β-Substituent Effects in the ^{13}C NMR Chemical Shifts of Styrenes

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The effects of *meta* and *para* ring substituents on the ^{13}C NMR chemical shifts of the β-carbon of a series of β-heteroaryl styrenes has been investigated. The results show that the contribution of the resonance effect of *para* substituents to the C-β chemical shift depends on both the polar and resonance effect of the β-substituent, and not, as was previously believed, on the resonance effect alone.

In recent years ^{13}C NMR chemical shift measurements have become one of the principal tools used for the investigation of substituent electronic effects and their mechanisms of transmission within molecules. The systems studied most widely have been aromatic ones, especially those with unsaturated side-chains such as styrenes.[1]

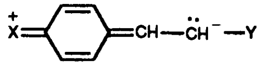
The influence of ring substituents on the chemical shifts of the two side-chain carbons of styrenes has been used by Reynolds to investigate the mechanism by which the polar effect of the substituent is transmitted to the probe site.[2] Other workers,[3,4] ourselves included,[5] have been less concerned with how the electronic effects are transmitted than with their magnitudes, and the relative contributions of polar and resonance effects to the observed shifts, *i.e.* they have aimed at using the observed shifts as a probe for measuring substituent effects and the factors that influence them. Among the most suitable systems for such studies have been *meta*- and *para*-substituted styrenes bearing a constant substituent on C-β, the terminal carbon of the side-chain vinyl group. For these, the substituent-induced changes in chemical shifts (SCSs) for C-β appear to be directly related to the polar and resonance effects of the ring substituents.

For *meta* substituents, excellent correlations are obtained using Hammett σ^{meta} constants, showing that any contributions from resonance effects represent a 'leakage' phenomenon.[5] In the *para* case, however, resonance effects contribute substantially to the observed shifts.

The mechanism by which the polar and resonance effects of a ring substituent influence the electron density at C-β are still not clear. Reynolds[6] has suggested that, in the case of the styrenes, the polar effect arises as a result of the field effect of the substituent dipole, and that this alters the electron density at C-β by two mechanisms: (*i*) field-induced polarization of the side chain vinyl group (direct π polarization), and (*ii*) field-induced π electron transfer (extended π polarization).

The second was considered to be the major contributor, provided the system was planar. Reynold's view that the polar effect was of field, rather than inductive origin, is supported by the observation that its influence on C-β is approximately the same from the *meta* and *para* positions.

The means by which the resonance effect influences the electron density at C-β is less certain. Its magnitude appears to be related to the expected strength of the resonance interaction between the *para* and the β-substituents present.[5] The degree of sensitivity observed is quite surprising, as an interaction of this type would not automatically be expected to have a major effect on the electron density at C-β. It cannot be due to an increase in the extent of coplanarity of the ring and side chain, as this would have affected the $\rho_I^{meta}/\rho_I^{para}$ ratio, and there was no evidence for this. Also of interest was the observation that there is no indication that the polar effect of a β-substituent had a systematic effect on either ρ_R or σ_R for any system studied, even though the presence of a strongly electron-attracting group on C-β should enhance the contribution of resonance forms of the type shown.



It seemed to us that there was a general need for additional basic information on these systems, especially with regard to the role of the β-substituent. It was of particular importance to establish whether or not its polar effect really had no influence on the degree of electron transfer, or whether an effect did exist, but was masked by a more dominant resonance contribution. In order to achieve this, it is necessary to compare data for series where the variations in the electronic character of the β-substituent are more precisely controlled than has been the case to date. The simplest approach is to use *meta*- and *para*- substituted aryl groups as β-substituents. Comparison of the results for these with those for stilbenes should permit the investigation of polar and resonance effects free from the complications of proximity effects. However, a preliminary study showed that for these, the substituent-induced changes are far too small. We opted instead for heteroaryl groups, which, like aryl groups, minimise complications from proximity effects, but which are potentially capable of exerting much stronger electron-donating and electron-withdrawing effects. The series chosen for study were the 2- and 3-styrylfurans, the 2-, 3-, and 4-styrylpyridines (stilbazoles) and the 2-, 3-, and 4-styrylpyridine methiodides. These heteroaryl β-substituents vary quite significantly in their polar and resonance effects, and especially in the balance between the two. While their effects on the C-β shifts were still not as large as we would have wished, they were in most cases detectable, and open to rational interpretation. The results of our investigation are the subject of this paper.

Results and Discussion

The Electronic Effect of the β-Heteroaryl Groups.—Before considering the results, it is important to try and establish as far as possible the relative magnitudes of the electronic effects of the heteroaryl groups used as β-substituents in the study. Each will exert a constant polar effect, and a resonance effect for which the magnitude may vary according to the demand placed on it. A number of σ constants of various types have been reported for these groups, but many are of doubtful reliability. Representative values, selected from a review by Tomasik and Johnson,[7] are given in Table 1. Of them, only the Hammett σ values for 2-, 3-, and 4-pyridyl can be considered well established.

Table 1. Substituent constants for furyl, pyridyl, and *N*-methylpyridinium groups.[a,b]

	σ	σ^-	σ^+	σ_I(est)[c]	σ_R^+(est)[c]	σ_R^-(est)[c]
2-Furyl	+0.32		−0.85	+1.5	−2.4	
3-Furyl	+0.04		−0.44	+0.7	−1.1	
2-Pyridyl	+0.72	+1.00	+0.75	+0.6		+0.4
3-Pyridyl	+0.62	+0.59	+0.54	+0.5		
4-Pyridyl	+0.97	+1.17	+1.16	+0.8		+0.4
2-*N*-Methylpyridinium		+2.49		+2.0		+0.5
3-*N*-Methylpyridinium		+1.58		+1.5		
4-*N*-Methylpyridinium		+2.32		+1.8		+0.5

[a] These values represent σ(aryl) values based on σ(phenyl) = 0. [b] The σ, σ^+, and σ^- values listed are taken from the review of Tomasik and Johnson.[7] [c] With the exception of the ones for 3-Pyridyl and 3-*N*-Methylpyridinium, these derived values are very unreliable. The method of derivation is outlined in the text.

A reliable σ_I value has not been reported for any of the substituents. However, these can usually be estimated if other σ values for the substituent are available. Such estimates are based on the assumption that groups with similar strengths as resonance donors or withdrawing groups tend to show similar variations of σ_R with electron demand. The most useful data for the purpose are σ^{meta} values, as the resonance contributions to these are often small. For common resonance withdrawing substituents, σ_R^{meta} is typically *ca.* 20% of the σ_R^- value for the group. In practice this usually means it lies within the range +0.07 to +0.10, and so, if σ^{meta} is known, σ_I can be estimated with a fair degree of reliability. The situation with regard to resonance donors is a little more complicated, as their σ_R^- values can vary over a much wider range. The 20% rule works well for ones with magnitudes up to and including that of –OMe, but is not applicable for more powerful ones, a figure closer to 15% being more appropriate for groups such as $-NMe_2$. As a result, the margin of error in estimating σ_R^{meta} is greater, and this leads to less reliable σ_I estimates. (σ_R^+ and σ_R^- values may be estimated by comparing the differences between measured σ_p^+/σ_p^- and σ^{meta} substituents for which the σ_R^+/σ_R^- values are known.) The reliability of this approach to the estimation of the σ_I parameters will depend very much on the quantity and the quality of the data available. In the present case, these were both limited and not very reliable, with the result that derived parameters are subject to considerable uncertainty.

In the case of the 2- and 3-furyl groups, the estimates for σ_I must necessarily be based on the relationship between the reported σ and σ^+ constants. The differences between these are comparable in magnitude to those for *p*-NMe_2 and *p*-OMe respectively. Extrapolating to conditions of zero electron demand leads to estimated σ_I values for 2- and 3-furyl of approximately +1.5 and +0.7. While such values may seem high compared with those for most common $+M$ substituents, they arise from the close proximity of the highly electronegative oxygen to the sites in question. Estimates of σ_R^+ for the two are readily derived, since the σ^+ values for the two positions are known. No σ^- values have been reported. This is not a serious disadvantage for the interpretation of our results, as neither a 2-furyl nor a 3-furyl group would be expected to interact strongly with *para* $+M$ substituents.

Initially, attempts to estimate σ_I values for the pyridyl and *N*-methylpyridinium groups were based on the methods outlined above, but some modification was required, as inconsistencies were revealed. Both the 3-aza and 3-*N*-methylazonium groups are of the $(-I, -M)$ type, so it is not unreasonable to assume that the σ_I values for 3-pyridyl and 3-*N*-methylpyridinium are about 0.1 σ units lower than their reported σ values, that is *ca.* + 0.5 and +1.5 respectively. Problems arise, however, with the others. If one considers the relationship between the magnitudes of σ^{meta}, σ^{para}, and σ^- in the pyridyl series, then it becomes immediately apparent that the difference between the first two is very much greater than that observed for typical $-M$ substituents (for most of these this difference is less than 0.1 σ units). We believe that the apparent enhancement arises as a consequence of π polarization—the distortion of the aromatic π system by the electronegative aza nitrogen.

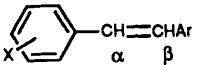
The major effect of such π polarization would be an abnormal decrease in the electron density at the ring carbon *para* to the nitrogen, which would lead to an apparent increase in the polar effect of the 4-pyridyl group relative to that of 3-pyridyl. Such an increase is, strictly speaking, due to a change in ρ_I rather than σ_I, but nevertheless the net effect is to make the former group behave as if it were at least 50% more electron attracting than the latter, *i.e.* 4-pyridyl behaves as if it had a σ_I *ca.* +0.8. The reported σ^- value of +1.17 for the group is consistent with a σ_R^- *ca.* +0.4. The value for σ^+ cannot be considered a well founded one, but it serves to establish that the group is not a good resonance donor, since it shows that σ_R^+ is positive.

In the case of 2-pyridyl, the normal increase in direct field and σ^- inductive effects expected from the closer proximity of the aza nitrogen would, if anything, tend to be offset rather than augmented by the aforementioned π polarization. The reported σ value for 2-pyridyl suggests an overall polar effect for this group of the same order as 3-pyridyl, an observation consistent with such an interpretation. It is not unreasonable to assume that, for the group, σ_R^- and σ_R^+ have similar values to those for 4-pyridyl.

Assessment of the polar and resonance effects for the 2-, 3-, and 4-*N*-methylpyridinium groups is hampered by the almost total lack of available σ values. Only σ^- values (+2.49, +1.58, and +2.32 respectively, based on the rates of methanolysis of halogen derivatives[8]) have been reported. However, these values, in the 3- and 4-cases at least, are supported to some extent in the present study (see below). Our estimates for the σ_I and σ_R^- values for the 2- and 4-*N*-methylazonium groups are based on the assumption that they and the aza groups are of similar types $(-I, -M)$, but the latter exerts both greater polar and resonance effects. The proposed value for σ_I^{para} is an estimate, based on the assumption that it must be at least 0.3 units greater than that for σ_I^{meta}, while σ_R^- cannot be less than +0.4. That for σ_I^{ortho} assumes that σ_R^- for the 2- and 4-substituents is the same. Both these values and the derived estimates for σ_R^- must be regarded as more unreliable than those for the other substituents. This is especially true of that for the 2-substituent, as the reported σ^- value ignores steric effects, yet is based on a reaction in which they are almost certainly significant. It is improbable that any of the three *N*-methylpyridinium groups are significant resonance donors.

Our estimated σ_I, σ_R^+, and σ_R^- values for the various heteroaryl groups are to be found in Table 1. It is important to note that they are only *estimates*, made to facilitate the interpretation of our results. For this reason we have only listed those σ_R^+ and σ_R^- values needed for this purpose.

Table 2. Positions of C-β resonances in *meta*- and *para*-*X*-substituted stilbenes, styrylfurans, stilbazoles, and stilbazole methiodides.[a,b]



X	Ph	2-Fur	3-Fur	2-Py	3-Py	4-Py	Ph[c]	2-PyMe$^+$ [c]	3-PyMe$^+$ [c]	4-PyMe$^+$ [c]
H	128.66	116.55	118.33	127.82	124.78	125.88	128.40	117.60	121.43	123.28
m-Me	−0.17	−0.18	−0.14	−0.16	−0.23	−0.21	−0.22	−0.24	−0.22	−0.19
m-OMe	0.34	0.29	0.33	0.18	0.33	0.30	0.22	0.28	0.33	0.26[d]
m-F	1.36	1.21	1.38	1.25	1.38	1.38	1.59	1.58	1.65	1.54
m-Cl	1.47	1.23	1.48	1.33	1.49	1.46	1.71	1.64	1.75	1.64
m-Br	1.48	1.27	1.53	1.37	1.51	1.50	1.70	1.61	1.72	1.60
m-CF_3	1.90	1.65	1.93	1.72	1.94	1.88	2.10	2.10	2.14	2.01
m-CN	2.69	2.25	2.68	2.40[d]	2.71	2.74	2.57	2.47	2.58	2.40
m-NO_2	3.10	2.67	3.16	2.79	3.21	3.17	2.94	2.91	2.92	2.72
p-NMe_2	−4.17	−3.91	−4.12	−4.42	−4.64	−4.92	−4.88	−7.02	−5.63	−6.18
p-OMe	−2.04	−1.86	−2.05	−2.11	−2.17	−2.38	−2.31	−2.84	−2.55	−2.60
p-Me	−0.94	−0.86	−0.98	−0.93	−1.02	−1.00	−1.00	−1.12	−1.05	−1.05
p-F	−0.18	−0.14	−0.18	−0.28	−0.21	−0.20	−0.12	−0.12	−0.10	−0.16
p-Cl	0.66	0.52	0.66	0.55	0.64	0.57	0.87	0.78	0.85	0.78
p-Br	0.76	0.61	0.77	0.62[d]	0.75	0.65	0.94	0.82	0.90	0.82
p-CF_3	2.55	2.23	2.56	2.36	2.58	2.59	2.93	2.89	2.89	2.75
p-CO_2R	2.48	2.24	2.60	2.33	2.53	2.50	2.83	2.63	2.75	2.59
p-CN	3.75	3.22	3.78	3.39	3.73	3.72	3.81	3.51	3.66	3.44
p-NO_2	4.64	3.95	4.72	4.20	4.59	4.53	4.86	4.26	4.49	4.23

[a] The positions of the resonances are expressed in the form of substituent chemical shifts except for the parent compounds, for which the shift relative to tetramethylsilane is given. [The substituent chemical shift (SCS) is the change in chemical shift that arises as a result of the introduction of the substituent X into the parent compound.] [b] Unless otherwise indicated, the shifts were determined in $CDCl_3$ solvent. [c] Measured in DMSO solvent. [d] Overlapping peak.

Interpretation of the C-β *Shifts.*—The C-β shifts of the nine series studied are summarised in Table 2. The methiodides were insoluble in deuteriochloroform and so spectra for these were determined in dimethyl sulphoxide. To facilitate comparisons, shifts for the stilbenes were measured in both solvents.

A preliminary inspection of the data shows that the effect of SCS of varying the β-substituent is relatively small in all of the *meta*-substituted compounds, in many instances less than would be anticipated from measurement errors alone. Quantitative comparisons based on consideration of ρ^{meta} values confirm this. As with our earlier study, no obvious pattern has emerged. In $CDCl_3$, ρ^{meta} for the 2-pyridyl and 2-furyl series are clearly lower than the others, but this does not appear to be related to polar effects, as a similar lowering is not observed in the 2-methiodide one.

Inspection of the data for the *para* series shows that for these, also, differences are relatively small, lying for many substituents within normal error limits. However, for the strong resonance donors (NMe_2, OMe) there is some dependence on β-substituent, shown most clearly in the 2- and 4-methiodide series. It should be remembered, however, that the β-substituents involved are not strong resonance withdrawing groups compared with, for example $-NO_2$ or −COMe.

In view of the relatively small differences between the series, quantifying changes in resonance interaction poses a problem. The approach adopted in our earlier study,[5] analysis of the *para* data by means of the DSP equation, is not satisfactory, as it is inherently incapable of distinguishing between small changes in σ_R and ρ_R, attributing them entirely to the latter. The alternative approach, of evaluating σ^{para} values by the normal Hammett method (*i.e.* by assuming $\rho^{meta} = \rho^{para}$) is likewise unsatisfactory, as it attributes the changes entirely to ones in σ_R, and yields σ^{para} values for resonance withdrawing substituents that are significantly greater than σ^-. Since it had been previously established[9] that, for stilbenes in DMSO, $\rho_I^{meta} = \rho_I^{para}$, such a result implies that $\rho_R^{para} \neq \rho_I^{para}$, rendering a conventional Hammett treatment invalid.

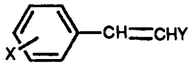
As a preliminary step in our analysis, the polar contributions to the *para* shifts were estimated using σ_I values based on styrenes, and by assuming that $\rho_I^{meta} = \rho_I^{para}$. The resonance contributions to the shifts could be obtained by difference. This reduced the problem to one of obtaining a realistic estimate for ρ_R. We believe that this is possible in our case.

In the styrenes it had been noted that the resonance components of the C-β shifts gave good correlations with σ_R^- in the case of *para* resonance withdrawing substituents. Examination of our data showed that this was also true for all of our series except the three methiodide ones. In the latter, the correlation with σ_R^- fell off in a manner consistent with the substituents exhibiting σ_R values smaller than their limiting σ_R^- ones. Derived ρ_R values for the series where good correlations with σ_R^- were observed proved to be 10–30% higher than ρ_I. Since the higher values of ρ_R/ρ_I tended to be associated with electron rich β-substituents, it was felt that the variations might be partly due to proportional changes in σ_R rather than changes in ρ_R. For this reason we elected to arbitrarily assume, for discussion purposes, that ρ_R/ρ_I ($=\lambda$) was constant, and assigned it a mean value of 1.2. This assumption had the advantage of allowing us to assign ρ_R values to series such as the methiodides. It is interesting to note that DSP analysis of data for the stilbenes, based on the use of *para* resonance donating substituents only, also yields λ values of around 1.2.[5]

Calculated σ_R values for our series made on this basis are presented in Table 3. Also listed for comparison are the ones for the β-methoxycarbonylstyrenes, a series previously studied, that yielded results close to those obtained for the methiodides.

The calculated σ_R values should reflect the combined influence of the polar and resonance effects of our β-substituents. The response to polar effects is best examined by comparing the results for the β-phenyl, β-3-pyridyl, and β-3-*N*-methylpyridinium series. The trends for both *para* $+M$ and

Table 3. Calculated σ_R values for *para* substituents based on C-β chemical shifts.[a]



	Y											
X	Ph	2-Fur	3-Fur	2-Py	3-Py	4-Py	CO_2Me[b]	Ph[c]	$2\text{-}PyMe^+$[c]	$3\text{-}PyMe^+$[c]	$4\text{-}PyMe^+$[c]	CO_2Me[d]
p-NMe_2	−1.05	−1.14	−1.04	−1.20	−1.12	−1.19	−1.31	−1.02	−1.36	−1.16	−1.45	−1.26
p-OMe	−0.65	−0.68	−0.65	−0.71	−0.64	−0.71	−0.74	−0.64	−0.73	−0.68	−0.75	−0.70
p-Me	−0.18	−0.20	−0.19	−0.20	−0.20	−0.19	−0.22	−0.17	−0.20	−0.18	−0.20	−0.18
p-F	−0.45	−0.45	−0.46	−0.48	−0.46	−0.46	−0.46	−0.44	−0.45	−0.44	−0.44	−0.45
p-Cl	−0.24	−0.25	−0.24	−0.25	−0.25	−0.26	−0.26	−0.22	−0.22	−0.22	−0.23	−0.24
p-Br	−0.20	−0.21	−0.20	−0.22	−0.21	−0.23	−0.24	−0.17	−0.18	−0.18	−0.19	−0.20
p-CF_3	0.17	0.19	0.18	0.18	0.17	0.17	0.17	0.20	0.20	0.19	0.20	0.16
p-CO_2R	0.32	0.35	0.35	0.34	0.31	0.31	0.28	0.34	0.33	0.32	0.31	0.27
p-CN	0.27	0.28	0.28	0.27	0.25	0.25	0.20	0.29	0.27	0.26	0.25	0.21
p-NO_2	0.41	0.41	0.43	0.40	0.37	0.37	0.31	0.42	0.37	0.35	0.33	0.27
ρ^{meta}	3.88	3.29	3.86	3.49	3.96	3.93	4.00	4.39	4.29	4.35	4.07	4.59
ρ_R^{para}	4.57	4.03	4.86	4.17	3.36	4.30	3.61	5.18	3.95	4.38	4.17	3.58

[a] Calculations are based on σ_I and σ^{meta} values from reference,[12] assuming that $\rho_I^{meta} = \rho_I^{para}$ with $\lambda = 1.2$. The ρ_R^{para} values are based on correlations for $-M$ substituents using σ_R^- values from the same reference. [b] Calculations based on published data obtained in $CDCl_3$ solvent.[10] [c] DMSO solvent. [d] Calculations are based on data obtained in DMSO solvent.[11] Shifts for the *para* $-M$ substituents have not been previously reported. The relevant SCS values are 2.84 (CF_3), 2.47 (CO_2Me), 3.57 (CN), and 4.24 ppm (NO_2) respectively.

para $-M$ substituents are not large, but there is evidence that, as the polar effect of the β-substituent increases, σ_R for the former becomes more negative, while that for the latter becomes less positive. It is useful to compare these values with the corresponding ones for the two furyl series, which have very similar polar effects to the 3-pyridyl and 3-methiodide series respectively, but are strong resonance donors. Only the σ_R values for the $-M$ substituents should be affected, and this is what is observed.

Analysis of the situation for the four series bearing resonance-withdrawing β-substituents is more difficult, as polar and resonance effects are operating in the same direction, and are potentially capable of influencing the σ_R values for both $+M$ and $-M$ substituents. In addition, the σ_R^- and σ_I values for the 2- and 4-methiodide groups are unreliable, although there are reasonable grounds for believing that $\sigma_I \gg \sigma_R$ for both. The situation with regard to the 2-group is further confused by the possibility of the involvement of proximity effects.

Overall, the most useful comparisons are those between 3-furyl and 2-, 3-, and 4-pyridyl. The polar effects of all four groups are approximately the same, but only the second and fourth are capable of exerting a significant $-M$ effect. It can clearly be seen that the σ_R values for the strong resonance donors (*p*-NMe_2, *p*-OMe) are enhanced for these, and the most obvious explanation for this is that it is a result of resonance interaction with the β-substituent. A comparison of the results for 2-furyl and the three methiodide series reveals similar trends, although in view of the uncertainties in the σ_I and σ_R^- for 2- and 4-methiodides, the evidence for the involvement of resonance effects is weaker. It may be noted that, just as there was no evidence for $+M$ β-substituents influencing σ_R for *para* $+M$ ones, there is likewise none for $-M$ β-substituents affecting σ_R for *para* $-M$ ones. In both cases any variations are best explained in terms of polar effects.

The overall results, therefore, support a much greater role for the polar effect of β-substituents than had been expected on the basis of the earlier study. However, in the systems of greatest interest, where the electron demand on a *para* $+M$ ring substituent is responding to both the polar and resonance effects of a $(-I, -M)$ β-substituent, it has not proved possible to assess the relative contributions of each. There are indications, however, that the $-M$ effect is potentially capable of making the greater contribution, possibly by a factor of three or more. This raises the question as to why, if polar effects do make substantial contributions, this was not obvious in our earlier investigation? One possible explanation is that the value of ρ_R/ρ_I is higher for a substituent directly linked to the β-carbon, than when it is more distant. There is, in fact, a precedent for this. For the chemical shifts of *para* ring carbons, λ has a value of 4–5,[13] while for C-β of styrenes it is approximately unity.[5]

Estimation of Substituent Constants for Heteroaryl Groups.— In the preceding discussion the heteroaryl groups were considered as β-substituents in a series of ring-substituted styrenes. The parent compounds in each of the series examined can also be considered as substituted stilbenes, and, on this basis, substituent constants for the aryl groups involved may be evaluated. In the case of the 3-pyridyl and 3-*N*-methylpyridinium groups, these will represent σ^{meta} values and may be directly compared with the literature values listed in Table 1. For the others the situation is a little more complex in that one must take into account the value of λ for the system before direct comparisons with literature values are possible. The results of this exercise are summarised in Table 4. Comparison with the reported literature values (Table 1) shows that the values for the 3-pyridyl and 3-*N*-methylpyridinium groups are in excellent agreement, better indeed than we might anticipate, given the considerable differences in the solvents involved. Those listed for the 2- and 4-pyridyl groups and their *N*-methyl analogues should represent σ^- values. For all but the 2-*N*-methylpyridinium derivative, where proximity effects are likely to play a major role, agreement is also excellent. The situation with regard to the 2- and 3-furyl values is somewhat different. These are $+M$ substituents, and direct comparison with literature values is not possible. This is because, like other substituents of their class in the stilbene series, they do not yield σ values that correspond to any of σ°, σ, or σ^+. Instead, all appear to yield intermediate values with magnitudes slightly more negative (or less positive) than benzoic acid based σ values. Only in the case of the 2-furyl substituent does the correction for differing ρ_R and ρ_I values have much effect on the evaluated substituent constants. The much larger discrepancy observed here arises because this group is an extremely powerful resonance donor, and is accordingly much more sensitive to variations in electron demand.

Table 4. Calculated σ(aryl) constants for heteroaryl groups.

	Ph	2-Fu	3-Fur	2-Py	3-Py	4-Py	2-PyMe$^+$	3-PyMe$^+$	4-PyMe$^+$
SCS (ppm)	0	−1.51	−0.33	3.99	2.05	4.75	14.42	6.86	12.15
σ(aryl)[a]	0	−0.09	−0.04	0.96		1.16	3.08		2.64
σ(aryl)[b]	0	−0.40	−0.09	1.04	0.54	1.24	3.29	1.57	2.77

[a] Calculated on the assumption that $\rho_R/\rho_I = 1.2$. [b] Calculated on the assumption that $\rho_R/\rho_I = 1.0$.

Experimental

Preparation of Compounds.—The compounds used in the study were prepared by standard methods. New compounds were identified on the basis of their ^{1}H and ^{13}C NMR spectra coupled with either microanalysis or high resolution mass spectrometry.

The 2- *and* 4-*stilbazoles.* These were mostly prepared by refluxing the appropriately substituted benzaldehyde with an equimolar quantity of 2- or 4-methylpyridine in acetic anhydride.[14] In instances where this method proved unsatisfactory, they were made by dealkylation of the corresponding methiodides. This was best achieved by refluxing them for several hours in a solution of lithium iodide in dimethylformamide.

The 3-*stilbazoles.* These were prepared from the appropriate arylmethyltriphenylphosphonium salt and pyridine-3-carbaldehyde by the Wittig reaction, using NaOMe/MeOH (2 mol dm^{-3}) to generate the ylide. The isolated products proved to be mixtures of the *Z* and *E* isomers. Refluxing this mixture for 10 min in nitrobenzene containing a trace of iodine[15] yielded an all *E* product.

The 2- *and* 4-*stilbazole methiodides.* These were prepared either by the Knoevenagel condensation of the appropriate benzaldehyde with 2- or 4-stilbazole methiodide,[16] or by reaction of the stilbazole with a solution of methyl iodide in ether. The 3-stilbazole methiodides were all prepared by the latter route.

The 2-*styrylfurans.* These were mostly prepared by the reaction of the appropriately substituted benzaldehyde with *O,O*-diethyl 2-furylmethylphosphonate in NaOMe/DMF.[17] A few were prepared by the method used for the 3-stilbazoles.

All but one of the 3-*styrylfurans* were prepared by the method used for the 2-derivatives, except that for these, arylmethylphosphonates were reacted with furan-3-aldehyde. The *p*-NMe_2 derivative was prepared by the method used for the 3-stilbazoles.

The stilbenes and methyl cinnamates were available from earlier studies.[9,10]

^{13}C *NMR Measurements.*—The NMR spectra for all of the compounds except the 2-styrylfurans were determined on a Varian XL-300 spectrometer equipped with a 5 mm switchable probe operating at 75.426 MHz. Spectra were recorded at 23 °C on *ca.* 2% w/v solutions in deuteriochloroform or DMSO. Solvent peaks were used as internal references, and the values obtained subsequently converted into shifts relative to tetramethylsilane. The shifts for the 2-styrylfurans were measured on a Varian CFT-20 spectrometer operating at normal probe temperature.

For most carbons, assignment was straightforward. Where ambiguities were encountered, these were resolved by ^{1}H–^{13}C two-dimensional correlation spectroscopy.

Details on the characterization of new compounds together with full chemical shift data have been deposited as a Supplementary Publication [Sup. 56778 (31 pp)*].

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