Modelling ^{13}C Substituent Chemical Shifts in 3-Aryl-2-cyanoacrylamides. An Application of the Dual-substituent Parameter Non-linear Resonance (DSP-NLR) Method

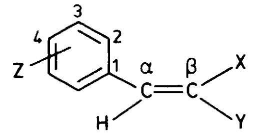
Sankar P. Bhattacharyya and Asish De
Departments of Organic and Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India
Ajit K. Chakravarty
Department of Medicinal Chemistry, Indian Institute of Chemical Biology, Calcutta 700032, India
John S. A. Brunskill
Department of Applied Chemistry, UWIST, Cardiff CF1 3XF
David F. Ewing *
Department of Chemistry, University of Hull, Hull HU6 7RX

^{13}C Substituent chemical shifts (SCS) in 3-phenyl- and 3-thienyl-2-cyanoacrylamides have been examined by multiple linear regression analysis using standard field parameters (σ_F) together with various resonance parameters. The side-chain SCS are best modelled by a method, DSP-NLR, which explicitly allows for a non-linear resonance response. A combination of polarization and resonance mechanisms accounts satisfactorily for substituent effects at all side-chain sites.

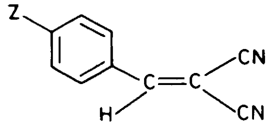
There has been a resurgence of interest in the mode of transmission of polar substituent effects[1] particularly in molecules containing an extended π-system. Styrenes (**1**; X = Y = H) are well suited to such studies owing to a well defined geometry, a non-polar side chain, and easy accessibility to a wide range of groups X and Y with a reasonable substituent set for Z. Thus ^1H and ^{13}C substituent chemical shifts (SCS) have been examined by Reynolds and co-workers[2,3] for the parent system (**1**; X = Y = H) with a range of 15 Z substituents. The correlation of these side-chain SCS with single- or dual-substituent parameter σ-scales (SSP or DSP) has contributed greatly to recent discussion of the nature of polar substituent effects[1] and of the general validity of SSP and DSP analyses.[4] N.m.r. data (^1H and ^{13}C chemical shifts) have been reported for *ca.* 30 other series of styrenes (**1**) in which one or both of X and Y substituents are groups such as CN, COR, Ph, Me, or CO_2R.[5] Unfortunately most of these investigations of substituent effects (*i.e.*, variation of Z for given X and Y) use inadequate data sets or inappropriate analysis.

Variation of X and Y in (**1**) is a means of altering the electron demand on the substituted aryl group and thus the response of the substituent Z. Several workers[6–10] have investigated the benzylidenemalononitriles (**2**), a system with very high electron demand by the side chain, and recently[11] we extended the scope of this powerful side chain to the investigation of substituent interactions in heteroaryl analogues of system (**1**). The 5-substituted thiophene derivatives (**3**) are much more difficult to synthesize than those in series (**2**), thus imposing certain limitations on the number and variety of Z substituents. Other workers have examined the substituent effects in system (**3**) for two derivatives, Z = Me, Br.[12]

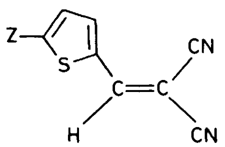
We report now on the SCS in systems (**4**) and (**5**) in order to extend the study of series (**2**) and (**3**) to a side chain of lesser electron demand using a data set of reasonable size (11) in the benzene series and to examine further the transmissivity of the thiophene ring, with a more limited set of five. A side chain containing a carbonyl group in the γ-position was selected for investigation since there is some controversy[13,14] about the interpretation of SCS for γ-carbons in similar systems.



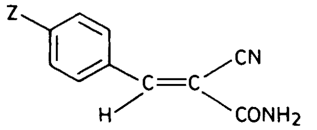
(**1**)



(**2**)



(**3**)



(**4**)

Results and Discussion

The chemical shifts for the 11 compounds in series (**4**) are given in Table 1 in terms of SCS with respect to the parent compound. Assignment of these shifts was achieved readily using decoupled and gated-coupled spectra, together with standard SCS values[15]

Table 1. ^{13}C SCS[a] in 3-(4-substituted phenyl)-2-cyanoacrylamides (**4**)

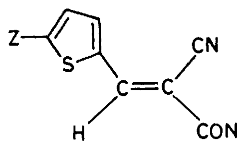
Substituent	C-1	C-2	C-3	C-4	C-α	C-β	CN	$CONH_2$
H	132.0	129.2	130.1	132.4	150.7	106.7	116.5	162.8
NMe_2	−13.3	3.5	−18.6	20.5	−0.1	−9.6	1.8	1.2
NEt_2	−13.6	4.3	18.7	18.6	0.4	−10.6	2.2	1.8
OMe	−7.6	3.3	−15.3	30.2	−0.4	−3.9	0.6	0.6
Cl	−1.3	2.4	−1.1	4.4	−1.5	0.5	−0.4	−0.3
F	−3.4	−1.2	−13.7	31.7	−1.1	−0.6	0.0	0.0
NHAc	−5.4	2.6	−10.8	10.8	−0.1	−2.9	0.7	0.8
NO_2	5.9	1.6	−6.1	16.2	−2.6	3.7	−0.9	−0.9
CO_2H	3.7	0.6[b]	−0.2[b]	1.1	−1.3	2.1	−0.5	−0.3
CN	4.7	1.1	2.7	−14.3	−2.0	3.1	−0.7	−0.8
Me	−2.8	1.0	−0.3	10.7	0.0	−1.6	0.2	0.2

[a] Relative to the parent compound, all shifts in DMSO relative to Me_4Si. [b] Assignments uncertain, chemical shifts 129.8 and 129.9, respectively.

Table 2. ^{13}C SCS[a] in 3-(5-substituted thienyl)-2-cyanoacrylamides (**5**)

Substituent	C-2	C-3	C-4	C-5	C-α	C-β	CN	$CONH_2$
H	135.9	137.5	128.5	134.7	143.7	102.0	116.8	162.9
Me	−2.0	1.0	−1.2	15.1	0.0	−1.9	0.0	−0.1
Cl	−1.1	0.2	−0.3	2.0	−0.7	0.4	−0.4	−0.8
Br	1.5	0.9	3.2	−13.7	−1.0	0.5	−0.3	−0.8
NO_2	5.1	−1.7	1.0	19.2	−1.4	5.4	−1.1	−1.6

[a] Relative to the parent compound, all shifts in DMSO relative to Me_4Si.



(**5**)

Table 3. Correlations[a] between SCS in systems (**2**) and (**4**) and in systems (**3**) and (**5**)

Systems	Carbon	p^b	q^c	r^d	f^e	n^f
(**2**)–(**4**)	C-4 (*ipso*)	0.99	0.61	0.998	0.046	11
(**2**)–(**4**)	C-1 (*para*)	0.94	−0.13	0.9997	0.022	11
(**2**)–(**4**)	C-α	1.09	0.26	0.917	0.248	8[g]
(**2**)–(**4**)	C-β	0.79	0.10	0.999	0.047	11
(**3**)–(**5**)	C-5 (*ipso*)	1.04	−0.30	0.998	0.061	5
(**3**)–(**5**)	C-2 (*para*)	1.22	−0.10	0.996	0.087	5
(**3**)–(**5**)	C-α	2.28	−0.01	0.954	0.200	5
(**3**)–(**5**)	C-β	0.84	−0.01	0.9999	0.016	5
(**3**)–(**5**)	CN_Z	0.94	−0.27	0.942	0.250	5

[a] Analysis according to equation (1). [b] Slope of regression line. [c] Intercept. [d] Correlation coefficient. [e] Taft's coefficient. [f] No. in data set. [g] NHCOMe, NMe_2, and NEt_2 omitted.

for the ring carbons. The side-chain carbons* C-α and C-β had characteristic shift values differing by *ca.* 50 p.p.m. and the nitrile and amido carbons showed couplings of *ca.* 14 and 8 Hz, respectively, with the vinyl proton, confirming that the aryl group is *cis* to the CN group. Chemical shifts in the thiophene series (**5**) were assigned using the same techniques, and are given in Table 2.

In order to be able to use the SCS data for series (**4**) and (**5**) as a potential enlargement of our data set[11-16] for series (**2**) and series (**3**) it is important to establish that these two pairs of series show strictly analogous behaviour. Table 3 gives the results of correlating some of the data in Tables 1 and 2 with the corresponding substituent effects (S) for the series of nitriles[11-16] according to equation (1). It is evident that for the

$$S(\text{amide}) = p{\cdot}S(\text{nitrile}) + q \qquad (1)$$

important sites C-1, C-4, and C-β there is an extremely good linear relationship between both sets of amides and nitriles, the correlation coefficient being greater than 0.995 in all cases. As might be expected in the benzene series the *para*-SCS (C-1 SCS) show the most regular behaviour and the correlation between the amides (**4**) and the nitriles (**2**) is slightly better than that for either of these with the parent styrene system (**1**; X = Y = H). Data are only available for C-1 in the parent system for measurements in CCl_4 solution[3] but the common eight-point set (omitting NEt_2, CO_2H, NHAc) gives equation (2) with r =

$$S(4, \text{C-1}) = 1.13\,S(\text{styrene, C-1}) + 0.02 \qquad (2)$$

0.996 and f = 0.084. Small specific solvent effects may account for this slightly poorer correlation, but this cannot be the case for the correlation with the *para*-SCS for monosubstituted benzenes in DMSO,[17] equation (3), which has r = 0.995, f =

$$S(4, \text{C-1}) = 0.98S(\text{benzene, C-4}) - 0.31 \qquad (3)$$

0.094 for an eight-point set. Close inspection of these correlations reveals that the most deviant point in both cases is that for NMe_2. Omission of this datum from the analyses gives r = 0.999 for both correlations and it is clear that this strong π-donor group participates in enhanced conjugation with the acceptor group $CH{=}C(CN)CONH_2$. Such behaviour is similar to that found by Taft and co-workers[18] in other series of 1,4-disubstituted benzenes for which a non-linear resonance response is evident. From a comparison of the *para*-SCS for the NMe_2 group in the amides (**4**) and the other series studied by Taft and co-workers[18] it appears that the group $CH{=}C(CN)$-$CONH_2$ has a similar effect to the group CO_2Et on the conjugative interaction of *para*-substituents.

---

* The α-carbon is adjacent to the ring. This is consistent with the labelling used by most workers[5] for systems related to (**1**).

Although the SCS at C-β in series (**4**) show an excellent correlation with the SCS in series (**2**) the substituent effect is only about 80% of that in the nitriles (**2**), probably due to the reduced π-acceptor ability of $CONH_2$ relative to CN. This parallels the behaviour of C-*para* SCS in 1,4-disubstituted benzenes[18] where the values found in *para*-substituted esters are about 85% of those in the corresponding nitriles. Clearly the β-SCS are influenced by variations in the β-substituent in a similar manner to the well established variations at a *para*-site. It has been suggested that the substituent at the *para*-site in 1,4-disubstituted benzenes can alter the shift-to-charge ratio[5,18] for that site mainly through π-electron delocalisation, and a similar control appears to operate at the β-position in the styrene system (**1**).

The range of SCS at the γ-sites in series (**2**) and (**4**) is small, 2—3 p.p.m., and the regression statistics reflect a greater uncertainty. Nonetheless, the *cis*-CN data are closely parallel in both series with residuals of 0.2 p.p.m. or less. The one site that does not show any correlation between series (**2**) and (**4**) is the α-carbon. Gross deviations are shown by donor substituents and if, for example, the data for NMe_2, NEt_2, and NHAc are omitted a tolerable correlation is found (Table 3), with OMe the most deviant point. Although Reynold *et al.*[2] found that C-α and C-β in styrene derivatives can both be almost equally well explained by DSP analysis, Robinson, *et al.*[10] commented that the α-carbon in several series of type (**1**) shows poor correlations with σ^+. We shall return to this point below when we examine the efficacy of a DSP model for these SCS but it is evident from the comparison of the amides with the nitriles that in side chains with high electron demand the α-carbon behaves in an anomalous way.

The restricted set of substituents available in the thiophene series (**5**) precludes a detailed comparison with series (**3**). However, even using a five-point data set the close parallel between the thiophene and benzene series is apparent in the regression coefficients in Table 3. The correlations are excellent for C-2, C-5, and C-β sites, confirming our previous observation in the benzene series that these three positions respond in a well behaved way to a change in the side chain. The sensitivity at the *ipso*-site is essentially the same in both phenyl and thienyl series and a similar reduction at the β-site is also apparent. In contrast the *quasi-para* position (C-2) has enhanced SCS values in the thiophene amides. Since substituent effects at the γ-carbons of the side chain are small (*ca.* 1.5 p.p.m. or less) some values have a large uncertainty and this is reflected in the poorer quality of the inter-set correlations of CN carbons.

It is now well established[5,19] that two substituent parameters are both necessary and sufficient to model long-range substituent effects in styrenes. Most previous attempts[6–10,20] to examine the relationship of α- and β-SCS to substituent parameters in systems containing a side chain with high electron-demand characteristics have relied on SSP or DSP analyses using inappropriate parameters. Craik and Brownlee[5] have summarised this work and shown that β-SCS values for most systems of type (**1**) are well correlated by an equation of type (4),

$$S = \rho_I\sigma_I + \rho_R\sigma_R \qquad (4)$$

where σ_R represents one of the resonance parameters first defined by Taft and co-workers.[21] Data for the styrene series (**1**; X = Y = H), and data for related α-methyl- and α-t-butyl-styrenes have been used[2] to refine σ_I values and redefine these as σ_F (in accord with the current view[1] that this parameter is a measure of field effects). We have examined, by regression analysis,* the modelling of the SCS in (**4**) and (**5**) with these new σ_F values in combination with the $\sigma_R{}^\circ$ values of Reynolds (also refined on the basis of the styrene data[2]) or the $\sigma_R{}^+$ values of Charton,[22] or the $\sigma_R{}^+$ values of Taft and co-workers.[21] A selection of the results is given in Table 4. Whilst the work of Reynolds and co-workers[2] has identified σ_F and $\sigma_R{}^\circ$ as pure field and resonance parameters, respectively, these two scales alone cannot account for long-range effects in all situations since a continuum of resonance response is to be expected.[21,23] The need for differing σ_R scales can best be accommodated by the use of the dual-substituent parameter non-linear resonance (DSP-NLR) method[18] which allows the resonance scale to vary with the electron demand of the site. This is achieved with a parameter ε, characteristic of the group attached to the site, and an equation of type (5) gives an almost perfect explanation

$$S(para) = \rho_F\sigma_F + \rho_R\sigma_R{}^\circ/(1 - \varepsilon\sigma_R{}^\circ) \qquad (5)$$

of *para*-SCS in 15 series of disubstituted benzenes[18] with ε ranging from 0.25 for NMe_2 to -0.72 for NO_2. This method has been applied† to series (**4**) with the results shown in Table 5.

The *para*-carbon is best correlated with $\sigma_R{}^\circ$ although the quality of the fit is not very different for correlation with Taft's $\sigma_R{}^+$ values. Inspection of a plot of *S*(*para*) against fitted values reveals that these two simple models give smooth curves of opposite sense confirming that the best fit must correspond to a resonance scale of a type intermediate between $\sigma_R{}^\circ$ and $\sigma_R{}^+$. Using the DSN-NLR method a value of $\varepsilon = -0.38$ results in a correlation (Table 5, entry 1) of high quality with an improvement in the *f* fitting parameter significant at the 99.9% level.[24] This value of ε confirms that the $CH{=}C(CN)CONH_2$ group has similar electron-demand characteristics to the CO_2Et group.[18]

The DSP-NLR method is a powerful tool for checking the quality of the data in well behaved systems such as (**4**) and the only deviant points are for the NEt_2 and NHAc substituents for which parameters had had to be estimated. (These groups were not included in the set of styrenes from which the refined σ_F and $\sigma_R{}^\circ$ values were determined.[2]) Exclusion of these two data points gives results (Table 5, entry 2) that model the SCS within experimental error, with an improvement in the *F*-test of variance.

It is notable (*i*) that refining the model for *para*-SCS reveals a greater sensitivity to the resonance component, (*ii*) that the SCS for series (**4**), determined in DMSO, are successfully reproduced by substituent parameters derived from data determined in CCl_4 (thus indicating a wider applicability of

---

* In all correlations with either equation (4) or (5) we have included a constant term in the regression equation, since we regard this as a better approach. Whilst the exclusion of the constant term increases the degrees of freedom the same result is achieved by including a datum for H. If the model is good the constant term should be less than the experimental uncertainty.

† Objections could be raised that this procedure involves fitting to three parameters, which is intrinsically less desirable than a genuine DSP analysis (which has itself been criticized by purists who deplore any departure from the approach of Hammett). We agree with the view[4,5,14] that a two-parameter model is incontrovertibly more meaningful than a one-parameter model and that the latter is of restricted value at least for spectroscopic studies. Both concepts have allowed the need for different resonance scales and the use of the DSP-NLR method formalizes and characterizes this requirement of a general theory of substituent effects. It should be noted that although equation (5) contains three parameters it does *not* represent a formal extension to an analysis in terms of three variables since ε has a constant value over the substituent set in a given analysis. Thus the statistical factors in Tables 4 and 5 are directly comparable, since both analyses have the same number of degrees of freedom. The principle virtue of the DSP-NLR method lies in its explanatory capability and only marginal improvement in the quality of the correlation is expected in most cases. It is becoming increasingly evident that inadequacies in the data itself have often had an obscuring effect on the nature of the model required to explain observed trends and that only with high-precision spectroscopic data will accurate modelling be possible.

Table 4. Evaluation of DSP models for SCS in systems (**4**) and (**5**)

Entry	System	Site	Model[a]	ρ_F	ρ_R	c[b]	r[c]	f[d]	n[e]
1	4	C-1	A	5.66	21.91	−0.44	0.995	0.088	11
2	4	C-1	B	5.25	11.57	−0.22	0.985	0.156	11
3	4	C-1	C	5.28	8.12	−0.05	0.991	0.120	11
4	4	C-α	A	−3.12	−1.11	−0.17	0.954	0.217	11
5	4	C-α	A	−3.20	−1.15	−0.19	0.980	0.134	9[f]
6	4	C-α	C	−3.26	−0.29	−0.14	0.963	0.188	11
7	4	C-β	A	5.56	14.42	−0.59	0.963	0.250	11
8	4	C-β	B	4.74	8.19	0.07	0.998	0.055	11
9	4	C-β	C	4.87	5.67	0.04	0.995	0.090	11
10	4	CN	B	−1.12	−1.67	−0.03	0.989	0.114	11
11	4	CO	B	−1.18	−1.29	0.06	0.973	0.221	11
12	5	C-2	A	5.36	13.05	−0.13	0.954	0.289	5
13	5	C-α	A	−2.03	−0.50	−0.01	0.985	0.113	5
14	5	C-β	A	5.87	12.44	−0.15	0.999	0.049	5
15	5	CN	A	−1.21	−1.43	−0.07	0.984	0.131	5
16	5	CO	A	−2.04	−1.06	−0.09	0.993	0.076	5

[a] A, DSP model is used in the form SCS = $\rho_F\sigma_F + \rho_R\sigma_R + c$. Models A, B, and C use $\sigma_R{}^{\circ}$ (Reynolds),[2] $\sigma_R{}^{+}$ (Charton),[22] and $\sigma_R{}^{+}$ (Taft),[21] respectively. The estimated constants used for NEt_2 were 0.10 (σ_F), −0.60 ($\sigma_R{}^{\circ}$), −1.32 ($\sigma_R{}^{+}$, Charton), −1.85 ($\sigma_R{}^{+}$, Taft) and for NHAc were 0.28 (σ_F), −0.30 ($\sigma_R{}^{\circ}$). [b] Intercept for a plot of observed against fitted SCS values. [c] Multiple correlation coefficient. [d] Taft *f* value. [e] Number in set. [f] NEt_2 and NHAc omitted.

Table 5. Evaluation of the DSP-NLR model[a] for SCS in systems (**4**) and (**5**)

Entry	System	Site	ρ_F	ρ_R	ε	c	r	f	s[b]	F[c]	n[d]
1	4	C-1	5.49	18.23	−0.38	−0.23	0.9989	0.0422	0.345	1 815	11
2	4	C-1	5.53	17.25	−0.49	−0.15	0.9994	0.0344	0.252	2 497	9
3	4	C-β	4.94	7.43	−0.99	−0.24	0.9965	0.0781	0.445	568	11
4	4	C-β	4.91	6.54	−1.10	−0.17	0.9981	0.0601	0.288	787	9
5	4	C-α	−3.15	−1.61	3.6	−0.03	0.9935	0.0754	0.123	228	9
6	4	CN	−1.16	−1.11	−1.19	0.02	0.9969	0.0788	0.074	482	9
7	4	CO	−1.23	−1.24	−0.81	0.05	0.9972	0.0752	0.057	533	9
8	5	C-β	6.2	11.63	−0.85	−0.11	0.9989	0.0442	0.180	453	5

[a] The standard DSP model was used in form SCS = $\rho_F\sigma_F + \rho_R\sigma_R$ + c. The σ_R values were evaluated according to the method of Taft.[18] Symbols have the same standard meaning as indicated in the footnotes to Table 4. [b] Standard deviation. [c] *F* test of variance. All correlations are significant at a level >99.9%. [d] For nine-point sets, NEt_2 and NHAc were omitted.

Reynolds' refined substituent parameters[2]), and (*iii*) that the presence of β-substituents (CN, $CONH_2$) on the vinyl group results in a reduction of the resonance mechanism and an increase in the field mechanism at the *para*-site (*cf.* the coefficients in Table 4, entry 1, with those for the corresponding regression equation[2] for styrenes, $\rho_F = 4.33$, $\rho_R = 19.74$).

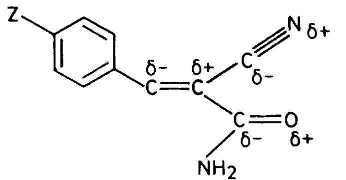
The side-chain SCS in (**4**) were also investigated by DSP and DSP-NLR methods. The best correlation for C-β (*cf.* entries 7—9, Table 4) requires a $\sigma_R{}^{+}$ parameter, and a small residual curvature in the plot of observed against fitted values (with Taft $\sigma_R{}^{+}$ scale) indicates an optimum scale corresponding to slightly less enhancement. This optimum value of ε = −0.99 is found using equation (5) to give the results in entry 3, Table 5, falling to ε = −1.10 with omission of the NEt_2 and NHAc points. This latter value is approximately what would be expected if the two substituents at the β-site (CN, $CONH_2$) have an additive enhancing effect on the resonance interaction of the remote substituent. The ε factors for CN and CO_2Et are −0.60 and −0.48, respectively, at the *para*-site in benzene.[18]

This result for the β-carbon emphasises the inadequacy of previous attempts[13,14,24] to correlate side-chain SCS with standard $\sigma_R{}^{+}$ scales. The Taft scale was derived[21] by finding the best scale to explain two sets of kinetic data. This scale gave excellent results for many other sets of similar rate and equilibrium data but was acknowledged to have 'limited generality'. A good correlation for SCS using the $\sigma_R{}^{+}$ scale can generally only be fortuitous.

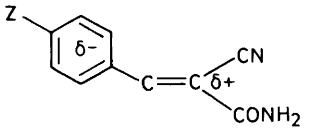
Correlation of C-α SCS (Table 4, entries 4 and 6) appears to require $\sigma_R{}^{\circ}$ rather than $\sigma_R{}^{+}$ although neither scale provides a good fit. All reports hitherto[2,7,8,10,13,14] have indicated that C-α is not as well explained as C-β by DSP analysis in *any* series of type (**1**), including series (**2**). For the styrene series[2] a value of *r* = 0.9915 was obtained for C-α compared with *r* = 0.9992 for C-β and other examples in this work show greater divergence. Using literature data for series (**2**) Bromilow and Brownlee[25] found that the correlation of C-α with σ_I and $\sigma_R{}^{+}$ had *f* = 0.27 compared with *f* = 0.08 for the β-correlation. With remeasured data[14] a value of *f* = 0.11 was obtained for C-α (using σ_I and $\sigma_R{}^{-}$) but only at the expense of omitting the datum for NMe_2. The power of the DSP-NLR method is shown by our results for C-α. The correlation is nearly as good as that for C-β (*cf.* entries 4 and 5 in Table 5). The value of ε = 3.6 is slightly less than that corresponding to the $\sigma_R{}^{-}$ scale, an unexpected result, since most workers use the same σ_R scale to correlate C-α and C-β SCS.

This result strengthens our belief that the DSP-NLR method is the best approach since it models all substituents in terms of two fundamental scales (σ_F and $\sigma_R{}^{\circ}$) and an electron-demand parameter. However, the differential of ε with respect to the standard deviation is low in this case and further work is required with a range of systems to establish the uncertainty in ε. Nonetheless, it is clearly established that the required resonance scale is close to $\sigma_R{}^{-}$, confirming that C-α and C-β not only show a resonance response of opposite sign (as expected) but also show an exaltation in that response of opposite type.

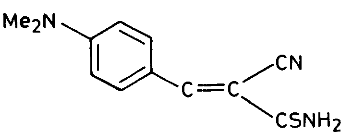
The SCS for the CN site in series (**4**) correlate well with a



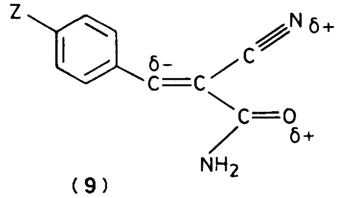
(6)



(7)



(8)



(9)

literature $\sigma_R{}^+$ scale (Table 4) and optimisation of the resonance scale gives a value of ε almost the same as that required by C-β (Table 5). The ρ_R value is negative as required by an alternating resonance response and is similar to the values found for γ-sites in other substituted styrenes.[14] The carbonyl site shows virtually the same values of regression coefficients as the CN site although the ε value is somewhat lower. It is interesting that the order of ε values for the first carbon of these two substituents is the same as that found for the site carrying CN and COR substituents in disubstituted benzenes.[18]

All of the results for the side-chain carbons (Table 5, entries 4—7) are in keeping with a model of substituent interactions comprising two major components. The alternating sign of ρ_R for C-α, C-β, and C-γ sites and the negative ε values for the C-β and C-γ sites indicate an enhanced resonance interaction, as is expected if the ring is nearly coplanar with a side chain of high electron demand. It is difficult to account for the positive value of ε for C-α but it is undoubtedly related to the presence of acceptor substituents at C-β. The main field effect in this system is direct polarization[1] of the side chain π-electrons as three independent moieties (6). Thus ρ_F is negative at C-α, CN, and CO sites. The large positive value of ρ_F for C-β indicates some extended polarization[1] between vinyl and phenyl groups (7) although this is less than in the case of styrene[2] where $\rho_F = 5.11$ for C-β. Increased twisting is indicated for (4) and this is supported by the 15° twist between phenyl and vinyl determined from an *X*-ray analysis of thioamide (8).[26]

The most notable difference between the styrene system and (4) is the magnitude of ρ_F for C-α. The value of -2.59 for styrene has been taken[2] to represent direct vinyl polarization and hence the value of -3.15 in (4) is indicative of significant extended polarization of type (9). Similar results are apparent in other substituted styrenes.[5]

DSP analysis of the SCS in series (5) are of limited value owing to the poorly balanced nature of the substituent set. Results for C-2, the *quasi-para* position, are poor (Table 4) but this is largely due to the anomalous effect of the bromo substituent. Most substituents at the 2-position in thiophene[27] have an effect at C-5, similar to that found at *C-para* in benzene. Bromo has an SCS of -1.5 in benzene but a value of $+2.6$ is found in thiophene and analogous values are $+1.48$ and $+1.5$ in series (3) and (5), respectively. These values reflect a strong repulsive interaction between the bromine and sulphur atoms.

The range of available SCS was large enough for C-β in (5) to warrant optimisation of the resonance scale and the result is shown in Table 5, entry 8. The resonance scale is close to $\sigma_R{}^+$ as found in the benzene series, but ρ_R is nearly double. This is in keeping with a greater resonance transmissivity for the thiophene ring.[11,25] Increased extended polarization analogous to (7) is to be expected in the less crowded thiophene and this accounts for the increased ρ_F values. The ρ values for C-α, CN, and CO sites are generally as expected, showing that a similar combination of mechanisms operates in both series (4) and (5).

Experimental

All compounds were prepared by base (Et_3N)-catalysed condensation of the appropriate aldehyde with 2-cyanoacrylamide. Satsifactory elemental analysis data were obtained in all cases and no impurities were detected by ^1H spectroscopy. The ^{13}C spectra were recorded on a JEOL FX-100 FT n.m.r. 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, and 8K f.i.d. and an average of 1 500 scans. The central line of the DMSO multiplet (39.5 p.p.m.) was used as internal reference.

References

1 W. F. Reynolds, *Prog. Phys. Org. Chem.*, 1983, **14**, 165.
2 W. F. Reynolds, A. Gomes, A. Maron, D. W. MacIntyre, A. Tanin, G. K. Hamer, and I. R. Peat, *Can. J. Chem.*, 1983, **61**, 2376.
3 G. K. Hamer, I. R. Peat, and W. F. Reynolds, *Can. J. Chem.*, 1973, **51**, 897, 915; W. F. Reynolds, G. K. Hamer, and A. R. Bassindale, *J. Chem. Soc., Perkin Trans. 2*, 1977, 971.
4 W. F. Reynolds, P. Dais, D. W. MacIntyre, G. K. Hamer, and I. R. Peat, *J. Magn. Reson.*, 1981, **43**, 81.
5 D. J. Craik and R. T. C. Brownlee, *Prog. Phys. Org. Chem.*, 1983, **14**, 1.
6 T. B. Posner and C. D. Hall, *J. Chem. Soc., Perkin Trans. 2*, 1976, 729.
7 D. A. R. Happer, S. M. McKerrow, and A. L. Wilkinson, *Aust. J. Chem.*, 1977, **30**, 1715.
8 A. Cornélius, S. Lambert, and P. Laszlo, *J. Org. Chem.*, 1977, **42**, 381.
9 R. E. Bilbo and D. W. Boykin, *J. Chem. Res. (S)*, 1980, 332.
10 C. N. Robinson, C. D. Salter, J. S. Covington, C. R. Chang, L. S. Dewey, J. M. Franceschini, J. L. Fritzche, J. E. Hamilton, C. C. Irving, J. M. Morris, D. W. Norris, L. E. Rodman, V. I. Smith, G. E. Stablein, and F. C. Ward, *J. Magn. Reson.*, 1980, **41**, 293.
11 A. De, S. P. Battacharyya, J. S. A. Brunskill, K. K. Sidhu, and D. F. Ewing, *J. Chem. Res. (S)*, 1982, 312.
12 G. Musumarra and F. P. Ballistreri, *Chem. Scr.*, 1981, **18**, 209.
13 A. Cornélius, S. Lambert, P. Laszlo, and P. Schaus, *J. Org. Chem.*, 1981, **46**, 2130.
14 D. J. Craik, R. T. C. Brownlee, and M. Sadek, *J. Org. Chem.*, 1982, **47**, 657.
15 D. F. Ewing, *Org. Magn. Reson.*, 1979, **12**, 499.
16 D. F. Ewing, unpublished work.
17 J. Bromilow, R. T. C. Brownlee, V. O. Lopez, and R. W. Taft, *J. Org. Chem.*, 1979, **44**, 4766.
18 J. Bromilow, R. T. C. Brownlee, D. J. Craik, M. Sadek, and R. W. Taft, *J. Org. Chem.*, 1980, **45**, 2429.
19 W. F. Reynolds, A. Gomes, A. Maron, D. W. MacIntyre, R. G. Maunder, A. Tanin, H. E. Wong, G. K. Hamer, and I. R. Peat, *Can. J. Chem.*, 1983, **61**, 2367.

20 D. A. R. Happper, *Aust. J. Chem.*, 1976, **29**, 2607.
21 S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1973, **10**, 1.
22 M. Charton, *Prog. Phys. Org. Chem.*, 1981, **13**, 119.
23 W. F. Reynolds, P. Dais, D. W. MacIntyre, R. O. Topsom, S. Marriott, E. von Nagy-Felsobuki, and R. W. Taft, *J. Am. Chem. Soc.*, 1983, **105**, 378.
24 S. Ehrenson, *J. Org. Chem.*, 1979, **44**, 1793.
25 J. Bromilow and R. T. C. Brownlee, *J. Org. Chem.*, 1979, **44**, 1261.
26 J. S. A. Brunskill, A. De, D. F. Ewing, and A. J. Welch, *Acta Crystallogr.*, 1984, **C40**, 493.
27 S. Gronowitz, I. Johnson, and A.-B. Hörnfeldt, *Chem. Scr.*, 1975, **7**, 76.

Received 13*th July* 1984; *Paper* 4/1215