^{13}C Nuclear Magnetic Resonance Chemical Shifts in Styrenes; Substituent and Solvent Effects

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The ^{13}C n.m.r. chemical shifts of a series of *meta*- and *para*-X-substituted styrenes (X = H, NMe_2, OMe, Me, F, Cl, Br, I, CF_3, CO_2Me, Ac, CN, NO_2, NMe_3^+) have been determined in seven different solvents (75% EtOH–D_2O, EtOH, Me_2SO, Me_2CO, $CDCl_3$, CCl_4, and C_6H_6). The data for the side-chain carbons and for the ring carbon *para*- to the substituent (C_6) in the *meta*-series have been analysed and used as a basis for assessing the effect of solvent on σ_I, $\sigma_R{}^0$, $\sigma_R{}^{BA}$, and $\sigma_R{}^-$.

In 1937 Hammett introduced the equation that now bears his name as an aid to systematising the reactions of *meta*- and *para*-substituted benzene derivatives.[1] While itself of relatively limited applicability, it provided the first quantitative scale of inductive and resonance effects, and many subsequent quantitative structure–reactivity relationships proposed amount simply to modifications and extensions aimed at enlarging the number and type of systems to which it can be applied.

The most widely used of these at the present time is that of Ehrenson *et al.*[2] This is based on the original equation of Hammett, expressing it in a more general form (1). This equation, usually referred to as the dual substituent parameter (or d.s.p.) equation, is obviously of greatest value in circumstances where ρ_I and ρ_R are significantly different (the Hammett equation assumes that they are the same), and has been widely used in the interpretation of substituent effects in systems where this is often the case, such as spectroscopic data.

$$\log \frac{k^X}{k^H}\left(\text{or } \log \frac{K^X}{K^H}\right) = \rho_I\sigma_I{}^X + \rho_R\sigma_R{}^X \qquad (1)$$

In common with a number of other groups, we have used the equation to examine substituent effects on ^{13}C n.m.r. chemical shifts. These shifts can be measured with a relatively high degree of accuracy and we have observed that differences between calculated and experimentally measured shifts are often greater than can be accounted for reasonably in terms of measurement errors. The problem therefore is to decide whether this is due to the use of inappropriate σ_I and σ_R parameters or to contributions from substituent effects other than inductive and resonance ones.

There are three reasons why the σ_I and σ_R values used might be incorrect. First, the original data on which they were based might have been unreliable. Measurement errors in equilibrium and rate data, the principal source of these values, are usually higher than those found in ^{13}C n.m.r. chemical shifts. Secondly, σ_I and σ_R for some substituents might be solvent dependent. The listed parameters were mostly derived from data obtained in either aqueous solution or aqueous–organic solvent mixtures. Solvents used for ^{13}C n.m.r. studies, on the other hand, are usually non-protic and frequently non-polar. Differences in solvent character could easily lead to differences in solvent–substituent interactions that could affect σ_I and σ_R. Finally, there is the problem of choice of σ_R scale. Ehrenson *et al.* recognised that σ_R was a continuous function but decided that this could be approximated by offering a choice of four discrete sets of values corresponding to the σ_R components of the four common σ^{para} scales (σ^0, σ, σ^+, and σ^-). It is generally accepted that in reactions of benzene derivatives there is a remarkable tendency for reactions to fall into one of these four classes, but this need not necessarily apply to systems of other types. Selection of the appropriate σ_R scale ($\sigma_R{}^0$, $\sigma_R{}^{BA}$, $\sigma_R{}^+$, $\sigma_R{}^-$) is based solely on best fit to the data, and limiting the choice to one of these in a case where none is appropriate could conceivably result in not only a poorer fit, but also incorrect values of ρ_I and ρ_R. This problem has been recognised and at least two attempts have been made to overcome it by expressing σ_R as a mathematical function.[3,4]

We had been investigating the effect of substituents on the ^{13}C n.m.r. chemical shifts of the β-carbons of styrene derivatives (the β-carbon is the more distant of the two alkenic carbons from the ring) and felt that in some cases the limited choice of σ_R scales was responsible for poor correlations. However, we also established that, for at least some substituents, σ_I and/or σ_R showed some degree of solvent dependence. We were primarily interested in resonance effects, but found that the contributions of inductive effects to the overall chemical shifts were sufficiently large for us to require a reliable scale of σ_I values in order that we could make allowance for these. The most commonly used scale of σ_I values is that proposed by Ehrenson *et al.* for use with the d.s.p. equation.[2] Although the method used to derive these was not specified, the values lie close to those proposed by Charton[5] based on reactions in protonic solvents, and are likely to be of similar origin. Most of our data were obtained in either deuteriochloroform or dimethyl sulphoxide, the majority of our compounds being insoluble in water or aqueous–organic solvents.

A set of σ_I and σ_R values appropriate for solvents such as ours would clearly be highly desirable. In addition to ourselves, two groups have made efforts to tackle the problem. In all cases the approach has been based on the use of n.m.r. chemical shift data rather than reactivity measurements.

The first attempt was that of Brownlee, Taft, and their coworkers,[6] and their intention was to set up a more reliable $\sigma_R{}^0$ scale. Their investigations had led them to believe that the ^{13}C n.m.r. chemical shifts of the *para*-ring carbons in monosubstituted benzenes obey the relationship (2) where SCS^X is the

$$SCS^X = \rho_I\sigma_I + \rho_R\sigma_R{}^0 \qquad (2)$$

change in chemical shift induced by the substituent X. Using σ_I values considered appropriate for hydrocarbon solvents, they determined $\sigma_R{}^0$ values for a number of substituents suitable for use with weakly interacting solvents such as carbon tetrachloride and cyclohexane. These σ_I and $\sigma_R{}^0$ parameters were assumed to apply to the other solvents used ($CDCl_3$, Me_2CO, Me_2SO, and DMF), and any effect of solvent was attributed entirely to changes in ρ_I and ρ_R. Their system tended to be dominated by resonance effects (ρ_R/ρ_I *ca.* 4—6) so any solvent dependence of σ_I might well be masked.

More recently Adcock[7] has constructed a series of σ_I scales applicable to seven different solvents (C_6H_{12}, CCl_4, $CDCl_3$, CH_2Cl_2, DMF, CH_3OH, and CF_3CO_2H) from the results of an investigation of the solvent dependence of the ^{19}F n.m.r. chemical shifts of a series of 1-X-4-(*p*-fluorophenyl)bicyclo-[2.2.2]octanes. In doing this he assumed that only inductive effects are involved, and that σ_I for the bromo substituent had the value +0.44 in all the solvents. Since the latter is the figure assumed by Ehrenson *et al.* for their σ_I scale,[2] the effect of solvent may be seen by comparing his values with theirs. The agreement varies from excellent to fair. Adcock did establish, however, that for some substituents σ_I was solvent dependent.

Like the other two groups we looked to n.m.r. chemical shifts as a probe for measuring substituent effects, and undertook an investigation of the effect of solvent on SCS for the ^{13}C n.m.r. chemical shifts for the β-carbon of a series of *meta*- and *para*-substituted styrenes.[8] Previous investigations[3,9] had led us to believe that these data could be well correlated by means of the Hammett equation, provided one assumed σ^{para} values intermediate between σ and σ^+. Such a study provided two series, one dominated by inductive effects (the *meta*) and one by resonance effects (the *para*). The only assumption made was that ρ^{meta} was equal to ρ^{para}. Solvent dependences of SCS were observed for many substituents, but these could not be resolved with certainty into individual dependences on σ and ρ. It was tentatively proposed that in the *meta*-series, changes in SCS reflected changes in σ_I rather than changes in ρ. Such a conclusion led to results that were inconsistent with one of the basic assumptions of the other two groups, that the σ_I values for halogeno substituents show little variation with solvent, since it predicted that these were *ca.* 20—30% lower in non-polar ones. In view of this conflict it was felt important that confirmation (or otherwise) be sought by investigating other systems. Our search for evidence, we feel, has been successful, but unfortunately, fails to support our findings. In most of the systems considered, substituent chemical shifts for halogeno-substituted compounds showed relatively small variations with solvent. Where variations were observed these seemed more compatible with changes in ρ_I than in σ_I.

In seeking suitable systems to study we were aided considerably by the publication by Brownlee and his co-workers of the results of a study on the effect of *meta*- and *para*-substituents on the ^{13}C n.m.r. chemical shifts of side-chain sp^2 carbons immediately adjacent to an aromatic ring.[10] The observed substituent effects appeared to result, in the main, from localized polarization of the side-chain π system, induced by the field effect of the substituent. This meant that the available, but unpublished, shift data for the α-carbons of the styrenes comprised two additional series that we could make immediate use of. D.s.p. analysis of the data confirmed that the inductive effects of ring substituents represented the dominant influences on the substituent chemical shifts, especially in the *para*-case, although values of f (= s.d./r.m.s.) were significantly higher than those observed for correlations of the β-carbon data. The most important feature, however, was a relative lack of variation in the SCS values of the halogeno substituents over the range of solvents used (see Table 7). This lack of variation was significant, because, whereas a pattern of variation different from that for the C_β data would be inconclusive, lack of variation over a series of solvents of such different types is strongly indicative of a solvent independence of σ_I for these groups.

Further support for this solvent independence of σ_I was subsequently provided by two studies commenced by us prior to Brownlee's report, and which involved the use of $-CH_2-$ groups to isolate the substituent from the aromatic ring. The first of these was an investigation of the ^{19}F n.m.r. chemical shifts for a number of *meta*- and *para*-XCH_2-substituted fluorobenzenes, the results of which have been published.[11] The effect of solvent was more pronounced than that observed in the styrene C_α data, but the pattern differed from that for C_β.

The second study was an investigation of the ^{13}C n.m.r. shifts of the *meta*- and *para*-XCH_2-substituted β-methoxycarbonylstyrenes. Here the original two series expanded to four as a result of Brownlee's investigations permitting the use of the C_α data also. Initial measurements, carried out in ethanol solvent, and subsequently published,[12] confirmed that for most substituents, the inductive effects of X dominated both C_α and C_β sufficiently to suggest that a solvent dependence study would yield useful information. This was undertaken, and the results, which we hope to report in detail at a later date, once again failed to show any evidence for a solvent dependence of σ_I for halogeno substituents of the form predicted by the styrene-C_β data.

All this does not, of course, require that they be solvent independent, but there seem to be enough instances where SCS values showed only small variations over the solvent range to make this probable and justify a re-interpretation of our original C_β data for the styrenes.

Along with this re-interpretation it was decided to increase the number of substituents covered from 8 to 13 by adding to the former series data for the NMe_2, OC_6H_5, I, CO_2Me, and COMe groups. In addition, data were obtained for the NMe_3^+ I^- derivatives in those solvents in which they were sufficiently soluble, in order to examine the validity of our earlier assumption that $\rho_I^{meta} \approx \rho_I^{para}$.

Results and Discussion

The shifts for the β-carbons of the side chains of our 12 new styrenes together with the 17 reported previously are listed in Table 1. Examination of those for the trimethylammonio derivatives in both 75% ethanol and dimethyl sulphoxide (the only solvents in which both isomers were soluble) reveals that, in these solvents at least, $\rho_I^{meta} \approx \rho_I^{para}$, and there is no reason to believe that this is not so for all. This means that by considering the differences between the shifts in the two series, contributions due to inductive effects can be eliminated. Consequently, if the effect of solvent on σ_R is negligible, plotting the differences in one solvent against the corresponding ones in any other should yield a straight line passing through the origin of the graph, the slope of which is a measure of the relative magnitudes of the ρ_R in the two solvents. Variations of σ_R with solvent result in displacements of points from the line, while non-zero intercepts would indicate that the assumption that $\rho_I^{meta} = \rho_I^{para}$ is invalid. Graphs in which the shift differences in the various solvents are plotted against the corresponding ones in ethanol are given in Figure 1. They show that σ_R for $+R$ substituents, with the exception of NMe_2, may be regarded as solvent independent over the range of solvents studied. For $-R$ substituents, however, if the values applying in 75% ethanol are to be regarded as 'normal' then lower than normal ones (by *ca.* 20% in $CDCl_3$, Me_2SO, Me_2CO and C_2H_5OH, and *ca.* 30% in CCl_4 and C_6H_6) apply in the other solvents. The lines through the $+R$ substituents in every case pass through or close to the origin, confirming that $\rho_I^{meta} \approx \rho_I^{para}$. Their slopes are all close to unity, implying that ρ_R is not markedly solvent dependent.

Determination of σ^{meta} Values.—The discovery that many substituents show negligible variation of σ_R with solvent is of considerable importance since there are now available a number of substituents (H, Me, F, Cl, Br) for which both σ_I and σ_R are invariant. For these σ^{meta} may therefore be regarded as solvent independent. These σ^{meta} values can be used to derive ρ^{meta} for each *meta*-series and hence σ^{meta} values for the other substituents in all solvents. The results of such a series of calculations are presented in Table 2.

Table 1. Positions of C_β resonances in *meta*- and *para*-X-substituted styrenes[a]

	meta-Series							*para*-Series						
X	75% EtOH	EtOH	Me_2SO	Me_2CO	$CDCl_3$	CCl_4	C_6H_6	75% EtOH	EtOH	Me_2SO	Me_2CO	$CDCl_3$	CCl_4	C_6H_6
H	113.83	113.62	114.10	113.99	113.76	113.22	113.61	113.83	113.62	114.10	113.99	113.76	113.22	113.61
NMe_2	−0.42	−0.65	−0.68	−0.76	−0.44	−0.68	−0.59	−4.08	−4.27	−5.03	−4.90	−4.44	−4.25	−4.38
OMe	0.46	0.22	0.31	0.24	0.28	0.12	0.24	−2.14	−2.31	−2.48	−2.44	−2.20	−2.18	−2.24
OPh	1.12	0.99	1.07	1.03	0.84	0.82	0.89	−0.59	−0.80	−0.86	−0.83	−0.92	−0.90	−0.88
Me	−0.18	−0.24	−0.23	−0.26	−0.20	−0.24	−0.22	−1.05	−1.03	−1.13	−1.08	−1.01	−1.02	−1.04
F	1.72	1.65	1.76	1.73	1.40	1.44	1.37	0.01	−0.11	−0.11	−0.04	−0.26	−0.17	−0.33
Cl	1.89	1.82	1.93	1.90	1.55	1.57	1.55	1.09	0.97	1.00	1.02	0.68	0.76	0.64
Br	1.97	1.90	1.91	1.95	1.61	1.67	1.51	1.21	1.09	1.07	1.05	0.78	0.86	0.69
I	1.81	1.78	1.62	1.80	1.51	1.53	1.46	1.35	1.19	1.03	1.21	0.93	0.94	0.87
CF_3	2.48	2.39	2.40	2.32	2.04	2.17	1.97	3.31	3.13	3.23	3.09	2.73	2.74	2.60
CO_2Me	1.81	1.67	1.54	1.57	1.34	1.28	1.34	3.39	3.14	3.12	2.95	2.68	2.45	2.52
$COCH_3$	1.85	1.73	1.44	1.46	1.50	1.45	1.31	3.58	3.31	3.05	2.96	2.93	2.74	2.59
CN	3.28	3.16	2.92	2.92	2.84	2.90	2.46	4.57	4.24	4.19	4.05	3.92	3.78	3.37
NO_2	3.69	3.56	3.41	3.50	3.31	3.32	2.87	5.43	5.11	5.22	5.08	4.79	4.54	4.18
$NMe_3^+I^-$	3.86	3.88	3.08	3.52	*b*	*b*	*b*	3.81	*b*	3.16	*b*	*b*	*b*	*b*

[a] The positions are given in the form of substituent chemical shifts (see text) except for X = H, for which values are given in p.p.m. downfield of tetramethylsilane. [b] Insoluble.

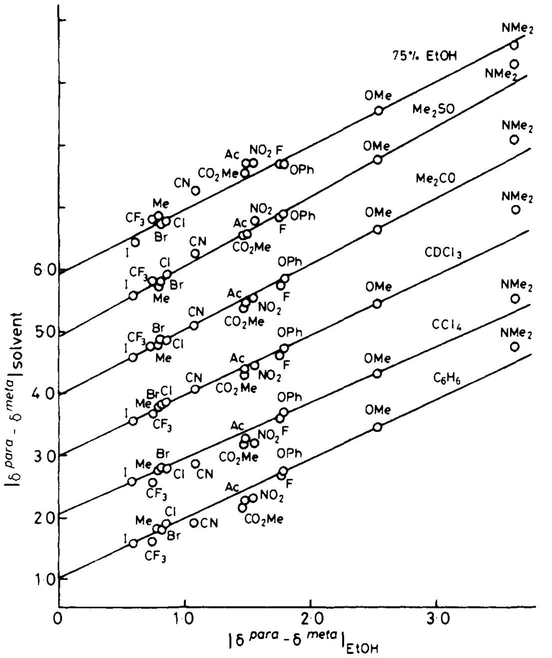

Figure 1. Effect of solvent on *meta*/*para* shift differences. Graphs are successively displaced by 1.00 p.p.m.

For many substituents variations in σ^{meta} are quite small and probably represent measurement errors. In other cases variations are substantial (> 0.03 units) and clearly represent real effects. In cases where the values for 75% ethanol–water differ significantly from the water-based literature ones we believe that real solvent effects may be involved, since for three of the substituents (OMe, CF_3, and CN) the chemical shifts of the corresponding alkenic carbon in cinnamate ions measured in aqueous solution are in better agreement with the literature σ^{meta} values than our 75% ethanol ones.[9]

The ρ^{meta} values listed in Table 2 have been calculated on the basis that ρ_I/ρ_R is not solvent dependent. This is not in fact true (see Table 6) but is a good enough approximation for no corrections to σ^{meta} values to be necessary.

The Solvent Dependence of σ_I *and* σ_R.—Any changes in σ^{meta} with solvent noted in Table 2 represent the combined effect of solvent on the inductive component (σ_I) and a resonance contribution. The latter is normally considered to represent a 'leakage' effect and to be of the $\sigma_R{}^0$ type.[2] Values of σ_I in any of the solvents can be easily determined therefore if we know (a) the value in any one solvent, and (b) the solvent dependence of $\sigma_R{}^0$. There is no way in which our data can be used to determine the first. It was therefore decided to assume, provisionally, that the σ_I scale of Ehrenson *et al.*[2] applied in 75% ethanol. The determination of the solvent dependence of $\sigma_R{}^0$ turned out to present a problem, in that it required some knowledge of the solvent dependence of σ_I. As a result of this interdependence it was found necessary for overall consistency to modify one or two of the 75% ethanol σ_I values used.

A careful examination of the *para*-shift data for 75% ethanol showed that for a d.s.p. analysis to yield a ρ_I value of 4.92, $+R$ substituents required a hypothetical scale of values slightly higher than $\sigma_R{}^{BA}$, while for $-R$ substituents a good fit could be obtained using $\sigma_R{}^-$. This meant that consideration of the *meta*/*para* shift differences could provide a reliable guide to the likely solvent dependence only for σ_R parameters of around these magnitudes. The lack of solvent dependence observed for the OMe, OPh, Me, F, Cl, Br, and I substituents suggests that $\sigma_R{}^{BA}$ for these is not solvent dependent and this probably applies to $\sigma_R{}^0$ as well. For the remainder the observed variations do not necessarily provide a reliable guide to the effect of solvent on their $\sigma_R{}^0$ values. In fact, as it turns out, they do not. It is possible to say this because additional data acquired during the investigation allow us to determine $\sigma_R{}^0$ for these substituents independently. The method is as follows.

It is generally accepted that the chemical shifts of *para*-ring carbons in monosubstituted benzenes can be satisfactorily correlated by the d.s.p. equation using the $\sigma_R{}^0$ scale.[6] While complications arise in the 1,4-disubstituted benzenes,[4] the presence of a constant *meta*-substituent should have no effect. Accordingly, the shifts for the ring carbons *para* to the substituents in the *meta*-substituted styrenes (C_6) provide us with sets of data that can be used to determine $\sigma_R{}^0$ values. These data are presented in Table 3. In analysing them we did not adopt the iterative method used by Brownlee and Taft,[6] because it was not only unnecessary, but led to incorrect parameters.

The analysis relies heavily on the results of the C_β study,

Table 2. Calculated σ^{meta} values based on the C_β shifts of *meta*-X-substituted styrenes[a]

X	Lit.[b]	75% EtOH	EtOH	Me_2SO	Me_2CO	$CDCl_3$	CCl_4	C_6H_6
NMe_2	−0.16	−0.10	−0.14	−0.14	−0.16	−0.11	−0.16	−0.15
OMe	0.11	0.08	0.04	0.05	0.04	0.06	0.03	0.06
OPh	0.25	0.22	0.20	0.20	0.20	0.20	0.19	0.22
Me	−0.06	−0.06	−0.05	−0.05	−0.06	−0.05	−0.06	−0.06
F	0.34	0.34	0.33	0.34	0.34	0.34	0.34	0.34
Cl	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.38
Br	0.39	0.39	0.39	0.37	0.38	0.39	0.39	0.37
I	0.35	0.36	0.36	0.31	0.35	0.36	0.36	0.36
CF_3	0.46	0.49	0.49	0.47	0.46	0.49	0.51	0.49
CO_2Me	0.38	0.36	0.34	0.30	0.31	0.32	0.30	0.33
Ac	0.38	0.36	0.35	0.28	0.29	0.36	0.34	0.32
CN	0.61	0.65	0.65	0.57	0.58	0.69	0.68	0.61
NO_2	0.74	0.74	0.73	0.69	0.69	0.80	0.78	0.71
$NMe_3^+I^-$	1.04	0.78	0.80	0.60	0.70			
ρ^{meta}		4.92	4.85	5.04	5.02	4.11	4.26	4.02

[a] Calculations are based on ρ values determined using the data for the H, Me, F, Cl, Br, and I substituents except for the case of Me_2SO, where the Br and I substituents have been omitted. [b] Values listed by Charton.[5]

Table 3. Positions of C_6 resonances in *meta*-X-substituted styrenes[a]

	SCS_{para}						
X	75% EtOH	EtOH	Me_2SO	Me_2CO	$CDCl_3$	CCl_4	C_6H_6
H	126.69	126.78	126.06	126.93	126.24	125.92	126.56
NMe_2	−10.40	−11.04	−12.02	−11.68	−11.37	−10.97	−11.24
OMe	−7.15	−7.39	−7.58	−7.46	−7.26	−7.35	−7.38
OPh	−4.61	−4.83	−4.74	−4.79	−4.87	−5.02	−4.93
Me	−2.79	−2.81	−2.82	−2.87	−2.87	−2.74	−2.78
F	−3.79	−3.94	−3.64	−3.75	−4.07	−4.15	−4.22
Cl	−1.46	−1.64	−1.33	−1.50	−1.77	−1.93	−2.00
Br	−1.02	−1.21	−1.02	−1.09	−1.33	−1.52	−1.62
I	−0.57	−0.68	−0.77	−0.66	−0.76	−0.86	−1.05
CF_3	3.48	3.21	3.53	3.38	3.19	2.94	2.72
CO_2Me	4.77	4.51	4.35	4.27	4.27	3.90	3.96
Ac	4.91	4.58	4.25	4.12	4.35	3.89	3.74
CN	5.13	4.91	4.59	4.93	4.87	4.70	4.38
NO_2	6.45	5.97	6.11	6.03	5.80	5.17	4.92
$NMe_3^+I^-$	4.97	4.68	4.06	4.30	*b*	*b*	*b*

[a] See Table 1 for layout. The C_6 carbon is the one *para* to the substituent. [b] Insoluble.

Table 4. The variation of σ_R with solvent

+*R* Substituents

The σ_R^0 and σ_R^{BA} values of OMe, OPh, Me, F, Cl, Br, and I show negligible variation with solvent

	NMe_2[a]							
	Lit.[b]	75% EtOH	EtOH	Me_2SO	Me_2CO	$CDCl_3$	CCl_4	C_6H_6
σ_R^0	−0.52	−0.56	−0.58	−0.60	−0.61	−0.64	−0.64	−0.61
σ_R^{BA}	−0.83	−0.83	−0.84	−0.90	−0.91	−0.97	−0.97	−0.91
−*R* Substituents[c]								
	σ_R^0							
CF_3	0.08	0.02	0.02	0.02	0.03	0.03	0.03	0.03
CO_2Me	0.14	0.13	0.13	0.12	0.13	0.15	0.13	0.14
Ac	0.16	0.15	0.14	0.13	0.13	0.14	0.12	0.13
CN	0.13	0.05	0.06	0.04	0.08	0.07	0.07	0.09
NO_2	0.15	0.10	0.10	0.09	0.10	0.09	0.08	0.10
	σ_R^-							
CF_3	0.17	0.18	0.15	0.16	0.14	0.15	0.14	0.13
CO_2Me	0.34	0.38	0.35	0.35	0.32	0.34	0.28	0.30
Ac	0.47	0.44	0.41	0.37	0.37	0.39	0.36	0.35
CN	0.33	0.32	0.26	0.29	0.27	0.27	0.23	0.23
NO_2	0.46	0.44	0.39	0.42	0.30	0.39	0.33	0.35

[a] No attempt has been made to estimate the solvent dependence of σ_R^+ for this substituent. [b] These are the values listed in ref. 2. Other values in the Table are not based on them as a starting point, but have been derived independently. [c] The values listed for σ_R^0 for CF_3, CN, and NO_2 may not be reliable (see text).

Table 5. Suggested σ_I values for substituents in various solvents[a]

X	Solvent Lit.[a]	75% EtOH	EtOH	Me_2SO	Me_2CO	$CDCl_3$	CCl_4	C_6H_6
NMe_2	0.06	0.15	0.12	0.11	0.11	0.18	0.13	0.12
OMe	0.27	0.27	0.23	0.24	0.23	0.25	0.22	0.25
OPh	0.38	0.35	0.33	0.33	0.33	0.33	0.32	0.35
Me	-0.04	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02
F	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Cl	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46
Br	0.44	0.44	0.44	0.42	0.44	0.44	0.44	0.42
I	0.39	0.39	0.39	0.34	0.39	0.39	0.39	0.39
CF_3	0.45	0.45	0.45	0.43	0.42	0.45	0.47	0.45
CO_2Me	0.30	0.30	0.28	0.24	0.25	0.26	0.24	0.27
Ac	0.28	0.28	0.27	0.20	0.21	0.28	0.26	0.24
CN	0.56	0.60	0.60	0.52	0.53	0.64	0.63	0.56
NO_2	0.65	0.65	0.64	0.60	0.60	0.71	0.69	0.62
$NMe_3^+I^-$		0.78	0.80	0.61	0.70			

[a] Taken from ref. 2.

which established that $\sigma_R{}^0$ for the OMe, OPh, Me, F, Cl, Br, and I groups were solvent independent, and, also *via* the σ^{meta} constants, good estimates of σ_I for these substituents. D.s.p. analyses of the C_6 data for these derivatives yielded values for ρ_I and ρ_R in each solvent, which were subsequently used to derive $\sigma_R{}^0$ values for the NMe_2, CF_3, CO_2Me, Ac, CN, and NO_2 substituents. In four of the solvents (75% EtOH, EtOH, Me_2SO, and Me_2CO) ρ_I values were also determined independently using the σ^{meta} ($= \sigma_I$) values for $NMe_3{}^+$ listed in Table 2. These ρ_I values agreed with the d.s.p. ones to within ±5%. Analysis of Brownlee and Taft's monosubstituted benzene data[6] by our method yielded $\sigma_R{}^0$ parameters virtually identical to those based on the C_6 shifts.

The $\sigma_R{}^0$ values obtained by the above method are found in Table 4. Only three (NMe_2, CO_2Me, and Ac) are in good agreement with the literature ones. The others are all *ca.* 0.05 units lower than expected. They are also inconsistent with other accepted σ values, including the σ^{meta} values listed in Table 2. There have been claims in the recent literature[13,14] that in favourable circumstances, groups such as these are capable of stablising electron-deficient centres, presumably by acting as π donors. In a previous investigation of β-nitrostyrenes, evidence was found for simultaneous $+R/-R$ behaviour for the cases of the C_6H_5, 3,4-(CH_4), and $C_6H_5N_2$ substituents,[9] but these are much more clearly amphielectronic. We are reluctant to accept π donation as an explanation for the discrepancies, since the effects are quite large, while the demand on the substituents are small.

For the NMe_2 group the effect of solvent on $\sigma_R{}^0$ is in good agreement with that predicted by the C_β shifts, but for the others, variations are much smaller than expected. It would appear, therefore, that the effect of solvent on $\sigma_R{}^-$ is proportionally greater than that on $\sigma_R{}^0$, and this suggests that the observed lack of variation of σ_R with solvent for the $+R$ substituents may not apply to their $\sigma_R{}^+$ values.

Our combined results lead to the conclusion that only in the case of the NMe_2 group is the effect of solvent on the resonance contribution to σ^{meta} likely to be significant, and this makes the task of assessing the effect of solvent on σ_I a relatively simple one. A proposed set of σ_I scales suitable for use in our seven solvents is given in Table 5. The approach to modifications of the base values of Ehrenson *et al.* has been a conservative one, these being modified only when it was felt that they were inconsistent with relationships between the other substituent parameters (both ours and those listed in the literature). In two instances (Ac, CO_2Me) the parameters were left unchanged because it was considered that literature σ^{meta} values had not been established with a sufficient degree of reliability. In general, variations in σ_I of 0.02 or less are probably not significant.

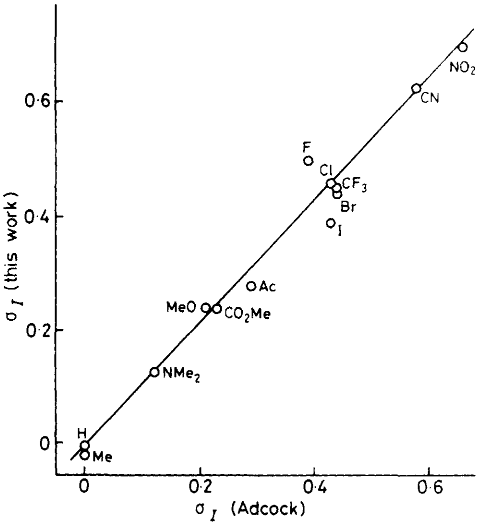

Figure 2. Comparison of $\sigma_I(CCl_4)$ values with those of Adcock[7]

The greatest effects of solvent on σ_I were observed, not unexpectedly, for the strongly dipolar substituents. A direct comparison of the values with those proposed by Adcock based on the ^{19}F chemical shifts of 1-X-4-(*p*-fluorophenyl)bicyclo-[2.2.2.]octanes[7] is only possible in CCl_4 and $CDCl_3$, although his results for dimethylformamide and methanol should be similar to ours for Me_2SO and 75% ethanol, respectively. The results for CCl_4 solvent are compared in Figure 2. Comparisons in the other solvents show a very similar pattern, suggesting that discrepancies are not reflecting variations in the effect of solvent on σ_I, but rather, different basic σ_I values. Since the halogeno substituents are among those for which this is the case, Adcock's choice of bromo as a standard must be regarded as unfortunate.

The Solvent Dependence of ρ_I *and* ρ_R.—The various ρ_I and ρ_R parameters for C_6 and C_β obtained as a by-product of our analysis of substituent effects are listed in Table 6. The falloff in ρ_I is considerably less than the predicted falloff in the strength of the inductive (field) effect. It is scarcely legitimate to compare the two sets of values, however, since the environments of the two carbons are not the same. If one assumes that, for C_β,

Table 6. The solvent dependence of ρ_I and ρ_R[a]

	75% EtOH	EtOH	Me_2SO	Me_2CO	$CDCl_3$	CCl_4	C_6H_6
$\rho_I(C_\beta)$[b]	4.92(1.00)	4.85(0.99)	5.07(1.03)	5.02(1.02)	4.11(0.84)	4.26(0.87)	4.02(0.82)
$\rho_I(C_6)$[c]	6.75(1.00)	6.03(0.89)	7.16(1.04)	6.46(0.96)	5.50(0.82)	5.20(0.77)	4.87(0.72)
$\rho_I(C_{para})$[d]			7.70	7.17	5.61	5.31	
$\rho_R(C_\beta)$	(1.00)	(1.00)	(1.06)	(1.03)	(0.91)	(0.93)	(0.90)
$\rho_R(C_6)$[c]	20.45(1.00)	20.21(0.99)	21.11(1.03)	20.44(1.00)	19.57(0.96)	19.71(0.96)	19.39(0.95)
$\rho_R(C_{para})$[d]			22.35	22.10	20.73	20.72	

[a] Numbers in parentheses are values relative to those for 75% ethanol. Unless otherwise stated correlations were based on $+R$ substituents only (excluding NMe_2). [b] These represent ρ^{meta} values. See footnote to Table 2 for substituents used. [c] The C_6 carbon is the one *para* to the substituent in the *meta*-substituted styrenes. [d] The C_{para} carbon is the one *para* to the substituent in the monosubstituted benzenes. The same series of substituents were used as for the other correlations. The data were taken from ref. 6.

Table 7. Positions of C_α resonances in *meta*- and *para*-X-substituted styrenes[a]

	meta-Series							*para*-Series						
X	75%EtOH	EtOH	Me_2SO	Me_2CO	$CDCl_3$	CCl_4	C_6H_6	75% EtOH	EtOH	Me_2SO	Me_2CO	$CDCl_3$	CCl_4	C_6H_6
H	137.62	137.81	136.64	136.80	136.96	136.85	137.37	137.62	137.81	136.64	137.80	136.95	136.85	137.37
NMe_2	0.77	0.88	0.91	1.01	0.77	0.94	1.12	−0.07	−0.05	−0.10	−0.07	−0.36	−0.29	0.00
OMe	−0.08	−0.05	−0.14	−0.01	−0.07	−0.09	−0.02	−0.61	−0.69	−0.55	−0.59	−0.67	−0.68	−0.56
OPh	−0.65	−0.60	−0.67	−0.61	−0.64	−0.62	−0.74	−0.90	−0.87	−0.92	−0.88	−0.92	−0.87	−0.91
Me	0.11	0.11	0.09	0.07	0.06	0.09	0.13	−0.13	−0.18	−0.18	−0.15	−0.20	−0.19	−0.12
F	−1.18	−1.12	−1.12	−1.13	−1.09	−1.02	−1.32	−1.22	−1.27	−1.23	−1.25	−1.20	−1.25	−1.36
Cl	−1.35	−1.36	−1.37	−1.42	−1.30	−1.30	−1.58	−1.31	−1.31	−1.27	−1.30	−1.22	−1.25	−1.40
Br	−1.45	−1.44	−1.47	−1.47	−1.40	−1.41	−1.65	−1.26	−1.26	−1.27	−1.23	−1.14	−1.17	−1.34
I	−1.53	−1.52	−1.55	−1.54	−1.53	−1.54	−1.74	−1.10	−1.11	−1.10	−1.11	−1.14	−1.11	−1.24
CF_3	−1.42	−1.40	−1.40	−1.43	−1.23	−1.36	−1.68	−1.40	−1.41	−1.31	−1.43	−1.29	−1.30	−1.57
CO_2Me	−0.94	−1.01	−1.01	−0.92	−1.01	−0.88	−1.11	−1.02	−0.97	−1.00	−0.89	−0.87	−0.81	−1.04
$COCH_3$	−0.99	−0.92	−0.82	−0.77	−0.95	−0.84	−0.99	−1.04	−0.97	−0.94	−0.91	−1.02	−0.89	−1.04
CN	−2.14	−2.14	−2.00	−2.01	−2.05	−2.03	−2.37	−1.56	−1.59	−1.42	−1.47	−1.51	−1.50	−1.78
NO_2	−2.16	−2.11	−1.95	−1.99	−2.16	−2.14	−2.50	−1.98	−1.89	−1.75	−1.82	−1.92	−1.91	−2.23
$NMe_3^+I^-$	−1.82	−1.81	−1.63	−1.74	*b*	*b*	*b*	−2.17	*b*	−2.04	*b*	*b*	*b*	*b*

[a] See footnote to Table 1 for layout of Table. [b] Insoluble.

localized polarization of the ethenyl group is the major contributor to the observed shifts, then one may conclude that the ethenyl π system is more polarizable than an aromatic one. The effect of solvent on ρ_I for the two carbons is very similar, and may be taken as evidence that the mode of operation of the inductive effect is the same in both cases.

Comparison of ρ_R values for the two carbons is hampered by our not being able to assign values for C_β unequivocally. There are, as was mentioned earlier, indications that $\rho_I \approx \rho_R$ for the *para*-series. On this basis ρ_R for C_6 is considerably greater than that for C_β (by a factor of 4—5). The difference between the two is not a good guide to differences in the extent of resonance interaction, since different σ_R parameters apply in the two cases. The effect of solvent on ρ_R is very similar to that on ρ_I, but less marked. Such a similarity would suggest that the π system plays a key role in the relay of both inductive and resonance effects. For this to be consistent with the inductive effect being a field effect, the lines of force must pass through the molecule itself rather than through the solvent.

Substituent Effects on the C_α *Shifts*.—The chemical shifts for the α carbons of our two series of styrenes, in all solvents, are given in Table 7. The most striking feature is the relative lack of variation of shift with solvent. Only in benzene, in which shifts are *ca.* 15% higher than for the others, can any effect of solvent on the efficiency of transmission of substituent effects be considered significant. D.s.p. analyses of the data show that inductive effects are a dominant influence on the shifts, particularly in the *para*-series, where λ ($= \rho_R/\rho_I$) < 0.1. Just as with the correlations of the C_6 and C_β data, the shifts for the NMe_3^+ derivatives can be used as a check on the validity of the d.s.p. analysis. For the *para*-series, the analysis yields ρ_I values that, in the two cases where this can be checked, are very similar to those obtained using the NMe_3^+ shift data. The actual resonance contributions are invariably small, but clearly upfield for $-R$ substituents and downfield for $+R$, making ρ_R, like ρ_I, negative in sign. They parallel quite closely, although in attenuated form, the resonance contributions to the C_β shifts, which would suggest that they are a consequence of the normal resonance interaction existing between the latter and *para*-substituents.

For the *meta*-series we have much less confidence in the results of the d.s.p. analyses. The fit to the data is poorer than that for the *para*-series and the ρ_I values obtained (*ca.* −3.3) are substantially different from those obtained using the NMe_3^+ data (*ca.* −2.5). If the latter value is correct, then the resonance contributions for several of the substituents are inconsistent with their expected character. On the other hand if it is incorrect, then the C_α shifts must be subject to proximity effects from *meta*-substituents, which invalidates any d.s.p. analysis for this series.

Because of the uncertainty of fit, d.s.p. analysis of the C_α data does not provide a particularly useful check on the validity of our proposed σ_I and σ_R parameters. However, if instead the effects of solvent on the shifts themselves is examined carefully, and the assumption made that inductive effects are a dominant influence, then the variations observed are, in almost all cases, at least in the same direction as would be predicted on the basis of the proposed changes in σ_I.

Experimental

Preparation of Compounds.—Many of the styrenes were commercially available. Those that were not were synthesised by standard methods. The only new compound was the *m*-NMe_3^+ derivative, which was prepared by reaction of *m*-dimethylaminostyrene with a solution of methyl iodide in benzene as crystals, m.p. 137 °C (Found: C, 44.8; H, 5.7; N, 4.7. $C_{12}H_{16}IN$ requires C, 45.7; H, 5.6; N, 4.8%). The ^{13}C n.m.r. spectrum was consistent with the proposed structure.

^{13}C *N.m.r. Measurements.*—The conditions have been described previously.[8] The measured shifts could normally be reproduced to within ±0.05 p.p.m.

Acknowledgements

I am grateful to the Research Committee of the New Zealand University Grants Committee for financial support.

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Received 19*th December* 1983; *Paper* 3/2229