The Investigation of π Polarization Effects in Stilbazoles, Stilbazole Methiodides, and Styrylfurans by ^{13}C NMR Spectroscopy

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The ^{13}C NMR chemical shifts of the heterocyclic ring carbons of a number of 2-, 3-, and 4-(2-arylvinyl)pyridines, their methiodides, and 2- and 3-(2-arylvinyl)furans have been measured. The values obtained are compared with those for stilbenes, and show that ring size has a far greater influence on field-induced π polarization than the presence of a highly electronegative hetero atom. There is clear evidence for localization of the π bonds in the 5-membered, but none in the six-membered rings.

The means by which the polar effect of a substituent influences the electron density at another part of the molecule has long been of interest to physical organic chemists.[1–4] It is generally recognized that there are two main ways by which the effect may be relayed. These are commonly referred to as the *field* and the *inductive* mechanisms. The field mechanism attributes the effect of a polar substituent at other points in the molecule to the electrostatic field generated by the substituent dipole (most substituents are dipolar in nature). In theory, therefore, it represents a 'through space' interaction. In practice however, the term 'through space' may be misleading, as the lines of force will mostly pass through the medium of lowest relative permittivity, and for a non-polar molecule dissolved in a relatively polar solvent, this would normally be the molecular framework.

The inductive effect, on the other hand, while its origin also lies in the electronegativity of the substituent, is relayed through the molecule by successive polarization of the constituent bonds of the molecular framework. It is currently widely accepted that, except for those cases where the substituent and the probe site are directly linked, the field mechanism is by far the more important of the two.[1]

Early investigations of polar effects were based on studies of chemical equilibria or rates of reactions.[5–7] For both of these, relatively strong electrostatic interactions between the substituent dipole and the reaction site usually exist. Recently, however, many studies of the operation of polar effects have involved the effect of substituents on NMR chemical shifts. These differ in one important way—the 'reaction-site', or, more correctly, the probe site, is rarely strongly dipolar, and so the influence of the substituent is one of change in electron density arising from the polarization of electron systems in the vicinity, rather than one of direct interaction.

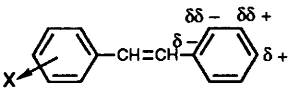
The response of such systems to the generated field will depend very much on the ease with which they undergo such polarization, and, in this respect, those involving π electrons are much more susceptible. This greater sensitivity has, not surprisingly, resulted in their receiving the most attention. Also for reasons of the sensitivity of response, most investigations have utilised either ^{19}F or ^{13}C chemical shifts as probes. Of these, the latter are the more generally useful, as they permit the investigation of the effect of a substituent on more than one site in the molecule simultaneously.

The influence of the polar effect of a substituent on the ^{13}C NMR chemical shifts of a π system isolated from it by a rigid, saturated framework was investigated by Adcock and co-workers.[8] The results were consistent with the field-induced π polarization model. There have also been investigations involving systems where the two are not isolated in this way, but are linked to one another by an extended π system. The most thoroughly investigated examples falling into this category are the mono-[9] and 1,4-di-substituted benzenes,[10] and benzene derivatives bearing unsaturated side chains.[11] In these, the polar effect is in a position to influence electron densities not only by polarization of the π system under study (direct polarization), but also by polarization of the entire system as a single unit (extended polarization). The most thoroughly investigated system of the latter type is the styrene one. For this, Reynolds has estimated that, in the case of the terminal vinyl carbon (C-β), about three-quarters of any change in ^{13}C chemical shift due to the polar effect of a *meta* or *para* ring substituent arises from extended polarization, and only one quarter from direct polarization of the vinyl group.[12]

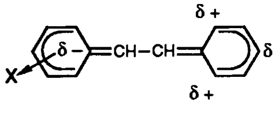
This result was surprising, as the results obtained by Adcock for the ^{13}C shifts of the phenyl ring carbons of a series of 1-*X*-4-phenyl[2.2.2.]bicyclo-octanes,[8] when compared with those for the corresponding biphenyls, suggested that, in the latter, the two effects are of comparable importance. Reynolds has proposed that the difference may be accounted for either by the greater polarizability of phenyl than vinyl, or the known lack of coplanarity of the two phenyl rings in biphenyls.[1]

Some time ago we reported the results of an investigation into the effect of substituents on the ^{13}C NMR chemical shifts in stilbenes.[13] The stilbene system is one that presents elements in common with both the styrenes and the biphenyls. It may be viewed either as a β-substituted styrene, or as a vinyl-bridged biphenyl. Considered from the former point of view, a relatively non-polar β-substituent such as phenyl would not be expected to have a major effect on ring-substituent induced changes in the chemical shift at either C-α or C-β. However, the β-phenyl substituent is capable of forming part of an extended π system involving the entire molecule; consequently, any field-induced polarization by the extended π polarization mechanism could well exert a levelling effect on the shifts at C-β. There does, indeed, turn out to be one, but it is quite small (< 10%). (Interestingly, greater changes are observed for C-α, which becomes about 20% more sensitive to polar effects).

If the system is viewed as a vinyl-bridged biphenyl, then we are concerned with substituent-induced polarization, not of the vinyl group, but of the β-phenyl. Direct and extended π polarization would give rise to different charge distributions for this ring; as shown schematically here. The overall pattern that



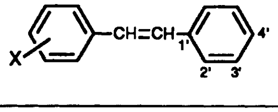
direct π polarization



extended π polarization

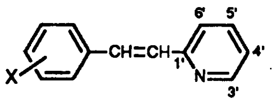
Table 1. ^{13}C NMR chemical shifts for side-chain ring carbons of 3- and 4-substituted stilbenes, stilbazoles, stilbazole methiodides, and styrylfurans.[a,b,c]

(a)



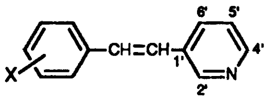
	meta series				*para* series			
	C-1′	C-2′	C-3′	C-4′	C-1′	C-2′	C-3′	C-4′
H	137.33	126.50	128.66*	127.60	137.33	126.50	128.66*	127.60
NMe$_2$					0.83	−0.48	−0.09	−0.97
OMe	−0.12	0.03	0.00	0.06	0.32	−0.26	−0.04	−0.40
Me	0.11	−0.04	0.00	−0.07	0.19*	−0.11	−0.01	−0.20
F	−0.50	0.14	0.07	0.39	−0.15	−0.06	0.05	0.07
Cl	−0.52	0.14	0.08	0.43	−0.34	0.05	0.07	0.27
Br	−0.55	0.14	0.08	0.44	−0.38	0.05	0.07	0.29
CF$_3$	−0.63	0.20	0.13	0.58	−0.70	0.26	0.18	0.68
CO$_2$Et					−0.55	0.27	0.11	0.61
CN	−0.97	0.28	0.17	0.84	−1.05	0.35	0.18	1.02
NO$_2$	−1.07	0.32	0.18	0.91	−1.16	0.51	0.22	1.23
ρ^{meta}	−1.37	0.41	0.23	1.18				
f	0.05	0.06	0.28	0.05				

(b)



	meta series					*para* series				
	C-1′	C-3′	C-4′	C-5′	C-6′	C-1′	C-3′	C-4′	C-5′	C-6′
H	155.47	149.50	121.96*	136.42	121.96*	155.47	149.50	121.96*	136.42	121.96*
NMe$_2$						0.93	−0.17	−0.97	−0.19	−0.70
OMe	−0.14	0.00	0.00*	0.09	0.00*	0.36	−0.07	−0.39	−0.05	−0.30
Me	0.10	−0.05	−0.07*	0.03	−0.07*	0.23	−0.02	−0.21	−0.05	−0.14
F	−0.50	0.11	0.34*	0.10	0.34*	−0.17	0.03	0.05*	0.06	0.05*
Cl	−0.54	0.12	0.37*	0.11	0.37*	−0.33	0.10	0.22*	0.07	0.22*
Br	−0.56	0.12	0.38*	0.10	0.38*	−0.39	0.10	0.24*	0.07	0.24*
CF$_3$	−0.67	0.15	0.52	0.19	0.45	−0.73	0.18	0.58	0.14	0.55
CO$_2$Me						−0.62	0.14	0.52*	0.15	0.52*
CN	−1.06	0.19	0.71*	0.19	0.71*	−1.12	0.24	0.85*	0.23	0.85
NO$_2$	−1.13	0.20	0.80*	0.26	0.80*	−1.24	0.29	1.01	0.25	0.89
ρ^{meta}	−1.45	0.24	1.01	0.26	1.00					
f	0.10	0.15	0.06	0.23	0.07					

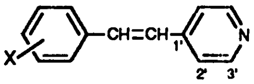
(c)



	meta series					*para* series				
	C-1′	C-2′	C-4′	C-5′	C-6′	C-1′	C-2′	C-4′	C-5′	C-6′
H	132.89	148.39*	148.39*	123.43	132.52	132.89	148.39*	148.39*	123.43	132.52
NMe$_2$						0.99	−0.32	−0.91	0.00	−0.48
OMe	−0.07	0.03*	0.03*	0.03	0.09	0.33	−0.21	−0.39	−0.03	−0.26
Me	−0.11	−0.01	−0.16	−0.02	−0.02	*d*	−0.10	−0.22	0.00	−0.09
F	−0.44	0.08	0.36	0.07	0.22	−0.16	−0.08	0.05	0.02	−0.02
Cl	−0.54	0.06	0.40	0.02	0.16	−0.30*	0.02	0.24	0.04	0.07*
Br	−0.60	0.06	0.38	0.00	0.14	−0.44	0.02	0.26	0.05	0.09
CF$_3$	−0.61	0.13	0.55	0.10	0.25	−0.68	0.19	0.64	0.10	0.29
CO$_2$Me						−0.55	0.21	0.56	0.08	0.27
CN	−0.94	0.15	0.76	0.11	0.32	−0.99	0.27	0.91	0.13	0.41
NO$_2$	−0.96	0.22	0.88	0.18	0.44	−1.08	0.35	1.07	0.17	0.49
ρ^{meta}	−1.30	0.25	1.17	0.19	0.48					
f	0.09	0.19	0.06	0.38	0.16					

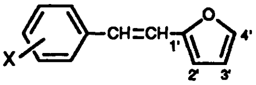
Table 1 (*continued*)

(*d*)



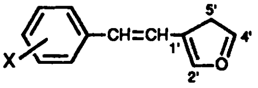
	meta series			*para* series		
	C-1′	C-2′	C-3′	C-1′	C-2′	C-3′
H	144.90	120.91	149.85	144.90	120.91	149.85
NMe_2				1.10	−0.38	−0.35
OMe	−0.16	0.00	0.07	0.68	*e*	−0.49
Me	−0.02	−0.04	0.08	0.03	−0.16	0.13
F	−0.60	0.05	0.18	−0.24	−0.10	0.12
Cl	−0.59	0.05	0.16	−0.30	0.01	−0.01
Br	−0.63	0.05	0.17	−0.22	0.06	−0.10
CF_3	−0.60	0.13	0.10	−0.85	0.13	0.30
CO_2Me				−0.77	0.09	0.30
CN	−1.20	0.08	0.37	−1.30	0.16	0.40
NO_2	−1.24	0.16	0.37	−1.37	0.23	0.42
ρ^{meta}	−1.50	0.20	0.39			
f	0.11	0.34	0.27			

(*e*)



	meta series				*para* series			
	C-1′	C-2′	C-3′	C-4′	C-1′	C-2′	C-3′	C-4′
H	153.28	108.51	116.62	142.09	153.28	108.51	111.62	142.09
NMe_2					0.83	−1.87	−0.15	−0.79
OMe	−0.03	0.16	0.02	0.08	0.32	−0.86	−0.06	−0.36
Me	0.07	−0.17	−0.06	−0.06	−0.44	−1.06	−0.20	−0.20
F	−0.48	0.84	0.13	0.42	−0.16	0.03	0.01	0.04
Cl	−0.50	0.88	0.10	0.41	−0.34	0.49	0.06	0.25
Br	−0.50	0.91	0.09	0.42	−0.36	0.57	0.09	0.28
CF_3	−0.55	1.17	0.24	0.57	−0.56	1.44	0.23	0.69
CO_2Me					−0.37	1.40	0.23	0.69
CN	−0.91	1.70	0.18	0.78	−0.87	2.25	0.40	1.07
NO_2	−0.96	1.92	0.29	0.91	−0.95	2.72	0.47	1.26
ρ^{meta}	−1.26	2.44	0.36	1.13				
f	0.07	0.03	0.24	0.03				

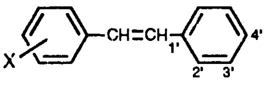
(*f*)



	meta series				*para* series			
	C-1′	C-2′	C-3′	C-4′	C-1′	C-2′	C-3′	C-4′
H	124.47	140.82	143.58	107.34	124.47	140.82	143.58	107.34
NMe_2					0.60*	−0.90	−0.15	0.07
OMe	−0.08	0.09	0.02	0.00	0.17	−0.49	−0.10	−0.02
Me	0.06	0.03	0.08	0.06	0.12	−0.29	−0.06	0.01
F	−0.33	0.43	0.16	−0.08	−0.14	−0.05	0.05	−0.08
Cl	−0.33	0.47	0.18	−0.09	−0.22	0.24	0.12	−0.09
Br	−0.34	0.49	0.18	−0.10	−0.23	0.27	0.13	−0.10
CF_3	−0.40	0.61	0.25	−0.11	−0.38	0.77	0.28	−0.12
CO_2Me					−0.26	0.77	0.25	−0.10
CN	−0.63	0.86	0.32	−0.20	−0.56	1.17	0.40	−0.20
NO_2	−0.67	1.00	0.37	−0.19	−0.54	1.47	0.50	−0.21
ρ^{meta}	−0.86	1.19	0.41	−0.29				
f	0.06	0.04	0.14	0.14				

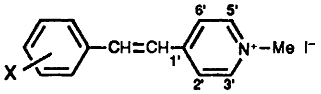
Table 1 (*continued*)

(*g*)



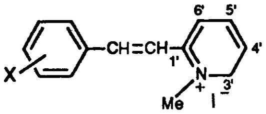
	meta series				*para* series			
	C-1′	C-2′	C-3′	C-4′	C-1′	C-2′	C-3′	C-4′
H	137.00	126.47	128.69	127.64	137.00	126.47	128.69	127.64
NMe_2					0.81	−0.68	−0.11	−1.07
OMe	−0.04	0.02	0.00	0.03	0.35	−0.33	−0.05	−0.49
Me	0.05	−0.05	−0.01	−0.06	0.14	−0.15	−0.03	−0.17
F	−0.36	0.17	0.04	0.34	−0.06	−0.05	0.00	−0.01
Cl	−0.33	0.20	0.04	0.37	−0.25	0.08	0.01	0.20
Br	−0.37	0.19	0.03	0.36	−0.26	0.09	0.02	0.22
CF_3	−0.39	0.26	0.06	0.47	−0.54	0.37	0.07	0.63
CO_2Et					−0.45	0.37	0.08	0.60
CN	−0.52	0.28	0.09	0.58	−0.66	0.48	0.10	0.82
NO_2	−0.59	0.38	0.08	0.66	−0.73	0.65	0.15	1.05
ρ^{meta}	−0.88	0.55	0.13	0.99				
f	0.09	0.05	0.20	0.03				

(*h*)



	meta series			*para* series		
	C-1′	C-2′	C-3′	C-1′	C-2′	C-3′
H	152.39	123.56	145.10	152.39	123.56	145.10
NMe_2				0.94	−1.47	−0.80
OMe	−0.04	−0.02[b]	0.01	0.44	−0.56	−0.27
Me	0.05	−0.07	−0.03	0.19	−0.21	−0.11
F	−0.41	0.20	0.16	−0.04	−0.06	0.01
Cl	−0.42	0.21	0.18	−0.24	0.10	0.09
Br	−0.42	0.20	0.17	−0.27	0.11*	0.09
CF_3	−0.45	0.28	0.25	−0.61	0.44	0.25
CO_2Me				−0.56	0.39	0.20
CN	−0.65	0.33	0.28	−0.81	0.51	0.29
NO_2	−0.67	0.39	0.29	−0.85	0.64	0.31
ρ^{meta}	−1.04	0.62	0.47			
f	0.09	0.07	0.10			

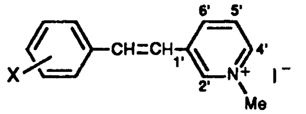
(*i*)



	meta series					*para* series				
	C-1′	C-3′	C-4′	C-5′	C-6′	C-1′	C-3′	C-4′	C-5′	C-6′
H	152.30	144.34	125.21	146.06	125.00	152.30	144.34	125.21	146.06	125.00
NMe_2						0.93	−1.26	−2.20	−0.77	−1.44
OMe	−0.03	0.00	0.03	0.02	0.01	0.42	−0.40	−0.74	−0.25	−0.57
Me	0.06	−0.03	−0.07	−0.02	−0.08	0.17	−0.17	−0.30	−0.11	−0.25
F	−0.34	0.18	0.37	0.23	0.15	−0.01	0.02	−0.01	0.05	−0.10
Cl	−0.35	0.17	0.38	0.20	0.15	−0.20	0.07	0.18	0.12	0.04
Br	−0.33	0.18	0.38	0.22	0.15	−0.19	0.08	0.20	0.13	0.05
CF_3	−0.33	0.27	0.51	0.28	0.25	−0.50	0.31	0.59	0.32	0.39
CO_2Me										
CN	−0.48	0.31	0.60	0.34	0.23	−0.66	0.33	0.76	0.39	0.43
NO_2	−0.49	0.35	0.68	0.36	0.36	−0.77	0.40	0.89	0.45	0.53
ρ^{meta}	−0.81	0.52	1.05	0.56	0.52					
f	0.14	0.09	0.04	0.11	0.13					

Table 1 (*continued*)

(*j*)



	meta series					*para* series				
	C-1′	C-3′	C-4′	C-5′	C-6′	C-1′	C-3′	C-4′	C-5′	C-6′
H	137.06	143.19[b]	143.19[b]	127.51	140.92	137.06	143.19[b]	143.19[b]	127.51	140.92
NMe_2						1.17	−0.86	−1.45	−0.13	−1.20
OMe	−0.12	0.00[b]	0.00[b]	0.01	−0.01	0.48	−0.37	−0.58	−0.05	−0.51
Me	0.05	0.00	−0.04	0.01	−0.05	0.21	−0.14	−0.25	−0.03	−0.20
F	−0.39	0.17	0.36	0.07	0.21	−0.04	−0.03	−0.03[b]	0.00	−0.07
Cl	−0.41	0.16	0.36	0.07	0.18	−0.22	0.10	0.17	0.03	0.08
Br	−0.40	0.18	0.35	0.07	0.18	−0.23	0.11	0.18	0.03	0.09
CF_3	−0.40*	0.22	0.45	0.10	0.21	−0.60	0.40	0.56	0.06	0.40
CO_2Me						−0.50	0.37	0.50	0.07	0.38
CN	−0.62	0.25	0.48	0.11	0.32	−0.74	0.59	0.92	0.32	0.50
NO_2	−0.63	0.40	0.65	0.13	0.33	−0.84	0.61	0.83	0.11	0.59
ρ^{meta}	−0.90	0.51	0.94	0.18	0.53					
f	0.11	0.14	0.07	0.10	0.11					

[a] The positions of the resonances are expressed in the form of substituent chemical shifts, except for the parent compound in each series, 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 compound.] [b] Unless otherwise indicated, the solvent used is deuteriochloroform. [c] Shifts for carbons that overlap with those for other carbons in the molecule are indicated by an asterisk. Such shifts are less reliable than others. [d] Not observed. [e] The resonance for this carbon was broad and weak. The actual shift position could not be determined reliably. [f] Spectra were obtained in dimethyl sulphoxide solvent.

resulted would reflect the relative contributions of each of these, and some idea of their relative importance could possibly be gained by consideration of trends in the shifts of the *ortho* carbons.

Reynold's studies of substituent effects in α-substituted styrenes[12,14] suggested that, in potentially planar systems, extended polarization has a built in advantage. There is little doubt that the stilbene system is coplanar, or at least spends a good deal of its time in this state—DSP analysis of the substituent induced ^{13}C chemical shifts for the ring carbons of the side chain phenyl group showed clear evidence for significant resonance interaction between it and *para* resonance donors and withdrawing groups in the other ring.[13] It is possible, therefore, that the dominance of extended polarization observed for the styrenes is retained.

Recently we prepared several series of β-heteroarylstyrenes for an investigation into the effect of varying the polar character of a β-substituent on the ^{13}C NMR chemical shifts of the β-carbon.[15] The shifts for the ring carbons of the heteroaryl substituents naturally became available during the course of this study. We felt that a comparison of the results obtained with those of the corresponding stilbenes would be of interest, as they introduce factors such as differences in ring size, the presence of highly electronegative groups, and tendencies towards bond-localization into what are otherwise similar systems. The results of this comparison are presented in this paper.

Results and Discussion

A Note on the Analysis of the Results.—In the course of the investigation the ^{13}C NMR spectra of approximately 170 compounds were obtained. Only those data relevant to the discussion are reported here. These are to be found in Table 1, listed in the form of substituent chemical shifts (SCSs), except for the parent compounds, for which the shifts relative to tetramethylsilane are given.

Inspection shows that, because the substituents and the probe sites are a considerable distance apart, the measured SCSs are rather insensitive to substituent effects, raising the question as to whether it is more desirable to discuss the results in a semi-qualitative fashion (*e.g.* by consideration of the data for the *m*-NO_2, *p*-NO_2, and *p*-NMe_2 derivatives) or whether a quantitative correlation analysis is of more value. While both lead to the same conclusions, quantitative treatment has the advantage of allowing some sort of assessment as to the degree to which the observed changes arise from polar and resonance effects alone.

For the quantitative analysis of data such as ours, the most common approach is to correlate them using Taft's DSP (dual substituent parameter) equation.[16] In the present case this takes the form of equation (1) where C_a is the carbon for which the

$$SCS(C_a) = \rho_I\sigma_I^X + \rho_R\sigma_R^X \qquad (1)$$

shift is being correlated, and σ_I^X, σ_R^X, are the appropriate substituent parameters for the substituent X. The DSP equation is well suited for the analysis of spectroscopic data, as, in contrast with the Hammett equation, it does not assume any relationship to exist between ρ_I^{meta}, ρ_I^{para}, and ρ_R^{para} (the latter assumes all three to be equal). From the results of such an analysis, it is possible to not only estimate the efficiencies with which polar and resonance effects are relayed from the substituent to the carbon in question (*via* the magnitudes of ρ_I and ρ_R), but also to assess the strength of resonance interaction between the two (by consideration of the type of σ_R parameter that gives the best correlation).

Data for *para* series are potentially the most useful, as a single analysis can give information on both polar and resonance effects. For *meta* series, the contributions of resonance effects to the overall shifts are usually small, and DSP analysis can only give useful information on the transmission of polar effects. However, the ρ_I values obtained for the latter are more reliable than those for the corresponding *para* series, and this can be important where systems of low sensitivity, such as the ones encountered here, are being analysed. For all of our series, analysis showed that $\rho_I^{meta} \approx \rho_I^{para}$, allowing us to use the data for *meta* series as a probe for polar effects, and that for *para* for resonance ones. In practice, preliminary DSP analyses for the *meta* data in general gave fits with σ_R° and values for λ ($= \rho_R/\rho_I$) within the range 0.3–0.5. In our experience, in such circumstances, one-parameter correlations using Hammett σ^{meta} constants yield more reliable ρ_I^{meta} values, and this approach was, therefore, adopted for all *meta* series.

DSP analysis of data for *para* series indicated unambiguously that resonance effects contributed to the observed shifts, confirming that extended π polarization represented a feasible mechanism for the relay of polar effects in our system. However, because of the low sensitivity of the shifts to substituent effects, quantitative assessment of their magnitudes could not be reliably achieved, nor dissection of these into ρ_R and σ_R contributions. The *para* analyses were all performed twice, once for all substituents, and once using $+M$ ones alone (see below).

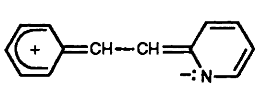
Polar Effects.—The effect on a phenyl group has been investigated previously,[13] and forms the most suitable basis of comparison with our heteroaryl systems. DSP analysis of the shifts for the various ring carbons showed clear evidence for the involvement of a planar conjugated system in the relay of both polar and resonance effects. The relative contributions of direct and extended polarization to the overall polar effect were not considered at the time, although the positive ρ_I value obtained for the *ortho* ring carbons required that the latter played an important role.

In order to facilitate comparisons with our results for heteroaryl systems, the shifts for the stilbenes in deuteriochloroform were remeasured, and the corresponding shifts in dimethyl sulphoxide solvent were also obtained. While the primary purpose of the Me_2SO data was to relate the results for the pyridyl and pyridinium methiodide systems, they yielded an important new result. In moving from $CDCl_3$ to Me_2SO the value of ρ_I for C-β increased by ≈15%.[15] This was expected, as a similar increase is observed for the same carbon in related systems.[17] In contrast, however, the magnitude of ρ_I for the *para* ring carbon (C-4′) decreased slightly. One possible explanation for this difference in behaviour is that it arises from changes in the relative contributions of direct and extended polarization to the shifts. Some support for this thesis is provided by consideration of the solvent dependence of the shifts for the *ortho* and *ipso* carbons. For the former, the magnitude and sign of ρ_I implies a major role for extended polarization, and the observed ρ_I is greater in Me_2SO than in $CDCl_3$. For the latter, however, the negative value for ρ_I indicates that direct polarization should dominate, and ρ_I in $CDCl_3$ its value is about 50% greater than that in Me_2SO.

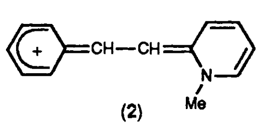
The replacement of the phenyl group by a heteroaryl one, in addition to drastically changing the nature of probe sites, is capable of influencing the degree of delocalization of the π system, as it introduces the possibility of new resonance forms such as (**1**)–(**6**), in addition to inducing changes in the contributions of others. Forms such as these can affect not only the extended polarization mechanism of electron transfer, but also, by inducing bond localization in the heterocyclic ring, direct polarization.

Because of the different natures of the interactions involved, it is convenient to discuss the series involving five- and six-membered rings separately. Let us first consider the pyridine and pyridinium systems, since these, being six-membered, are more formally similar to the phenyl group.

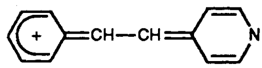
The smallest changes should be those encountered in the 3-stilbazoles and their corresponding methiodides, as, in these, no significant new resonance forms are involved. Any variations in ρ_I and ρ_R will accordingly, derive from the presence of the electron-attracting substituent into the side-chain ring. DSP analysis of the shifts for the ring carbons in these two series serves to confirm what a cursory inspection of the SCS data suggests, *i.e.* that the introduction of the heteroatom has relatively little effect on ρ_I in either case.



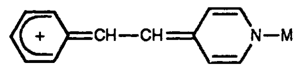
(**1**)



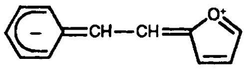
(**2**)



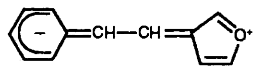
(**3**)



(**4**)



(**5**)



(**6**)

The placing of the heteroatom at the 2- or 4-positions is much more likely to lead to changes in both ρ_I and ρ_R. Any observed effect on ρ_I should arise predominantly as a result of contributions from resonance forms of the type (**1**)–(**4**). Potentially, these, by encouraging coplanarity of the system, could enhance the role of extended polarization, thereby increasing ρ_I at the ring carbons *ortho* or *para* to the vinyl group. In addition, if they contribute enough to the overall structure, they may induce a degree of bond localization in the heteroaryl group, and this would affect ρ_I for carbons *ortho* and *meta* to the styryl group. However, such localization would lead to an anomalously high negative value for the SCS for C-2′ of the *p*-F derivative in the 4-stilbazole methiodide series (the degree of localization depends on σ_R for the *para* substituent, while the resulting polarization depends on σ_I). Since this value appears normal, one may conclude that bond localization from this source is either unimportant or constant.

As substituents, both the pyridino and *N*-methylpyridinium nitrogens are of similar type ($-I$, $-M$), but differ in magnitude. The latter exerts a considerably more powerful polar effect (by a factor of around two[15]), but the results for the 3-series have shown that polar effects do not influence ρ_I and ρ_R to a major degree. Quantitative evidence on $-M$ values is lacking, but it is very probable that *N*-methylazonium exerts a substantially greater resonance effect also. The data for the 2- and 4-stilbazole methiodide derivatives should, therefore, be the most enlightening. Inspection shows that, as in the corresponding 3-derivatives, the SCSs of the *ipso* carbons are little affected. This suggests that the presence of a hetero atom into a six-membered ring, regardless of its position, has little effect on the latter's susceptibility to direct polarization. Consequently any observed changes in ρ_I should arise from variations in extended polarization.

For the *para* carbons there is no evidence for significant changes in ρ_I. For *ortho* and *meta* carbons the same holds true for the methiodide series, but there are variations in the pyridyl ones. This is surprising, as it implies that these variations may be of non-electronic origin. However, the difference in behaviour between the two may merely be the result of a different mix of opposed electronic effects. (The pattern of ρ_I values in the 2- and 4-stilbazoles in many ways resembles that found in the two styrylfuran series, ones in which the heterocyclic ring possesses a high degree of bond localization—see below).

In the two styrylfuran series, we are dealing with a five-membered rather than a six-membered heteroaryl group, and inspection immediately shows a very different pattern of behaviour from that observed in the six-membered ring systems. This is not really surprising, as most estimates suggest that furan has less than half the resonance energy of benzene,[18] and a decrease in resonance energy implies the existence of a greater degree of bond localization. Bond localization affects both the nature of the system undergoing polarization and the mechanism by which this is achieved.

The most important changes are those resulting from differences in the relative contributions of direct and extended polarization to polar effects. These arise because the latter is sensitive to perturbations to the extended conjugated system whereas the former is not. The operation of the extended polarization mechanism in the stilbenes inflicts some degree of bond localization on the β-phenyl group. Such localization is limited by the loss of aromatic resonance energy involved. If, as in the case of furan, the resonance energy of the system is not large in the first place, then the extended polarization mechanism should be able to operate more efficiently. The result of this would be an enhancement in the sensitivity of certain carbons (C-2′ and C-4′ in the 2-styrylfurans and the C-2′ in the 3-styrylfurans) to polar effects, *i.e.* ρ_I should be more positive than in the stilbenes. Furthermore, bond localization in the 3-styrylfurans would result in isolation of the C(4′)–C(5′) bond from the conjugated system, and to the extent that this occurs, contributions to ρ_I for C-5′ due to extended polarization will be lost.

The pattern of ρ_I values arising from the effect of bond fixation on transmission effects will be modified further by the changes in electron distributions that will arise as a result of the polarization of the double bonds as independent units. Briefly, these should show up, in the 2-styrylfurans as a tendency for ρ_I for C-2′ to become more positive and that for C-4′ less so, and in the 3-styrylfurans, in C-2′ and C-4′ becoming more positive and C-5′ less so.

Let us now examine the results in the light of all this. First, our predictions with regard to the increased role of extended polarization appear to have been fulfilled. Relative to the stilbene system, ρ_I values for C-2′ in the 2-series and C-2′ in the 3-series have increased substantially, while that for C-5′ in the latter has become reduced to such an extent that it is now negative. The figure for C-4′ in the 2-series remains essentially unchanged. This is perhaps a little surprising, but may be related to the presence of the oxygen on that carbon; certainly ρ_I for C-2′ in the 3-series is substantially less than that for C-2′ in the 2-series. The higher than normal ρ_I for C-3′ in the 2-series is puzzling, as we would have anticipated it to be smaller, even negative. On the other hand, that for C-4′ in the 3-series is as expected, as a result of the direct field effect now dominating polarization of the C(4′)–C(5′) bond.

It is evident, however, that polarization of the furan ring as an aromatic unit does still contribute to the overall electron distribution. The most clear-cut evidence supporting this is provided by the ρ_I values for C-4′ and C-5′ in the 3-series. Complete localization of this would lead to direct polarization being the only influence on the π-electron distribution, and this would result in ρ_I for C-5′ being at least as negative as that for C-4′ is positive.

Resonance Effects.—Inspection of the data in Table 1 shows that the shifts for all of the heteroaryl carbons in all series are affected by resonance interaction involving both $+M$ and $-M$ *para* substituents. The difficulties involved in quantifying the role of resonance effects have been pointed out previously. The rigid application of the DSP equation to these systems can in some cases yield misleading results, as for some positions, $-M$ substituents require σ_R^- values for good correlations, while for $+M$ ones, σ_R^{BA} or even σ_R^+ values give a superior fit. Accordingly, the DSP analyses were performed twice, once using data for all substituents, and once using those for $+M$ ones only. Where the results for the two analyses differed significantly, only those for the latter are given (full results are available in the supplementary publication [Sup 56778 (31 pp)*].

The results of our DSP analyses are given in Table 2. The f values show that the fit of the data to the equation varied from unsatisfactory to excellent. As was only to be expected, poorest correlations were observed for data sets where ρ_I and ρ_R were small, and the best when they were large. There were also indications that low f values tended to be associated with series where ρ^{meta}, ρ_I^{para}, and ρ_R^{para} were similar in magnitude.

The tendency for ρ_I^{para}, and ρ_R^{para} to have similar values is perhaps the most striking feature of the results. In cases where the two differ significantly, the evidence that the difference is real rather than an artefact of the DSP analysis is usually weak. This strongly suggests that the dominant mechanism of transmission for both polar and resonance effects involves the π system. It also serves to reinforce our earlier conclusion that, for most positions, extended π polarization plays a dominant role so far as polar effects are concerned.

Even in the case of correlations for the *ipso* carbons, where extended π polarization would not be anticipated to play a significant role, the observed ρ_R values appeared to be more of a function of ρ_I than of any electronic characteristic of the heteroaryl group. For all of these, both ρ_I and ρ_R are negative, with the best fits being obtained when σ_R^{BA} values are used. There is a close parallel between the observed behaviour and that for the α-carbons of the vinyl groups, and it is likely that the mechanism by which the electron density is being influenced is the same in both cases.

In contrast, the correlations for both the *ortho* and *para* ring carbons showed, in addition to the previously mentioned strong dependence on ρ_I, some response on the part of both ρ_R and σ_R to the nature of the heteroaryl group. In both the series, DSP analyses based on $+M$ substituents alone were considered more reliable, although differences were often small.

For the *ortho* carbons, the greatest specific effect was on σ_R in the three methiodide series. The latter gave much better correlations with σ_R^+ than with σ_R^0, the most satisfactory scale for all of the other *ortho* series. Of particular significance was the observation that this applied not only to the 2- and 4-series, but also to the 3-series. This implies that the observed enhancement of the resonance is a consequence of the powerful $-I$ effect of these groups, rather than their $-M$ one. This suggests that polar and resonance effects are not as independent of one another as is often assumed. One might have expected similar behaviour in the case of the 2-furyl group, as this is also a strong $-I$ one. This was not observed, but it should be noted that, for this particular series, ρ_R is much higher than for the others.

For the *para* series, very similar results are obtained. This is not surprising, as from an electronic point of view, the *ortho* and *para* positions bear a similar relationship to any *para* substituent in the far ring. A careful quantitative comparison of the two, however, reveals that, because of the different ρ_R values involved, the actual contribution of resonance effects to the shifts for *para* carbons is significantly greater than that to the *ortho* ones.

Summary.—Overall, the main conclusion that can be drawn from the results is that, in all of the systems studied, the π electrons play a leading role in the transmission of both the resonance and polar effect of a substituent from one ring to the other. In stilbenes, the polar effect exerts its influence on the side chain phenyl group by a combination of direct and extended π polarization, with the latter playing the dominant role. The introduction of an aza or even *N*-methylazonium group has

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* For details of the Supplementary Publication Scheme, see *J. Chem. Soc., Perkin Trans. 2*, 1990, Issue 1.

Table 2. Summary of results for DSP analyses for *para*-substituted derivatives.[a,b,c]

C_{ipso}

	Ph	2-Py	3-Py	4-Py	2-Fur	3-Fur	Ph	2-PyMe$^+$	3-PyMe$^+$	4-PyMe$^+$
σ_R	BA	BA[d]	BA	BA[d]	BA	BA[e]	BA	BA	BA	BA[d]
ρ_I	−1.45	−1.54	−1.40	−1.70	−1.22	−0.78	−1.12	−1.09	−1.27	−1.30
ρ_R	−1.16	−1.28	−1.23	−1.58	−1.04	−0.68	−1.05	−1.17	−1.40	−1.26
λ	0.80	0.83	0.88	0.93	0.86	0.88	0.94	1.07	1.10	0.97
f	0.06	0.07	0.07	0.17	0.08	0.14	0.07	0.06	0.08	0.11

C_{ortho}

	Ph	2-Py	3-Py(2′)	3-Py(6′)	4-Py	2-Fur	3-Fur(2′)	Ph	2-PyMe$^+$	3-PyMe$^+$(2′)	3-PyMe$^+$(6′)	4-PyMe$^+$
σ_R	0	BA	0	0	0	BA	0	0	+	+	+	+
ρ_I	0.51	0.92	0.30	0.59	0.39	2.26	1.31	0.78	0.78	0.60	0.72	0.91
ρ_R	0.89	0.89	0.61	0.91	0.74	2.37	1.81	1.24	0.84	0.53	0.73	0.87
λ	1.73	0.97	2.02	1.54	1.92	1.05	1.38	1.59	1.09	0.87	1.01	0.95
f	0.06	0.04	0.13	0.05	0.26	0.08	0.12	0.08	0.09	0.05	0.02	0.09

C_{para}

	Ph	2-Py	3-Py	2-Fur	Ph	2-PyMe$^+$	3-PyMe$^+$
σ_R	BA	BA[e]	BA[e]	BA	BA	+	+
ρ_I	1.21	1.11	1.11	1.05	1.13	1.47	1.03
ρ_R	1.21	1.18	1.14	1.02	1.30	1.28	0.88
λ	1.00	1.06	1.02	0.98	1.15	0.87	0.85
f	0.06	0.10	0.09	0.09	0.05	0.13	0.07

[a] Normally the results for correlations using the σ_R scale resulting in the lowest f value is listed. In a few instances, results using one of the other scales is given in order to facilitate comparisons, but only where differences between the two were not considered significant. [b] Correlations for *ipso* carbons were based on data for all substituents. Those for the *ortho* and *para* ones are based on the use of $+M$ substituents only (see the text). [c] DSP correlations were not carried out for C-3′ and C-5′ of the stilbazoles and their methiodides, for C-3′ of the 2-styrylfurans or for C-4′ of the 3-styrylfurans as the results were likely to be too unreliable to be of value. [d] The use of $\sigma_R{}^0$ parameters leads to a slightly superior fit. [e] The use of $\sigma_R{}^+$ parameters leads to a slightly superior fit.

surprisingly little effect on the balance between the two. However, if the phenyl group is replaced by a furyl one, changes reflecting the greater degree of bond fixation in the latter are observed.

Perhaps the most surprising feature is the very strong tendency for ρ_I and ρ_R to be of the same sign and approximately the same magnitude. This suggests that the strength of the dipole generating the field responsible for the polar effect is a function of the resonance effect of the substituent, calling into question the validity of the common convention of treating these as independent. On the basis of our results, quite a strong case could be made out for a partial separation, somewhat along the lines of that proposed by Yukawa and Tsuno[19] being more appropriate in systems such as ours.

Experimental

Details on the preparation of the compounds and the measurement of the NMR spectra have been reported elsewhere.[15] A more complete summary of the results of the DSP analyses are included in the accessory publication to that paper (Supplementary Publication Number 56778.)

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