0.90	0.998	0.02	0.07	330

that the resonance response at this carbon atom is of the same type as at the two adjacent carbon atoms.

4-*Substituted Cinnamonitriles* (**4**) *and* (**5**).—For a comprehensive investigation, 4-substituted *cis*- and *trans*-cinnamonitriles were then examined, compounds which are structurally related to the compounds under study, but devoid of the second electron-withdrawing group at the β-position. Butt and Topsom[20,21] earlier reported the DSP analysis of the ^{13}C SCS of these compounds. The DSP–NLR analysis are given in Tables 6 and 7. As expected, the absence of the electron-withdrawing group results in the overall reduction of electron demand at all sites. In the *trans*-series, SCS C-α is best correlated when σ_{R° (Reynolds) is used as the resonance parameter and no improvement in the fit is observed with the introduction of ε. The electron demand at C-α of the other isomeric series is feeble but still does not have a sign opposite to those at the adjacent carbon atoms. The nature of the blending of polar and mesomeric effects and the type of field-induced π-polarisation in these two series do not differ from the trends observed in those compounds which carry a second electron-withdrawing group in the β-position.

5-*Substituted* 2-*Thenylidenemalononitrile* (**2**; X = CN).—In the course of the DSP analysis[13] of the ^{13}C SCS of these compounds, we were earlier unable to correlate SCS C-2 and C-α. The DSP–NLR analysis of the ^{13}C SCS data (Table 8) has now been able to correlate the ^{13}C SCS at all the sites including these two, which are charcterised by a rather large electron demand. Apart from this high electron demand, compared with what is observed at the analogous positions in the related benzene derivatives, the thiophene series is also distinguishable from the benzene series with regard to the relative proportions of the polar and mesomeric effects at different positions. While the mesomeric effect at C-1 in different *para*-substituted β-cyanostyrenes is 3.5—4 times more important than the polar effect, the value of λ at C-2 in 5-substituted 2-thenylidenemalononitriles is only 1.82. It can be surmised that some secondary local polar effect due to the ring sulphur atom may be in some way related to this high electron demand and increased polar effect at C-2. The extent of direct polarisation of the C-α–C-β double bond is also more pronounced compared with the benzene analogue. There is considerably less twist[24] between the thiophene and the dicyanovinyl moiety compared with that between the benzene ring and the same side-chain in benzylidenemalononitriles.[25] This factor, together with the presence of the ring sulphur atom may be responsible for this augmentation in the π-polarisation.

meta-*Substituted Benzylidenemalononitriles* (**3**; X = CN), 2-*Cyano*-3-(meta-*substituted phenyl*)*prop*-2-*enoates* (**3**; X = CO_2Et), *and* 2-*Cyano*-3-(meta-*substituted phenyl*)*prop*-2-*enamides* (**3**; X = $CONH_2$).—ββ-Disubstituted styrenes under our investigation also included compounds which are endowed with substituents placed *meta* with respect to the probe function. ^{13}C SCS of these compounds are listed in Tables 9—11. It is more logical to consider these *meta*-substituted compounds separately from the *para*-substituted isomers, since the position of the substituent in the former with respect to the side-chain should result, unlike the latter, in the predominance of the polar effect being exerted at the probe site. The mesomeric

Table 9. ^{13}C SCS[a] of 3-substituted benzylidenemalononitriles (**3**; X = CN)

Sub-stituent	C-1	C-6[b]	C-α	C-β	CN_Z	CN_E
H	131.2	134.3	161.4	81.5	113.1	114.1
Me	0.0	−2.8	−0.4	−0.4	−0.1	0.0
OMe	1.1	−7.3	−0.5	0.1	−0.1	−0.1
F	1.0	−3.7	−1.4	1.9	0.0	−0.6
Cl	1.8	−1.8	1.6	2.0	−0.4	−0.3
Br	2.0		1.8	1.9	−0.4	−0.4
CF_3	0.8		1.6	2.7	−0.4	−0.3
NO_2	0.2	5.4	2.3	2.0	−0.6	−0.5
CN	1.0	3.8	2.1	3.2	−0.6	−0.5

[a] Relative to the parent compound. [b] Correlation of SCS C-6 in this series was carried out with a seven-point data set due to the difficulty of accurately assigning the chemical shift of Br- and CF_3-substituted compounds.

Table 10. ^{13}C SCS[a] in ethyl 2-cyano-3-(*meta*-substituted phenyl)prop-2-enoates (**3**; X = CO_2Et)

Sub-stituent	C-1	C-6	C-α	C-β	CN	CO
H	131.4	130.1	155.0	102.7	115.5	161.8
Me	0.1	−3.0	−0.1	−0.4	0.0	0.0
OMe	1.2	−7.7	0.0	0.2	0.1	0.0
F	2.0	−4.0	−1.5	1.6	−0.3	−0.7
Cl	1.7	−1.9	−1.6	1.8	−0.3	−0.4
Br	1.7	−8.6	−1.7	1.7	−0.3	−0.4
CF_3	−0.9	−3.8	−1.6	2.3	2.1	−0.4
NO_2	2.5	5.6	−2.2	3.0	−0.4	−0.5
CN	0.9	3.1	−0.9	2.6	0.2	−0.4

[a] Relative to the parent compound.

Table 11. ^{13}C SCS[a] in 2-cyano-3-(*meta*-substituted phenyl)prop-2-enamides (**3**; X = $CONH_2$)

Sub-stituent	C-1	C-6	C-α	C-β	CN	CO
H	132.0	130.1	150.7	106.7	116.5	162.8
Me	0.0	−3.0	0.0	−0.2	0.1	0.0
OMe	1.3	−7.5	−0.1	0.2	0.1	0.0
F	2.4	−3.7	6.0	1.5	−0.8	−0.4
Cl	1.9	−1.6	−1.6	1.6	−0.3	−0.4
Br	2.3	−1.3	−1.7	1.7	−0.4	−0.4
NO_2	1.5	3.7	−2.6	2.8	−0.6	−0.6
CN	1.3	5.9	−2.0	2.7	−0.6	−0.7

[a] Relative to the parent compound.

effect, if any, can be the result only of some kind of 'relay' *via* another site which is mutually conjugating with both positions.[26] This is corroborated by the results of the DSP analysis of the SCS, listed in Table 12. Indeed, not all the sites were amenable to the DSP analysis; correlations of SCS C-β and in some cases SCS C-γ were no better than mediocre. SCS C-1 showed particularly poor correlation. On the other hand, SCS C-6 had excellent correlation with σ_F and σ_{R° (Reynolds) in (**3**; X = CN and CO_2Et). The quality of correlation was inferior in (**3**; X = $CONH_2$). The nature of the blending of polar and mesomeric effects is similar to that observed in the case of C-1 in *para*-substituted derivatives. There was little point in carrying out DSP–NLR analysis of SCS C-β and C-γ since the sensitivity to resonance effects at these sites is manifestly small. DSP–NLR analysis of a SCS C-6 showed that in (**3**; X = CN and CO_2Et) best correlations were obtained with a σ_{R° scale and the quality of fit was not improved with the introduction of the electron-demand parameter. With (**3**; X = $CONH_2$), however, the best fit was observed with ε −0.45. The regression equation can be written as (*e*).

$$\text{SCS C-6 } (\mathbf{3}; X = CONH_2) = 4.47\,\sigma_F + 17.08\,\sigma_R - 0.01\ (r\,0.971,\ \text{s.d. } 0.34, f\,0.23) \qquad (e)$$

Shift Charge Ratios (*SCR*).—In order to measure the effect of the various vinylic side-chains carrying a nitrile function in the β-position, on the sensitivity of the site of its attachment to the benzene ring to the substituent effect of the variable substituent R, the shift-charge ratios (SCR) at C-1 in (**1**), (**4**), and (**5**) and C-6 in (**3**) were determined. They were calculated[27] by scaling up, with the usual factor of 189, the ratios of the respective ρ_R values of the series concerned and that of the monosubstituted benzene.[28] The results are given in Table 13. The values indicate that different side-chains exert this 'sensitivity' effect to different extents and the results of the three *meta*-series demonstrate that this effect is not localised solely at the point of attachment of the side-chain.[26]

The Anomalous ε *Value at* C-α *in* (**1**; X = $CONH_2$).—The DSP–NLR analysis of four β-cyanostryenes (with or without a second electron-withdrawing group at the β-position) and one of their heteroaryl analogues indicates that the rather high positive value of 3.5 for ε at C-α in 2-cyano-3-(*para*-substituted phenyl)prop-2-enamides noted by us[12] earlier is probably unique to that series. Since the only feature that distinguishes that series from the rest is the carboxamide group at the β-position, we briefly examined another series (**10**) whose ^{13}C SCS have been reported.[29] The data set is smaller than the different *para*-substituted series we have so far examined, but the DSP–NLR analysis of the SCS C-α showed an ε value higher than 4.0. Although it is difficult to make a final pronouncement before examining more related series with well balanced data sets, some link between a demand parameter related to σ_{R^-} scale at C-α and the presence of the CONH function at C-β is suggested.

Conclusions.—The exhaustive DSP and DSP–NLR analysis of the seven β-substituted styrenes and one of their heteroaryl analogues reported above brings out the nature of the substituent-induced electronic effects in these systems. The blending of polar and mesomeric effects in unequal proportions at different probe sites demonstrates once more the necessity and the virtue of the DSP approach and the inadequacy of using a single substituent parameter in the correlation of SCS in these systems. Any objection that may be raised about the use of more than one independent variable can be discounted by the absence of any linear relationship between these variables themselves and the rigorous statistical support of the results obtained. The largely different nature of the relative importance of polar and mesomeric effects in the *para*- and *meta*-series indicate that they should be treated separately. The principal polar effect is found to be the field-induced polarisation of the side-chain π-electrons, with both direct and extended polarisation being observed. Our results also indicate that a direct comparison between the chemical shifts at identical positions in different related series cannot bring out all the subtle features mentioned above and thus cannot replace the methodology of the DSP and DSP–NLR approaches in investigating substituent-induced electronic effects in substituted benzene or heteroaryl system, through an analysis of the substituent-induced chemical shifts in their n.m.r. spectra. That in spite of the common mode of transmission of substituent-induced electronic effects there are gross variations in their nature and magnitude in different individual systems is

Table 12. DSP Analysis† of ^{13}C SCS in the series (3; X = CN, CO_2Et, $CONH_2$)

Entry	X	Site	Model[a]	ρ_F	ρ_R	λ	Intercept	r	S.d.	f	F
1	CN	C-6	A	4.03	19.53	4.85	−0.01	0.999	0.06	0.04	120
2	CN	C-β	C	4.50	1.18	0.26	0.00	0.916	0.16	0.25	16
3	CN	CN_E	B	−0.75	−0.16	0.21	0.00	0.973	0.02	0.14	53
4	CN	CN_E	C	−0.81	−0.05	0.06	0.00	0.912	0.03	0.24	18
5	CN	CN_Z	B	−0.84	−0.08	0.10	0.00	0.595	0.02	0.16	33
6	CN	CN_Z	C	−0.90	−0.19	0.21	0.00	0.978	0.02	0.02	74
7	CO_2Et	C-6	A	4.24	20.06	4.73	−0.01	0.999	0.06	0.05	1 490
8	CO_2Et	C-β	A	4.70	1.55	0.33	−0.04	0.985	0.07	0.10	98
9	CO_2Et	C-β	B	4.24	0.51	0.12	−0.01	0.989	0.06	0.09	135
10	$CONH_2$	C-6	A	4.57	19.30	4.22	−0.01	0.969	0.35	0.24	38
11	$CONH_2$	C-β	A	4.24	1.75	0.41	−0.01	0.995	0.04	0.06	297
12	$CONH_2$	C-β	B	3.86	0.44	0.11	−0.24	0.964	0.10	0.17	39
13	$CONH_2$	C-β	C	4.24	1.27	0.30	−0.02	0.997	0.03	0.05	525
14	$CONH_2$	CO	A	−1.04	−0.44	0.42	0.00	0.963	0.02	0.17	38
15	$CONH_2$	CO	B	−0.94	−0.14	0.15	0.00	0.953	0.03	0.22	20
16	$CONH_2$	CO	C	−0.05	−0.34	0.32	0.00	0.973	0.02	0.14	44

† Only statistically significant correlations are reported. Entry 1 shows the result of a correlation carried out with a seven-point data set. In all other cases nine-point data sets were used.

[a] Models A—C use σ_{R° (Reynolds), σ_{R^+} (Taft), and σ_{R^+} (Charton) as resonance parameters, respectively.

Table 13. Shift-charge ratios (SCR) in β-substituted styrenes examined

Compound	Carbon	SCR
4-Substituted benzylidenemalononitrile	C-1	154
Ethyl 2-cyano-3-(*para*-substituted phenyl)prop-2-enoate	C-1	162
2-Cyano-3-(*para*-substituted phenyl)prop-2-enamide	C-1	170
4-Substituted *trans*-cinnamonitrile	C-1	184
4-Substituted *cis*-cinnamonitrile	C-1	171
3-Substituted benzylidenemalononitrile	C-6	166
Ethyl 2-cyano-3-(*para*-substituted phenyl)prop-2-enoate	C-6	188
2-Cyano-3-(*meta*-substituted phenyl)prop-2-enamide	C-6	180

in their nature and magnitude in different individual systems is evident from comparison of the results of DSP–NLR analysis in systems (1; X = CN) and (2; X = CN). This is also evident from the SCR values. Despite the common mode of transmission of substituent effects in related systems indicated by the direct comparison of ^{13}C chemical shifts, the SCR values demonstrate the different 'sensitivity effect' of the vinylic side-chain at the point of attachment to be benzene ring or in its neighbourhood.

The intriguing feature of the nature of the electron demand parameter at C-α in (1; X = $CONH_2$) still remains to be solved. The results obtained so far suggest that this may be due to the presence of the carboxamide function at the β-position. A calculation of the shielding tensors may, presumably, throw some light on this matter.

Experimental

The compounds examined were synthesized according to the literature procedure[9,16,30–32] and were crystallised from ethanol to constant m.p.s. Satisfactory elemental analysis data were obtained in all cases and no impurities were detected by ^1H n.m.r. spectroscopy. The ^{13}C spectra were recorded (in [$^2H_6$]DMSO) on a JEOL Fx-100 Fourier transform spectrometer operating at 25.05 MHz, with a pulse length of 4 μs (33°), a repetition time of 1.2 s, a spectral width of 6 024 Hz, 8k f.i.d., and an average of 1 500 scans. The central line of the DMSO multiplet (δ 39.5 p.p.m.) was used as internal reference. Assignments were made using broad-band decoupled, SFORD, and gated coupled spectra.

For multiple linear regression, a stepwise regression program was used. Computations were carried out at Regional Computer Centre, Jadavpur, Calcutta, on a Burroughs 6720 computer.

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