J. CHEM. SOC. PERKIN TRANS. II 1988

Side-chain ^{13}C Nuclear Magnetic Resonance Shifts in Ring-substituted Styrenes. The Effect of β-Substituents on β-Carbon Shifts

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A large number of compounds of the type XC_6H_4–CH=CYZ have been prepared and the effect of varying X, Y, and Z on the ^{13}C n.m.r. chemical shifts of the β-(terminal) carbon of the ethenyl group has been investigated. For Y and Z constant and X *meta* or *para* to the side-chain the dominant influence is the electronic effect of X. For *meta*-X, excellent correlations of the C_β shifts with Hammett σ^{meta} constants are obtained in all cases. For *para*-X, there is evidence that both the inductive and resonance effect of X influence the shift with the extent of the contribution of the latter being greatest in situations where resonance interaction between X and Y/Z is expected to be strongest. Attempts to investigate the degree of this interaction by means of Taft's Dual Substituent Parameter Equation were only partly successful, and showed that in our systems such analysis is better regarded as a qualitative guide to the extent of resonance interaction that a quantitative measure of it.

The quantitative determination of the magnitudes of the electronic effects of substituents has historically been based on measuring their influence on reaction rates or the positions of chemical equilibria. Measurements of these types are time-consuming and often of relatively low precision. During the last ten years, however, the effects of substituents on ^{13}C n.m.r. chemical shifts have been increasingly used for this purpose. The stimulus for this has been the ready availability of instruments capable of measuring such shifts with a high degree of precision, coupled with the recognition that in suitable systems the influence of substituents on these are predominantly a consequence of their polar and resonance effects. The most widely used systems for this purpose have been the shifts of the *para*-ring carbons in benzenes[1,2] and the side-chain carbons of ring-substituted styrenes.[3–6] Recently, Reynolds and his co-workers have used these and similar data as a basis for redefining $\sigma_F(\sigma_I)$ and $\sigma_R{}^\circ$ parameters with a claimed high degree of precision (standard errors of 0.01 and 0.005, respectively).[4,5] We also recently investigated styrenes, but with different and more limited objectives.[6] Our studies were confined to an investigation of the effect of *meta*- and *para*-ring substituents on the ^{13}C chemical shifts of the two ethenyl carbons of the side-chain, with the aim of establishing (a) whether good correlations with the inductive and resonance effects of substituents existed, and (b) the extent to which the latter varied with solvent. Where comparisons between Reynolds' results and ours can be made, differences appear greater than expected, but for the most part are solely a consequence of differences in basic assumptions made.

Our investigations revealed that the shifts of the terminal ethenyl carbons (hereafter referred to as C_β) were particularly useful. For *meta*-ring substituents excellent correlations existed between these and Hammett σ^{meta} constants. In addition there was evidence that their response to inductive effects was approximately independent of whether the ring substituent was *meta* or *para* to the side-chain. Such behaviour parallels that observed in normal reactivity studies, but contrasts with that often found for ^{13}C n.m.r. chemical shifts in other systems.

In earlier investigations we, among others, had noted that the effect of a *para*-ring substituent on a C_β chemical shift varied with the electronic character of any substituent(s) attached to the latter carbon.[3] Up to now, however, no systematic study of this phenomenon encompassing an adequate range of ring and β-substituents has been attempted.† Perhaps the major problem encountered in pursuing such an investigation to date has been a lack of suitable reliable substituent parameters with which to analyse the results with an adequate degree of precision. As a result of our investigation of the effect of solvent on σ_I and σ_R in the styrenes, we felt that we had obtained a set of parameters suitable for the purpose. This paper presents the results of our investigation.

There are considerable data on C_β shifts in styrene derivatives available in the literature. However, much are unsuitable for use, either because an insufficient range of ring substituents was covered (few studies included an acceptable range of *meta*-ones, for example), or else because the shifts were measured at relatively high concentrations. In this latter case the character of the solvent can be changed sufficiently for the shifts themselves to be affected. For this reason, we have preferred to construct our own series and measure the data ourselves rather than rely on that in the literature. The only exception to this we have made is those obtained by Reynolds and his co-workers. A total of ten new sets of data are reported. This is supplemented with three sets reported previously by our group and three sets published by Reynolds. Together we feel they constitute a range sufficiently great for useful conclusions to be drawn.

Results and Discussion

The ^{13}C n.m.r. chemical shift data for our ten new series are given in Table 1. The series chosen from the literature to supplement these were $Y = Z = H$,[6] $Y = H$, $Z = Ph$,[8] $Y = Z = CN$,[9] $Y = Z = F$,[10] and $Y = Z = H$ where C_α is substituted with a Me and Bu^t group respectively.[4,11] Of the latter six series, only the first two sets of data were obtained in $CDCl_3$ solvent. The third was measured in Me_2SO, while for the last three CCl_4 was used. In the case of the β,β-difluorostyrenes and α-t-butylstyrenes no data for *meta*-derivatives were available. However, we were reluctant to exclude them for this reason as each demonstrated an important substituent type.

Analysis of the Data.—Previous experience with data of the type listed in Table 1 had led us to the conclusion that they are best separated into three sub-sets, each analysed by a different method. The three categories are (a) all data involving *meta*-ring

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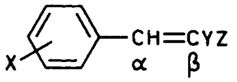
† Slater, Robinson, and their co-workers have obtained data for a considerable number of series, but the range of β-substituents in terms of electronic character is limited.[7]

Table 1. ^{13}C N.m.r. chemical shifts for $C_β$ in β-substituted styrenes in deuteriochloroform solvent[a]



	Y,Z									
X	Me,Me	H,Br[b]	H,Br	H,CO_2Me[c]	H,CN	H,CN[b]	H,$MeSO_2$	H,Ac	H,NO_2	$MeSO_2$,CO_2Et[d]
H	135.39	106.34	106.51	117.89	96.36	95.08	126.37	127.26	137.16	134.12
m-Me	−0.19	−0.26	−0.28	−0.28	−0.26	−0.27	−0.23	−0.19	−0.21	−0.26
m-OMe	0.34	0.15	0.31	0.32	0.36	0.22	0.19	0.22	0.17	0.29
m-F	1.47	1.39	1.55	1.39	1.68	1.64	1.50	0.95	0.97	1.46
m-Cl	1.57	1.59	1.64	1.47	1.73	1.77	1.55	0.98	0.91	1.46
m-Br	1.61	1.71	1.72	1.49	1.72	1.79	1.55	0.98	0.93	1.51
m-CF_3	2.07	2.15	2.22	2.01	2.37	2.43	2.14	1.37	1.37	2.09
m-CN	2.93	3.10	3.12	2.73	3.16	3.26	2.88	1.85	1.83	2.77
m-NO_2	3.34	3.47	3.63	3.20	3.66	3.72	3.30	2.22	2.15	3.05
p-NMe_2	−3.02		−4.95	−5.59	−6.93	−7.27	−6.61	−4.77	−5.11	−7.91
p-OMe	−1.47	−2.22	−2.50	−2.54	−2.98	−3.17	−2.81	−2.17	−2.10	−3.16
p-Me	−0.69	−0.92	−1.09	−1.13	−1.27	−1.29	−1.18	−0.92	−0.83	−1.30
p-F	−0.01	−0.12	−0.36	−0.21	−0.14	−0.32	−0.18	−0.31	−0.21	−0.22
p-Cl	0.84	0.83	0.67	0.59	0.71	0.67	0.57	0.31	0.32	0.53
p-Br	1.00	0.97	0.81	0.62	0.80	0.81	0.63	0.33	0.35	0.50
p-CF_3	2.55	2.58	2.91	2.59	2.99	3.00	2.63	1.91	1.85	2.52
p-CO_2Me	2.49		2.89	2.37	2.39	2.34	2.32	1.77	1.56	2.05
p-Ac				2.50	2.71	2.67		1.88		
p-CN	3.91	3.71	4.33	3.52	3.94	3.92	3.54	2.61	2.36	3.17
p-NO_2	4.83	4.39	5.14	4.30	4.68	4.59	4.14	3.21	2.73	3.73

[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.] The compounds are *trans*-isomers unless otherwise specified. [b] *cis*-Isomers. [c] Data for the *meta*-substituted derivatives are from ref. 12. [d] Configuration not known with certainty. Aryl group probably *trans* to $MeSO_2$.

substituents, (b) all data for *para* $+R$ substituents, and (c) data for *para* $-R$ substituents. While it may be argued that all three could be handled by the DSP analysis of Ehrenson *et al.*[13] (or some variant of it), we feel strongly that such an approach tends to mask important features of the system, and prefer ours.

For the *meta*-series we elected to correlate all the data against Hammett $σ^{meta}$ values. Excellent correlations were obtained with $σ^{meta}$ scales appropriate to the solvent used.[6] The $ρ^{meta}$ values obtained are listed at the foot of Table 2. The goodness of fit of the correlations may be judged from the values of f(= s.d/r.m.s.) listed. It will be noted that these appear slightly higher for the series on the right of Table 2. For the β-Ac and β-NO_2 derivatives the increase is considered due to the lower sensitivities of the shifts for these two series to substituent effects. However, for the other two series the increase in each case is a consequence of an anomalously low (by *ca.* 0.15—0.2 p.p.m.) substituent chemical shift for the *m*-nitro derivative. These latter variations were reproducible. No explanation can be offered for this anomaly, although it may be significant that in these two series the β-carbons are in a much more strongly electron-withdrawing environment than in any of the others.

There appears to be no obvious relationship between the magnitude of $ρ^{meta}$ and the nature of Y and Z. The values for the β-Ac and β-NO_2 series are both similar and substantially lower than the rest. These two substituents are both strongly $-R$ in character, but apart from this have little in common. However, if this factor were responsible for the variation, similar, but lesser, changes should be noted in other cases. None are to be found.

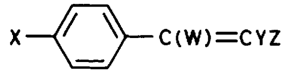
Analyses of data involving *para* substituents are customarily carried out using the DSP equation (1).[13] In this instance we elected to restrict the analysis to the $+R$ substituents, for reasons that will become apparent. A restriction of this type means that it is not possible to use what is normally regarded as the minimum basis set, which should include at least two $-R$ groups. The $σ_I$ and $σ_R$ parameters used were essentially those of Ehrenson *et al.*,[13] adjusted where necessary for the solvent used.[6] Since our earlier investigation had revealed that, of the $+R$ substituents, only the NMe_2 group showed a significant solvent dependence of $σ_I$ and $σ_R$, it is not surprising that the 'solvent-corrected' values of $ρ^I$ and $ρ^R$ obtained differed very little from unadjusted values. The results of our DSP analysis are presented in Table 2. Rather than report only the parameters for the 'best correlation' we have elected to give the results for all three $σ_R$ parameters.

$$SCS_β = δ^{13}C_β(X) - δ^{13}C_β(H) = ρ_Iσ_I + ρ_Rσ_R \quad (1)$$

The order of listing in Table 2 is as far as possible one of increasing $λ$ (= $ρ_R/ρ_I$). Moving from left to right the scale of best fit changes from $σ_R{}^o/σ_R{}^{BA}$ through $σ_R{}^{BA}$ to $σ_R{}^+$, and for all but one of the series it is possible to find one of the three scales that yields a value of f = 0.06 or less. Such a value would normally be regarded as very satisfactory, although it must be remembered that in our series we are not considering a minimum basis set of substituents. Comparisons of shifts calculated using the derived $ρ_I$ and $ρ_R$ values with the experimental values show that for most substituents agreement between the two is within the limits of experimental error in most series, and could well be improved if some of the basic $σ_I$ and $σ_R$ parameters were adjusted slightly (we elected not to do this).

All this suggests that the DSP equation would seem capable of satisfactorily correlating data for any reactions of benzene derivatives involving resonance interactions in the $σ_R{}^o/σ_R{}^{BA} \longrightarrow σ_R{}^+$ range. However, while this may well be true, it does not necessarily mean that the $σ_R$ scale for $+R$ substituents is a discontinuous one with a clustering around three fixed points ($σ_R{}^o$, $σ_R{}^{BA}$, and $σ_R{}^+$). Indeed, the developers of

Table 2. Dual substituent parameter correlations for *para* $-R$ substituents[a]



	Y,Z[b]															
	H,H[c]	Me,Me	H,Br[d]	H,H[e]	H,Ph[f]	H,H[g]	H,Br	H,CN	H,CO_2Me	H,CN[h]	H,$MeSO_2$	$MeSO_2$, CO_2Et	CN,CN[i]	H,NO_2	H,Ac	F,F[j]
σ_R°																
ρ_I	1.89	4.56	5.58	4.29	5.25	5.41	5.84	7.78	6.25	7.93	7.15	8.12	12.89	5.21	4.87	0.81
ρ_R	0.87	5.98	8.08	6.25	7.87	8.31	9.22	12.31	10.04	12.86	11.61	13.56	21.51	8.79	8.39	1.40
λ	0.46	1.31	1.45	1.46	1.50	1.54	1.58	1.58	1.61	1.62	1.62	1.67	1.67	1.69	1.72	1.73
f	0.10	0.11	0.10	0.05	0.07	0.06	0.06	0.13	0.11	0.13	0.14	0.18	0.23	0.17	0.12	0.07
σ_R^{BA}																
ρ_I	1.77	3.70	4.61	3.41	4.11	4.20	4.50	6.00	4.79	6.07	5.47	6.16	9.94	3.94	3.65	0.62
ρ_R	0.57	3.86	5.50	4.07	5.07	5.36	5.94	7.93	6.47	8.30	7.48	8.74	14.17	5.67	5.40	0.91
λ	0.32	1.04	1.19	1.19	1.23	1.28	1.32	1.32	1.35	1.37	1.37	1.42	1.43	1.44	1.48	1.47
f	0.09	0.06	0.03	0.06	0.05	0.03	0.03	0.12	0.09	0.10	0.13	0.17	0.21	0.15	0.11	0.08
σ_R^+																
ρ_I	1.67	3.00	4.07	2.70	3.22	3.25	3.45	4.65	3.68	4.66	4.21	4.71	7.26	2.99	2.73	0.42
ρ_R	0.30	1.99	3.25	2.13	2.63	2.77	3.08	4.15	3.37	4.33	3.92	4.60	7.23	2.98	2.82	0.47
λ	0.18	0.66	0.80	0.79	0.82	0.85	0.89	0.89	0.92	0.93	0.93	0.97	1.00	0.99	1.02	1.13
f	0.04	0.18	0.17	0.12	0.10	0.12	0.12	0.03	0.05	0.04	0.03	0.06	0.09	0.05	0.04	0.16
ρ^{meta}[k]		4.16	4.46	3.41	3.81	4.12	4.54	4.58	4.00	4.75	4.20	3.94	5.21	2.71	2.74	
f		0.02	0.03	0.02	0.03	0.01	0.01	0.03	0.03	0.03	0.03	0.05	0.06	0.05	0.04	

[a] All compounds are *trans*-isomers unless otherwise stated. Parameters have been corrected for the effect of solvent on X. Analysis has been based on data for NMe_2, OMe, Me, F, Cl, Br only. [b] W = H unless otherwise specified. [c] W = Bu^t. Measurements were made in CCl_4.[4,11] [d] *cis*-Isomer. Data for NMe_2 unavailable. [e] W = Me. Measurements were made in CCl_4.[4,11] [f] Data taken from ref. 8. [g] Data taken from ref. 6. [h] *cis*-Isomer. [i] Measurements were made in Me_2SO.[9] [j] Measurements were made in CCl_4.[10] [k] Based on data for the following *meta*-substituents: (H), Me, OMe, F, Cl, Br, CF_3, CN, NO_2.

the DSP equation never proposed that their fixed points were anything other than a reasonable approximation to a continuous range. That this is so can be seen by a careful examination of the ρ_I values listed in Table 2. The lowest f values are always associated with analyses for which $\rho_I \approx \rho^{meta}$. In those instances where substantial differences between the two exist, the natural conclusion is that we are operating in a region of the σ_R scale where none of the three parameters is truly applicable, even when the correlation, as judged by the f value alone, appears satisfactory. Series where significant differences between the two occur are the β,β-dimethylstyrenes, the stilbenes, the methyl cinnamates, the β,β-dicyanostyrenes, and the β-ethoxycarbonyl-β-methylsulphonylstyrenes. For all but the last two one would anticipate that intermediate σ_R scales would give an improved fit. For the latter some form of 'super' σ_R^+ scale would seem to be necessary for satisfactory correlations to be obtained.

The best fits are obtained using the σ_R^{BA} or σ_R^+ scale. Where it is the former, λ mostly has a value of *ca.* 1.2, while for the latter, one of *ca.* 0.9—1.0 would appear more typical. In their review,[13] Ehrenson *et al.* found that for reactivity data where correlations of the σ_R^{BA} type were observed, λ values were almost invariably less than unity, mostly lying in the 0.8—0.9 range. Values less than unity were also common for the σ_R^+ scale, although more widely scattered. In their analysis, unit λ values were associated with the ionization of benzoic acids in water and the solvolysis of aryldimethylcarbinyl chlorides in 90% acetone, respectively. It is possible that the differences may represent, at least in part, a solvent effect, as there is some evidence that, in the case of *para*-substituted styrenes, λ is higher in non-polar solvents such as $CDCl_3$ and CCl_4 than in hydroxylic ones.

Finally, with regard to Table 2, let us examine the relationship between the nature of the β-substituent and the form of correlation observed. Of the series under consideration, three have no β-substituent, seven have a single β-substituent bearing a *trans*-relationship to the aryl group, two a single *cis*-substituent, and four have two β-substituents. Electronically, most of the substituents are of $-I$ $-R$ type, but other types ($-I$ $+R$ and $+I$ $+R$) are also represented.

First let us consider the effect of a single β-substituent bearing a *trans*-relationship to the aryl group. Taking the results for the styrenes as the norm, the major factor that appears to influence the type of correlation obtained is the magnitude of the $-R$ effect of any attached group. Where this is small (Ph, σ_R^- $+0.04$)[13] or negligible (Br) the substituent has little effect. As it increases however, there is an increasing tendency towards a correlation of the σ_R^+ type. Where good σ_R^+ correlations are observed, series with the strongest $-R$ β-substituents appear to yield the highest λ values. Direct resonance interaction between $-R$ β-substituents and *para* $+R$ ring substituents is almost certainly responsible, but it is not obvious how the magnitude of such interactions are capable of influencing the election density at C_β as systematically as they do.

The inductive effect of the group attached to C_β apparently has little effect, as does any $+R$ effect; a substituent such as Br, which is a moderately strong inductive withdrawer and resonance donor, has little influence on either ρ_I or ρ_R. Furthermore, the effect of NO_2 or Ac on C_β is virtually identical even though the latter is a weak $-I$ group and the former a strong one. Of obviously much greater importance in the latter case is that their $-R$ effects are very similar in magnitude. Consideration of the results for the β-bromo- and β-cyano-styrenes would suggest that, provided the group is not too large, whether the substituent is *cis* or *trans* to the aromatic system is unimportant.

If we turn now to the cases where there are two β-substituents present, the situation becomes a little more complicated, since both electronic and steric factors may be involved. With regard to the first, there is obviously some tendency towards additivity. This is shown most clearly by comparing the results for the *cis*- and *trans*-β-cyanostyrenes with those for the β,β-dicyano-derivatives. There are signs of similar behaviour in the β-ethoxycarbonyl-β-methylsulphonyl derivatives, but here the situation is less clearcut, since the presence of two relatively bulky β-substituents can interfere with the coplanarity of the system as a whole. Solcaniova and her co-workers[14] have shown that in the β,β-diacetylstyrenes only one of two acetyl groups can be coplanar with the styrene system at a time; the combined $-R$ effect of the two groups as a consequence is about the same as one alone. For the β,β-dimethylstyrenes there may also be a small steric effect involved. In the absence of any, one would anticipate little difference from the parent styrenes, whereas there does appear to be a slight but real increase in tendency towards a $\sigma_R{}^\circ$ type correlation.

The result for the β,β-difluorostyrene series must be regarded as anomalous. Its actual position in the $\sigma_R{}^\circ \longrightarrow \sigma_R{}^{BA} \longrightarrow \sigma_R{}^+$ spectrum is in doubt, since, in spite of the relatively high f values obtained, all three correlations fit the data to within normal error limits. Our data for the β-bromostyrenes and the more limited data reported by Krabbenhoft[15] for the β,β-dichlorostyrenes would both predict that the introduction of two fluoro groups should have little overall effect. Instead, they have a very considerable one, especially on ρ_I for the system. It is likely that the very high combined $-I$ effect of the two fluorines is responsible for the observed result.

Lastly, there is the effect of an α-substituent. Little can be said as the data available are so limited. All that can really be examined is the effect of size, since the two groups involved are similar in all but this. The data show that while an α-methyl group has little effect, an α-t-butyl group has a considerable one. The natural conclusion is that the difference between the two series arises from interactions between the t-butyl group in the latter and the *o*-hydrogens of the aromatic ring. One would anticipate that this could have a considerable effect on ρ_R, and indeed it does. Less expected, however, is the effect on ρ_I, this being approximately halved in magnitude. This implies that extended polarization plays an important role in the relay of inductive effects to the β-carbon of styrenes. Such a suggestion is not new. The possibility that the relay of inductive effects to C_β by a combination of localized and extended polarization of the π-system has been discussed elsewhere, most recently by Reynolds.[16]

Correlations of Data for para $-$R *Substituents.*—In all of our series the side-chain must be regarded as amphielectronic in character, *i.e.* capable of interacting with both $+R$ and $-R$ *para*-ring substituents. Consequently, that interactions of *para* $+R$ substituents prove to require $\sigma_R{}^{BA}$ or $\sigma_R{}^+$ resonance parameters does not necessarily imply that, for the $-R$ ones, $\sigma_R{}^\circ$ values will apply, a pattern of behaviour the σ_R scales of the DSP equation assumes. It is possible to allow for such a situation very simply by broadening our choice of parameters to cover the $\sigma_R{}^\circ$–$\sigma_R{}^-$, $\sigma_R{}^{BA}$–$\sigma_R{}^-$, and $\sigma_R{}^+$–$\sigma_R{}^-$ combinations, but we were reluctant to take this step because parameters intermediate between $\sigma_R{}^\circ$ and $\sigma_R{}^-$ could have been involved. Instead, we used the ρ_I and ρ_R values derived using the $+R$ groups to evaluate σ_R values for our $-R$ ones, and examined these for constancy. For each series ρ_I and ρ_R for the scale giving the best $+R$ fit were used as a basis for our calculations. The resulting compilation of σ_R values is given in Table 3. The results are not entirely satisfactory, although there is a trend towards constancy in σ_R for all but the CF_3 substituent in a number of series. It is interesting to note that, in all of these, the fit of the $+R$ groups was particularly good, with $\rho_I \approx \rho^{meta}$. Those for which the fit was poorer, with ρ_I and ρ^{meta} differing substantially, yield rather different σ_R values for these substituents. A general observation that can be made is that if $\rho_I < \rho^{meta}$ (suggesting that the scale chosen for $+R$ groups used values more negative than they should have been), then the derived σ_R values for $-R$ groups are usually too high, while if the reverse is true, they are too low. The major exception to this generalization is the result for the β-acetylstyrenes. Here, ρ_I and ρ^{meta} are virtually identical, yet the derived σ_R values are closely similar to those for the β-methoxycarbonylstyrenes, both being higher than the others by *ca.* 30%. It may be that here the excellent agreement between ρ_I and ρ^{meta} is purely fortuitous, and that this is an instance where $\rho_I{}^{meta}$ is, in fact, significantly lower than $\rho_I{}^{para}$.

We believe that evidence for variations in σ_R with β-substituent in the case of $-R$ ring substituents is on the whole unconvincing. Where lower or higher than normal values are found, the ρ_I and ρ_R values used to obtain them may be considered suspect. This is not to say, however, that it does not occur in extreme cases. None of our series except the β,β-difluorostyrenes has a strong $+R$ substituent on the β-carbon, and, of those bearing strongly electron-withdrawing ones, any variations that might occur are difficult to establish in view of the problems in determining reliable values for ρ_I and ρ_R.

Finally, there is the problem of the CF_3 group. Examination of the results obtained using ρ_I and ρ_R values considered reliable suggests that this group apparently becomes significantly *more* electron withdrawing as the electron-withdrawing power of the β-substituent *increases*. That this actually occurs would seem highly improbable. The results, however, could be explained if this substituent were behaving purely as a $-I$ substituent and exerted no resonance effect whatsoever. Such an assumption requires that for CF_3, the influence of its inductive effect, unlike that for other substituents, be *ca.* 30% greater when it operates from the *para*-position than from the *meta*. The proposal is not new. The issue as to whether CF_3 is capable of exerting a $-R$ effect is a contentious one and is still unresolved.[17,18] Many workers believe that the observed differences between σ^{meta} and σ^{para} for this substituent can be adequately accounted for in terms of the mechanism of transmission of the inductive effect. Our results strongly suggest that, in our system, fluorine hyperconjugation is not involved. However, they do not support the favoured alternative transmission path (a π-inductive effect) anywhere near as strongly. While the magnitudes of the changes involved in the *meta*- and *para*-systems are about the same as those commonly observed in reactivity data, the relative contributions of π-inductive effects are believed to be rather different.[1]

Experimental

Preparation of Compounds.—The majority of compounds used in the study have been previously reported in the literature and were prepared by standard methods. New compounds were identified on the basis of their ^1H and ^{13}C n.m.r. spectra coupled with either microanalysis or high-resolution mass spectrometry.

^{13}C *N.m.r. Measurements*—The ^{13}C n.m.r. measurements were made on dilute (0.2M or less) solutions in $CDCl_3$ using a Varian CFT-20 spectrometer operating at normal probe temperature with tetramethylsilane as a reference.

Brief summaries of the methods used, including analytical data for previously unreported derivatives, are in Supplementary Publication No. SUP 56700 (19 pp.).*

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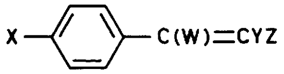
* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1988, Issue 1.

Table 3. Calculated σ_R values for $-R$ substituents in β-substituted styrenes[a]



	Y,Z[b]																
	σ_R^{o}[k]	σ_R^{-}[k]	Me,Me	H,Br[d]	H,H[e]	H,Ph[f]	H,H[g]	H,Br	H,CN	H,CO_2Me	H,CN[h]	H,$MeSO_2$	$MeSO_2$,CO_2Et	CN,CN[i,l]	H,NO_2	H,Ac	F,F[j]
Correlation			σ_R^{BA}	σ_R^{BA}	σ_R^{BA}	σ_R^{BA}	σ_R^{BA}	σ_R^{+}	σ_R^{+}	σ_R^{+}	σ_R^{+}	σ_R^{+}	σ_R^{+}	σ_R^{+}	σ_R^{+}	σ_R^{+}	σ_R^{+}
CF_3	0.03	0.15	0.23	0.19	0.15	0.15	0.16	0.15	0.22	0.28	0.21	0.19	0.09	0.04	0.17	0.24	0.16
CN	0.07	0.27	0.40	0.28	0.23	0.20	0.23	0.24	0.23	0.34	0.22	0.21	0.03	0.00	0.15	0.32	0.11
CO_2Me	0.15	0.34	0.40			0.24	0.30	0.29	0.28	0.42	0.26	0.31	0.18	0.16	0.26	0.38	
Ac	0.14	0.39			0.29	0.32	0.33		0.34	0.44	0.32					0.39	
NO_2	0.09	0.39	0.57	0.36	0.33	0.35	0.34	0.33	0.33	0.50	0.30	0.29	0.08	−0.02	0.20	0.45	0.19

[a] Values have been calculated using the ρ_I and ρ_R values listed in Table 2 that gave the best fit for $+R$ substituents. The results for the α-t-butylstyrenes have been omitted because of the very low contribution of resonance effects to the observed shifts. [b–j] See Table 2. [k] Estimated values in $CDCl_3$ solvent.[6] [l] Values for CF_3 and CO_2Me are based on measured SCS values of +3.43 and +2.56 p.p.m. for these substituents respectively.

Acknowledgements

We thank the Research Committee of the University Grants Committee for financial support.

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Received 17*th November* 1986; *Paper* 6/2209