^{19}F Nuclear Magnetic Resonance Studies of Aromatic Compounds. Part IV.[1] Transmission of Substituent Effects across Two Aromatic Rings connected by an N–N Linkage

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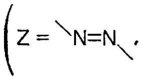
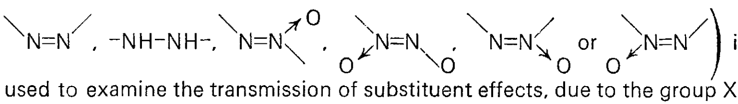
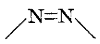
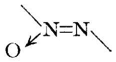
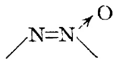
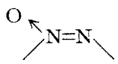
The synthesis of several series of dinuclear aromatic compounds of the type p-FC$_6$H$_4$·Z·C$_6$H$_4$X   is described. The ^{19}F n.m.r.spectra are used to examine the transmission of substituent effects, due to the group X, across the bridge Z. It is necessary to distinguish between 'transmission' (the *trans*-azo- and -azoxy-series) in which electron density is probably transferred from one ring to the other and 'relay' (in the *cis*-azo- and -azoxy-series, and the hydrazo-series) in which the substituent effects most probably occur by modification of the repulsive interaction between the non-bonding lone-pairs on the interconnecting nitrogen atoms. Support for this suggestion is given by observation of long range (11 bond) coupling between fluorine nuclei in n.m.r. spectra of the 4,4'-difluoro-members of the 'transmission' series and its absence in the spectra of the corresponding members of the 'relay' series. A recent examination of long range substituent effects in some analogous series is discussed and the results re-assessed. Some consideration is given to an analogous treatment of ^{13}C and ^{1}H n.m.r. shielding data in some 4-substituted styrene derivatives

Our recent study of long range substituent effects upon ^{19}F shielding in interconnected dinuclear aromatic compounds[1] and the later investigation by Taft *et al.*[2] of similar series, has prompted us to extend the work to series in which the connecting group consists of two nitrogen atoms. When the group is unsaturated (azo- or azoxy-) the existence of *cis–trans*-isomerism enables highly conjugated systems (the *trans*-isomers) to be compared with those in which there should be considerable steric inhibition of conjugation (*cis*-isomers), while the consequences of saturation may be studied by considering the hydrazo-linkage. Six series [(1)—(6)] of molecules were synthesised in which the substituents X and F are *para* to the linkage, p-FC$_6$H$_4$·Z·C$_6$H$_4$X-p; the various connecting groups Z are shown in Table 1.

Table 1

Structure of connecting groups in p-FC$_6$H$_4$·Z·C$_6$H$_4$X-p (1)—(6)

Series No.	Z
(1)	
(2)	
(3)	
(4)	
(5)	 or 
(6)	–NH–NH–

EXPERIMENTAL

^{19}F N.m.r. spectra were recorded for dilute solutions of the compounds in hexane as solvent, with C$_6$F$_6$ as internal reference; spectra were recorded for a variety of concentrations and the results extrapolated to infinite dilution.

A modified Varian HA 100 n.m.r. spectrometer was used for most observations, operating in extended field-frequency locked mode with fully automatic phase correction.[3] Chemical shifts were recorded, by use of the frequency difference technique, with a Beckmann frequency counter.

For the *cis*-azoxybenzenes, the small quantities which were prepared necessitated the use of signal-averaging techniques in order to observe useful spectra; a Varian XL 100–12 spectrometer operating in Fourier transform mode with noise decoupling of protons was used.

The compounds studied were prepared by the methods described below. They were identified by their spectroscopic properties (u.v., i.r., and n.m.r.) and by microanalysis (Table 2).

trans-4-*Dimethylamino-4'-fluoroazobenzene* (1; X = NMe$_2$) *and* trans-4-*Fluoro-4'-hydroxyazobenzene* (1; X = OH).—Compounds (1; X = NMe$_2$ and OH) were prepared by the action of 4-fluorobenzenediazonium chloride upon *NN*-dimethylaniline and phenol respectively. The latter gave a mixture of 4'- and 2'-hydroxyazobenzenes which were separated by chromatography (silica; dichloromethane).

4-Fluoronitrosobenzene was prepared as for nitrosobenzene.[4] It was stable at −5° for several days, m.p. 40° (lit.,[5] 39°).

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[1] Part III, I. R. Ager, L. Phillips, and S. J. Roberts, *J.C.S. Perkin II*, 1972, 1988.

[2] S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 9113.

[3] P. N. Jenkins and L. Phillips, *J. Phys.* (*E*), 1971, **4**, 530.

[4] G. H. Coleman, C. M. McCloskey, and F. A. Stuart, *Organic Synth.*, Coll. Vol. III, 1953, p. 668.

[5] G. Olah, A. Pavlàth, and I. Kuhn, *Acta. Chim. Acad. Sci. Hung.*, 1955, **7**, 65.

trans-4-*Fluoroazobenzene* (1; X = H).—A solution of 4-fluoronitrosobenzene (1·25 g, 10 mmol) in glacial acetic acid (4 ml) was added to a solution of aniline (0·93 g, 10 mmol) in glacial acetic acid (10 ml) and the mixture heated on a steam-bath for 20 min. The mixture was then poured into water (100 ml) and after 5 min the solid was filtered off and washed with water. Recrystallisation (charcoal) from aqueous ethanol gave the *product* (1·24 g, 62%).

TABLE 2

Melting points and quantitative elemental analysis

Compound	M.p. (°C)	Found (%)				Required (%)			
		C	H	N	F	C	H	N	F
(1; X = NMe_2)	154	68·9	5·85	17·45	7·85	69·1	5·8	17·3	7·8
(1; X = OH)	149—150	66·45	4·45	12·9	8·85	66·65	4·2	12·95	8·8
(1; X = OMe)	89—90	67·6	4·7	12·0	8·4	67·8	4·8	12·15	8·25
(1; X = H)	82	71·9	4·65	14·25	9·5	72·0	4·55	14·0	9·5
(1; X = Me)	101	73·0	5·3	13·2	8·75	72·9	5·2	13·1	8·85
(1; X = F)	103	66·2	3·85	13·05	17·7	66·05	3·7	12·85	17·4
(1; X = Cl) [a]	132	61·25	3·4	12·05	8·15	61·4	3·45	11·95	8·1
(1; X = Br) [b]	135	51·75	3·05	10·15	6·95	51·65	2·9	10·05	6·8
(1; X = I) [c]	133	44·05	2·6	8·8	5·95	44·2	2·45	8·6	5·85
(1; X = CF_3)	73	58·35	3·2	10·55	28·05	58·2	3·0	10·45	28·35
$4\text{-NO}_2\text{C}_6\text{H}_4\text{NO}$	114—115	47·6	2·9	18·5		47·4	2·7	18·4	
(1; X = NO_2)	133—134	58·9	3·4	17·35	7·7	58·8	3·3	17·15	7·75
(2; X = H)		71·9	4·5	14·0	9·4	72·0	4·5	14·0	9·5
(2; X = Me)		72·65	5·1	13·15	8·95	72·9	5·2	13·1	8·85
(2; X = F)		65·85	3·8	13·1	17·6	66·05	3·7	12·85	17·4
(2; X = Cl) [d]		61·1	3·55	12·25	8·3	61·4	3·45	11·95	8·1
(2; X = Br) [e]		51·4	3·05	10·25	6·95	51·65	2·9	10·05	6·8
(2; X = I) [f]		44·3	2·6	8·6	5·95	44·2	2·6	8·6	5·85
(2; X = OMe)		Structure and purity confirmed by mass spectrometry							
(2; X = CF_3)		Structure and purity confirmed by mass spectrometry							
(6; X = Me)	85·5—86	72·2	6·0	12·95	8·75	72·2	6·05	12·95	8·8
(6; X = H)	66·0—66·5	71·4	5·45	13·8	9·2	71·25	5·5	13·85	9·4
(6; X = F)	63·0—64·0	65·65	4·5	12·8	17·15	65·45	4·6	12·7	17·25
(6; X = Cl) [g]	65—65·5	60·75	4·2	11·8	7·95	60·9	4·25	11·85	8·05
(6; X = Br) [h]	80·5—81	51·45	3·7	10·08	6·9	51·25	3·6	9·95	6·75
(6; X = I) [i]	84—84·5	43·95	3·1	8·55	5·6	43·9	3·05	8·55	5·8
(6; X = CF_3)	48·5—49	58·05	3·9	10·5	28·15	57·8	3·75	10·35	28·1
(3 and 4; X = OMe)		Structure and purity confirmed by mass spectrometry							
(3 and 4; X = H)		66·85	4·4	13·0	8·85	66·65	4·2	12·95	8·8
(3 and 4; X = Cl) [j]		57·75	3·45	11·2	7·45	57·5	3·2	11·2	7·6
(3 and 4; X = Br) [k]		49·0	2·7	9·6	6·6	48·85	2·75	9·5	6·45
(3 and 4; X = I) [l]		42·2	2·45	8·1	5·8	42·15	2·35	8·2	5·55
(3 and 4; X = CF_3)		55·2	2·9	10·0	26·4	54·95	2·85	9·85	26·75
(3 and 4; X = NO_2)		55·5	3·25	16·05	7·2	55·2	3·1	16·1	7·25
(3 and 4; X = F)	89—89·5	61·4	3·45	11·95	16·4	61·55	3·45	11·95	16·2

[a] Found: Cl, 15·0. Required: Cl, 15·1%. [b] Found: Br, 28·7. Required: Br, 28·65%. [c] Found: I, 38·6. Required: 38·9%. [d] Found: Cl, 15·3. Required: Cl, 15·1%. [e] Found: Br, 28·9. Required, Br, 28·65%. [f] Found: I, 39·05. Required: I, 38·9%. [g] Found: Cl, 15·25. Required, 15·0%. [h] Found: Br, 28·65. Required: Br, 28·45%. [i] Found: I, 38·85. Required: I, 38·7%. [j] Found: Cl, 14·3. Required: Cl, 14·15%. [k] Found: Br, 26·75. Found: Br, 27·1%. [l] Found: I, 37·2. Required: I, 37·1%.

trans-4-*Fluoro-4′-methoxy-* (1; X = OMe), -4-*fluoro-4′-methyl-* (1; X = Me), -4,4′-*difluoro-* (1; X = F), -4-*chloro-4′-fluoro-* (1; X = Cl), -4-*bromo-4′-fluoro-* (1; X = Br), -4-*fluoro-4′-iodo-* (1; X = I), and -4-*fluoro-4′-trifluoromethyl-azobenzene* (1; X = CF_3) were prepared by the method described for (1; X = H), using the corresponding 4-substituted anilines.

4-*Nitronitrosobenzene*.—Peracetic acid (40% solution in water, 10·0 g; large excess) was added to a suspension of 4-nitroaniline (6·9 g, 50 mmol) and the mixture stirred at room temperature for 72 h. Steam-distillation of the mixture gave a green solid which turned yellow after drying *in vacuo*. The solid was recrystallised (ethanol) to give pale yellow needles (1·40 g, 18·5%), m.p. 114—115° (lit.,[4] 118·5—119·0°).

trans-4-*Fluoro-4′-nitroazobenzene* (1; X = NO_2).—4-Nitronitrosobenzene (1·32 g, 7·6 mmol) was dissolved in glacial acetic acid (20 ml) with slight warming and the solution added to 4-fluoroaniline (0·84 g, 7·6 mmol) in glacial acetic acid (5 ml). After gentle heating on a steam-bath for 10 min the product (1·41 g, 76%) was isolated as for (1; X = H).

cis-4-*Fluoroazobenzene* (2; X = H).—The procedure was based upon the method of Cook.[6,7] A solution of *trans*-4-fluoroazobenzene (1; X = H) (250 mg) in a little more than the minimum quantity of dry light petroleum (b.p. 40—60°) was irradiated for 45 min under nitrogen at 20° in a Pyrex flask using an unshielded quartz mercury vapour lamp. Chromatography on alumina (grade III), eluting with light petroleum, removed the unchanged *trans*-compound. The deep red cis-*isomer* (23 mg, 9·2%) was recovered by extracting the alumina with light petroleum–methanol (99 : 1).

cis-4-*Fluoro-4′-methyl-* (2; X = Me), -4,4′-*difluoro-* (2; X = F), -4-*chloro-4′-fluoro-* (2; X = Cl), -4-*bromo-4′-fluoro-* (2; X = Br), and -4-*fluoro-4′-iodo-azobenzene* (2; X = I) were prepared analogously. cis-4-*Fluoro-4′-methoxy-* (2; X = OMe) and cis-4-*fluoro-4′-trifluoromethyl-azobenzene* (2; X = CF_3) were formed by the same reaction as oils which

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[6] A. H. Cook, *J. Chem. Soc.*, 1939, 876.

[7] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 1939, 1309.

would not crystallise after standing at −5° for several days. All the *cis*-azobenzenes were stable for several days at −5° in the dark.

4-*Fluoro*-4′-*methylhydrazobenzene* (6; X = Me).—*trans*-4-Fluoro-4′-methylazobenzene (1; X = Me) (0·44 g, 20 mmol) was dissolved in the minimum quantity of acetone–methanol (1 : 1 v/v) and to it was added a saturated solution of ammonium chloride (0·54 g, 10 mmol). A further quantity of solvent was added until the precipitated azobenzene just redissolved. The solution was stirred and zinc dust (0·33 g, 5 mmol) was added. When the solution became completely colourless, it was filtered into ice–water. The precipitate was filtered off under nitrogen, washed with water, and dried *in vacuo*. The solid was extracted with hot, previously degassed, hexane and the crystalline *product* (0·26 g, 60%) was obtained by reducing the volume of hexane in a current of nitrogen.

TABLE 3

^{19}F chemical shifts (p.p.m. from C_6F_6 internal reference, extrapolated to infinite dilution in hexane as solvent) in series (1)—(6). Negative shifts are to low field

Substituent	Series (1)	(2)	(3)	(4)	(5)	(6)
NMe_2	−50·399					
OMe	−51·907	−47·683	−52·643	−53·122	−46·432	
Me	−52·495	−48·127			−46·514	−37·765
H	−53·033	−48·601	−53·453	−53·786	−46·780	−37·993
F	−53·327	−48·942	−53·943	−54·147	−47·246	−38·380
Cl	−53·789	−49·384	−54·193	−54·386	−47·585	−38·636
Br	−53·896	−49·471	−54·235	−54·446	−47·736	−38·703
I	−53·931	−49·498	−54·229	−54·479	−47·676	−38·724
CF_3	−54·897	−50·311	−55·067	−55·269	−48·353	−39·218
NO_2	−55·952		−55·930	−56·071		

4-*Fluoro*- (6; X = H), 4,4′-*difluoro*- (6; X = F), 4-*chloro*-4′-*fluoro*- (6; X = Cl), 4-*bromo*-4′-*fluoro*- (6; X = Br), 4-*fluoro*-4′-*iodo*- (6; X = I), and 4-*fluoro*-4′-*trifluoromethyl-hydrazobenzene* (6; X = CF_3) were prepared analogously.

trans-α and -β-4-*Fluoro*-4′-*methoxyazoxybenzene* (3 *and* 4; X = OMe).—*trans*-4-Fluoro-4′-methoxyazobenzene (III) (250 mg) was dissolved in glacial acetic acid (100 ml) and a large excess of 30% (w/v) hydrogen peroxide (10 ml) was added, with stirring. The mixture was heated to 85—90°. Further quantities of hydrogen peroxide were added periodically. After complete oxidation had occurred (3 h; t.l.c.) the mixture was left to cool and poured into water. After complete precipitation, the precipitate was filtered off, washed with water, and dried *in vacuo*. The pale yellow product was a pure mixture of the α- and β-isomers (α denoting that oxygen is bonded to the nitrogen atom α to the fluorine-containing ring), obtained in almost quantitative yield.

The same mixture of isomers of *trans*-4-fluoro- (3 and 4; X = H), -4-chloro-4′-fluoro- (3 and 4; X = Cl), -4-bromo-4′-fluoro- (3 and 4; X = Br), -4-fluoro-4′-iodo- (3 and 4; X = I), -4-fluoro-4′-trifluoromethyl- (3 and 4; X = CF_3), -4-fluoro-4′- nitro- (3 and 4; X = NO_2), and -4,4′-difluoro-azoxybenzene (3 and 4; X = F) was obtained analogously. In the case of (3 and 4; X = F) the possibility of an isomeric mixture did not arise.

cis-4-*Fluoro*-4′-*methoxyazoxybenzene* (5; X = OMe).—The procedure was based upon the method of Webb and Jaffé.[8] cis-4-*Fluoro*-4′-*methoxyazobenzene* (2; X = OMe) (48 mg, 0·22 mmol) was prepared by repeated irradiation of the *trans*-isomer (1; X = OMe), as described above, and dissolved in a chloroform solution of peracetic acid (5 ml). The solution was left at −5° for 24 h, washed with water (10 ml), 10% sodium carbonate solution (2 × 10 ml), and water (3 × 10 ml), dried ($MgSO_4$), and the solvent removed *in vacuo* at 25° to give a yellow solid. This was dissolved in n-hexane and its ^{19}F n.m.r. spectrum recorded by Fourier transform (Varian XL 100–12). It was shown that the solid contained the *trans*-azobenzene (50%) and *trans*-α-azoxybenzene (5%) but not the *cis*-azobenzene. The remaining peak in the n.m.r. spectrum was attributed to the *cis*-azoxybenzene (45%).

cis-4-Fluoro-4′-methyl- (5; X = Me), 4-fluoro- (5; X = H), -4,4′-difluoro- (5; X = F), -4-chloro-4′-fluoro- (5; X = Cl), 4-bromo-4′-fluoro- (5; X = Br), 4-fluoro-4′-iodo- (5; X = I), and 4-fluoro-4′-trifluoromethyl-azoxybenzene (5; X = CF_3) were prepared analogously. In the case of (5; X = Cl) both the α- and -β-*cis*- and the α- and -β-*trans*-azoxybenzenes were formed.

Table 3 lists the ^{19}F chemical shifts, measured from C_6F_6 as internal reference, for the compounds (1)—(6); Table 4 lists substituent chemical shifts for the same series (*i.e.* referenced to the compounds with X = H).

TABLE 4

^{19}F S.C.S. for series (1)—(6) (p.p.m. shifts to high field of X = H are positive)

Substituent	Series (1)	(2)	(3)	(4)	(5)	(6)
NMe_2	2·63					
OMe	1·13	0·92	0·81	0·67	0·35	
Me	0·54	0·47			0·21	0·23
H	0·00	0·00	0·00	0·00	0·00	0·00
F	−0·29	−0·34	−0·49	−0·36	−0·47	−0·39
Cl	−0·76	−0·78	−0·74	−0·60	−0·81	−0·64
Br	−0·86	−0·87	−0·78	−0·66	−0·96	−0·71
I	−0·90	−0·90	−0·78	−0·69	−0·90	−0·73
CF_3	−1·86	−1·71	−1·61	−1·48	−1·57	−1·23
NO_2	−2·92		−2·48	−2·29		

RESULTS AND DISCUSSION

In our previous study,[1] the ability of the linking group Z (Table 1) to transmit electronic interactions *via* the

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[8] D. H. Webb and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1964, **86**, 2419.

π electron system was discussed in terms of linear correlations of ^{19}F S.C.S. (substituent chemical shifts) in each series with those in 4-fluoro-4′-X-*trans*-stilbenes. After correcting for solvent effects, the slopes of these correlations were given the symbol T (referred to an arbitrary unity for the stilbene series) and the values of T were discussed in terms of the electronic structure of the group Z and the conformational properties of the molecule. We follow the same procedure in the current work, and Table 5 lists T values for the series (1)—(6).

TABLE 5

T Values for series of linked dinuclear aromatic compounds with various N–N bonds

Series	Slope of correlation with stilbene series	Correlation coefficient	T
(1)	1·38	0·9960	1·49
(2)	1·22	0·9990	1·28
(3)	1·05	0·9953	1·06
(4)	0·96	0·9981	0·95
(5)	0·95	0·9847	0·94
(6)	0·82	0·9910	0·77

Implicit in the analysis of these data is the assumption that when the fluorine atom and the substituent are so far apart (10 or 11 bonds and *ca.* 7·35 Å in *trans*-stilbenes and azobenzenes), any change which is observed in the ^{19}F shielding will be caused only by changes in the π electron distribution.* The change in shielding is assumed to be proportional to the change in π electron density on the carbon to which the fluorine is bonded [1, 9, 10] and the proportionality constant is assumed to be the same in all series. This ‘ constant ’ depends in part upon the reciprocal of a rather ill-defined ‘ average excitation energy ’ ΔE [11] concerned with wavefunctions which describe the total molecular electronic properties and may in fact be different for different series. It is probably a more reasonable assumption that for all members of one series the value of ΔE remains the same and that a proportionality constant holds throughout (*i.e.* there is no substituent effect upon ΔE); if ΔE is large compared with any substituent effects upon it then this approximation holds good, but if ΔE is small and the substituent effects are significant then the correlations will inevitably be imprecise with significant scatter or even curvature.

Table 5 lists slopes, correlation coefficients, and T values for the series (1)—(6). Consider, first, the *trans*- and *cis*-azobenzenes (1) and (2); as expected the *trans*-series shows a high degree of conjugation and a high T value of 1·49. This may imply that the π electron density changes at C-4 which accompany changes in the nature of the 4′-substituent are greater than in the stilbene series by *ca.* 50%; it is possible however that the proportionality constant relating observed ^{19}F shielding to π electron density variation may be larger for the azobenzene series than for stilbene because of a smaller average excitation energy ΔE. This latter explanation is supported to some extent by the highly coloured nature of the azo-series which implies easier access to excited states.

The *cis*-azobenzenes show a surprising result; the value of T, 1·28, is very nearly as large as in the *trans*-series even though π conjugation between the rings would be expected to be very much less than in series (1) because of ‘ steric inhibition ’. For maximum conjugation to occur both aromatic rings should be coplanar with the nodal plane of the bond of the unsaturated linkage (Figure 1a); in this conformation, which is closely approximated to in *trans*-stilbene and *trans*-azobenzene,[12] the π systems of the benzene rings have maximum overlap with the π bond of the *trans*-linking group. In the case of *cis*-azobenzenes however this type of conformation is strongly disfavoured because of steric interactions between the rings and *X*-ray studies [13] show that in the crystalline state the conformation resembles Figure 1b with the phenyl rings out of the C–N–N–C plane by an angle of 56°. The overlap between the π system of each ring and that of the N–N bond is a $\cos^2$ function of the dihedral angle between them, and therefore conjugation between the rings is reduced to $\cos^4 56°$, *i.e.* 9%, of that in the planar *trans*-compound.

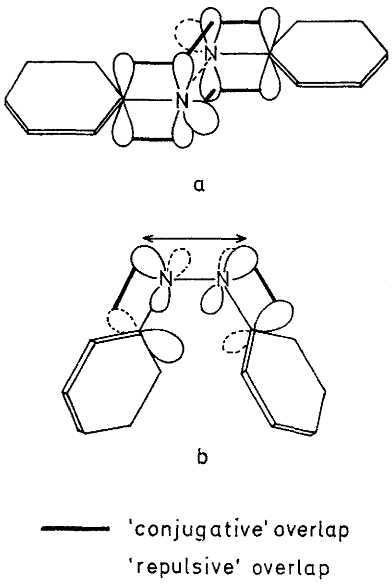

FIGURE 1 p Orbital overlap for a, *trans*-azobenzenes (1) and b, *cis*-azobenzenes (2)

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* Calculations show that even in the *cis*-derivatives (where there is closer approach of the fluorine and substituent) through-space effects such as electric fields or van der Waals fields have negligible influence.

[9] I. R. Ager, L. Phillips, T. J. Tewson, and V. Wray, *J.C.S. Perkin II*, 1972, 1979.

[10] J. W. Emsley, *J. Chem. Soc.* (*A*), 1968, 2523.

[11] F. P. Prosser and L. Goodman, *J. Chem. Phys.*, 1963, **38**, 374.

[12] J. M. Robertson, *Proc. Roy. Soc.*, 1939, *A*, **171**, 398.

[13] G. C. Hampson and J. M. Robertson, *J. Chem. Soc.*, 1941, 409.

Evidence that this situation pertains in solution is available from the electronic absorption spectra of the *trans*- and *cis*-azo-series. Figure 2 illustrates the spectra of *cis*- and *trans*-4,4′-difluoroazobenzenes, and Table 6 lists the frequencies of the maxima (together with molar extinction coefficients) of the bands in the spectra of the various members of the two series of compounds. The two bands which undergo significant change on going from the *trans*-series to the *cis* are the π–π* conjugation band [I, $\lambda_{max.}$ 318—349 nm ($\varepsilon_{max.}$ 17,000—24,200) in the *trans*-series; $\lambda_{max.}$ 281—327·5 nm ($\varepsilon_{max.}$ 5300—11,000) in the *cis*-series] and the *n*–π* band [II, $\lambda_{max.}$ 432—451 nm in both series ($\varepsilon_{max.}$ 630—1300 in the *trans* and 1400—3100 in the *cis*)].[14] The blue shift of the conjugation band, accompanied by a loss of intensity by a factor between two and three, shows that indeed the conjugation is very significantly attenuated upon going from the *trans*- to the *cis*-series; the concomitant increase in the intensity of the *n*–π* transition by a similar factor strongly suggests that the nitrogen lone-pair electrons (*n*) are in a more favourable orientation for excitation into the antibonding (π*) levels in the *cis*-series than in the *trans*, which is what would be expected if the relative conformations are as depicted in Figure 1.

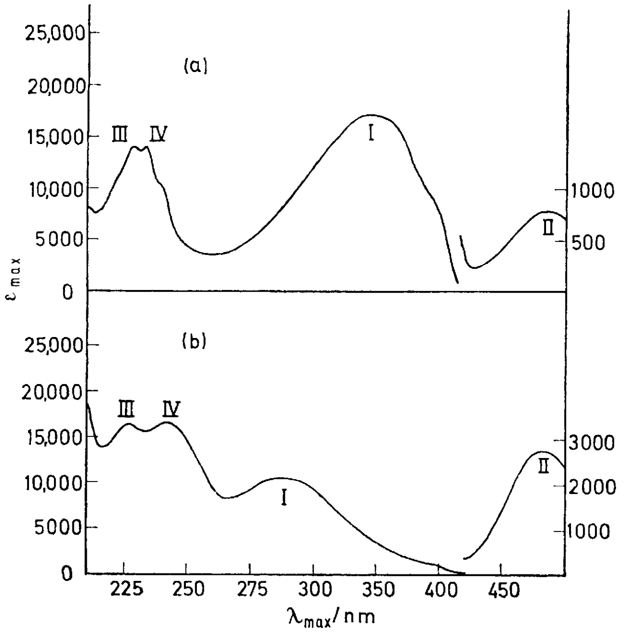

FIGURE 2 U.v. spectra of (a) *trans*-4,4′-difluoroazobenzene and (b) *cis*-4,4′-difluoroazobenzene

Comparison of the ^{19}F chemical shifts of the two series is also revealing. The azo-linkage, like the nitro- and cyano-groups, is unsaturated and has an electronegative atom with a *p* orbital of symmetry suitable for π overlap which is β to the ring; if fully conjugated, this causes the group to be powerfully π electron withdrawing, predominantly from the *ortho*- and *para*-positions. The consequences of this are shown, for example, by the fact that the fluorine nucleus in *trans*-fluoroazobenzene is deshielded compared with the fluorine in fluorobenzene (δ 53·03 p.p.m. to low field of C_6F_6; for fluorobenzene δ 50·08 p.p.m.; S.C.S. −2·95 p.p.m.). The chemical shift of fluorine in *cis*-fluoroazobenzene is 48·94 p.p.m. to low field of C_6F_6 however, *i.e.* the *cis*-phenylazo-group has an S.C.S. of +1·48 p.p.m. and is shielding compared

TABLE 6

Wavelength of maximum absorption and molar extinction coefficients for the electronic absorption spectra of *cis*- and *trans*-4-X-4′-fluoroazobenzenes (band assignments are in Figure 2)

trans-Azobenzenes		$\lambda_{max.}$/nm($\varepsilon_{max.}$)		
X	III	IV	I	II
NMe_2	218 (9400)	258 (9400)	408 (25,600)	
OMe	237·5 (12,500)		345 (19,700)	434 (1300)
OH	238 (12,200)		349 (24,200)	
Me	229·5 (13,100)	234 (13,300)	327 (18,700)	436 (830)
H	228·5 (13,100)		318·5 (17,000)	436 (750)
F	227·5 (14,000)	232·5 (13,900)	321 (17,300)	435 (740)
Cl	229·5 (13,400)	234·5 (13,900)	325·5 (19,700)	438 (830)
Br	230 (13,400)	235 (13,800)	326·5 (20,300)	438 (920)
I	230 (14,100)		334 (21,300)	438 (960)
CF_3	227·5 (12,100)		318 (17,800)	437 (630)
NO_2			333 (23,500)	451 (700)
cis-Azobenzenes				
OMe	222	229·5	317·5	438
Me	229·5 (16,000)	244 (17,500)	292·5 (10,400)	438 (3100)
H	227 (7800)	243·5 (9100)	285 (7900)	432 (1700)
F	226·5 (16,200)	241·5 (10,100)	287 (10,100)	432 (2600)
Cl	229(s) (9200)	247·5 (10,800)	289 (10,900)	435 (2700)
Br	229·5 (16,900)	248·5 (19,700)	289·5 (11,000)	434 (2900)
I	228·5(s) (9000)	250 (9300)	293 (5300)	438 (1400)
CF_3	227(s)	247	281	432
NO_2	228·5(s)		327·5	438

(s) = shoulder

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[14] P. P. Birnbaum, J. H. Linford, and D. W. G. Style, *Trans. Faraday Soc.*, 1953, **49**, 735.

with hydrogen; this must be a consequence of the diminished conjugation with the N–N π bond and may indicate that the non-bonding lone-pair of electrons on the α-nitrogen atom is overlapping to some extent with the aromatic π system and acting as a π electron donor. It is therefore very unlikely that π conjugation between the rings is of any great significance and some alternative explanation of the large T value must be sought.

The azo-linkage is conventionally regarded as consisting of two sp^2 hybridised nitrogen atoms, each of which has a non-bonding lone-pair of electrons in one of the sp^2 orbitals. In the *trans*-series these lone-pairs are in an antiperiplanar relationship to each other and there is minimum repulsive interaction between them; in the *cis*-compounds however their syncoplanar orientation must result in a significant repulsive interaction between them. If each of these non-bonding orbitals overlaps significantly with the π system of its neighbouring aromatic ring and thereby acts to some extent as a π electron donor (mesomeric effect) it must be considered as part of that π system. The π electron density at the nitrogen atoms will be affected by substituents in the *para*-position in the normal way, and since the repulsive interaction between the two nitrogen sp^2 orbitals will depend upon this electron density it will vary with the substituent nature. There may also be significant repulsive interaction between the ' undersides ' of the two aromatic rings, particularly between those carbon atoms which are α to nitrogen, and there is some evidence for this in the u.v. spectra;[14] this will also be subject to modification by substituent effects in the same way as the nitrogen lone-pair–lone-pair repulsion and it is impossible to separate the consequences of these two effects from each other. There exists, however, an important ' relay ' mechanism by means of which a substituent may affect π electron distribution in the ring to which it is not formally bonded without there being any transfer of charge from one ring to the other; 4′-substituents may therefore change the shielding of a 4-fluorine nucleus in a way which is parallel to the situation in which there *is* formal π conjugation between the rings with transfer of charge between them (*e.g.* the *trans*-azobenzenes).

There would be little point in discussing the two mechanisms of interaction if they do not lead to some demonstrable difference in properties of the two types of system, since substituent effects upon ^{19}F shielding parallel each other exactly (*e.g.* a plot of ^{19}F S.C.S. for the *cis*-series against the *trans* is very precisely linear, of slope 0·90 and correlation coefficient 0·9989). A very significant difference *does* exist between the spectra of *cis*- and *trans*-4,4′-difluoroazobenzenes; in the case of the *trans*-isomer there is a long range (11 bond) coupling between the two fluorines of 1·0 Hz, while in the *cis*-compound it is entirely absent. The coupling shows itself as a doubling of most of the lines in the fluorine spectrum, as compared with the normal ' X part of an AA′BB′X spectrum ' shown by all other members of the series; exactly the same phenomenon ($^{11}J_{FF}$ 0·4 Hz) is present in the spectrum of 4,4′-difluoro-*trans*-stilbene, and was confirmed by proton-noise-decoupling and observing the doublet splitting of the ^{13}C satellites of the singlet fluorine line which remains. The existence of such a coupling may be taken as *a priori* evidence of electron delocalisation between the two fluorine atoms,[15] in support of the ' transmission ' mechanism for substituent effects in the *trans*-series; its absence in the *cis*-compound demonstrates the lack of such electron delocalisation between the sites and is support (albeit of a negative nature) for a ' relay ' mechanism for substituent effects in the *cis*-series.

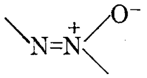
The data for hydrazobenzenes (6) lend some support to these ideas. The consequence of hydrogenation of the azo-linkage is to change the two nitrogens into amine-type sp^3 hybridised atoms; one sp^3 orbital on each is a doubly occupied non-bonding orbital, a ' lone-pair ' which can overlap favourably with the aromatic π system of its neighbouring ring to act as a lone-pair donor. The immediate consequence of this upon the ^{19}F n.m.r. spectrum is to shield considerably the fluorine compared with the unsaturated series; thus, the phenylhydrazino-group (PhNHNH) has a *para* ^{19}F S.C.S. of +11·70 p.p.m., which compares with +14·4 for NH_2. The π electron density upon nitrogen, in what may formally be described as the ' sp^3 lone-pair orbital ' is again subject to modification by ring substituents, hence the repulsive interaction between the two nitrogen lone-pairs will vary with substituent nature; again there is the possibility of ' relay ' of substituent effects from the 4′ to the 4 position. The size of the repulsion will, of course, depend upon the conformational properties of the molecule since the hydrazo-linkage is not rigid like the azo-group; nevertheless, if there *is* significant population of the two staggered conformations in which the nitrogen lone-pairs are considered to be *gauche* to each other, some degree of relay will occur (rapid inversion of the nitrogens will produce an equivalent situation and so may be neglected). Evidence for the predominance of such a conformation in simpler hydrazine derivatives has been given by Radom *et al.*[16] The observed value of T is high for a saturated linking group (0·77, *cf.* 0·0 for $CH_2{\cdot}CH_2$) and is *ca.* 67% of that observed for the *cis*-azo group; this seems reasonable in the light of the above discussion. There is no observable long-range coupling between the two fluorine nuclei in 4,4′-difluorohydrazobenzene.

The azoxy-compounds (3)—(5) were prepared in order to examine the consequences of occupying one of the nitrogen lone-pairs in bonding. In the two *trans*-series, the effect of oxygen is in both cases to deshield the 4-fluorine nucleus compared with the analogous fluorine in the *trans*-azo-compounds, and it would be expected that the largest effect would be observed when the oxygen is bonded to the nitrogen α to the fluorine-containing ring. On this basis, series (4) is assigned the α structure and series (3) the β structure. In the α series, the un-

[15] J. N. Murrell, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 1.

[16] L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 2371.

substituted *trans*-α-phenylazoxy-group has a *para* ^{19}F S.C.S. of −3·71 p.p.m. while in the β series the *trans*-β-phenylazoxy-group has a *para* ^{19}F S.C.S. of −3·37 p.p.m.; these should be compared with −3·25 p.p.m. for *trans*-phenylazo.

In both series the values of T are high (0·95 for α, 1·06 for β, T_α/T_β 0·88) and in the case of 4,4′-difluoroazoxybenzene (which is common to both series) there is an 11 bond J_{FF} of 0·5 Hz which indicates that the substituent effects are indeed transmitted across the bridge by a conjugative mechanism. The fact that T is different for the two isomeric series is interesting; the effect is real, and not an artefact of the analysis, for the S.C.S. in the two series are indeed linearly related with a slope of 0·91 and correlation coefficient of 0·9982. This consequence of the unsymmetrical bridge suggests that the polarisability of the π system along the axis of the  bond is anisotropic; the fact that both series have a smaller T value than *trans*-azobenzenes is probably a consequence of steric interaction between the two rings and the oxygen atom which causes the molecule to adopt a less coplanar conformation and reduces conjugation between the rings.

For the *cis*-azoxybenzenes (5) (probably those in which the oxygen is α to the ring containing fluorine) the T value is very similar to that for the *trans*-series (0·94). Presumably the mechanism is that of ' relay ', and the substituent variation causes modification of the repulsive interaction between the *cis*-oriented N–O bond and lone-pair on the neighbouring atom. There is no observable long range J_{FF} in the 4,4′-difluoro-compound.

Consider now the recent analysis by Taft *et al.*[2] of substituent effects upon ^{19}F shielding in some 18 series of interconnected dinuclear aromatic compounds, *p*-$FC_6H_4{\cdot}Z{\cdot}C_6H_4X$-*p*. This work encompasses data for one of the series discussed above (*trans*-azobenzenes) and for five series (Z = CH_2, HCOH, MeCOH, HC=CH, C=O) discussed by us previously.[1] The treatment is entirely different from that given in our paper, and it should therefore be considered in some detail.

Taft *et al.*[2] analyse substituent chemical shifts in terms of a ' Dual Substituent Parameter ' approach in which the S.C.S. for a given group i in a series j is determined by equation (1). The value of σ_I depends

$$\text{S.C.S.}\ (i,j) = \sigma_I{}^i\rho_I{}^j + \sigma_R{}^{ij}\rho_R{}^j \qquad (1)$$

only upon the nature of the group i, and the values are common to all series; they are determined by linear free energy relationships involving the dissociation constants of 4-substituted bicyclo[2.2.2]octanecarboxylic acids. The values of σ_R depend both upon the nature of the group i and the characteristic structure of the series j; they are intended to reflect not only the nature of the substituent but also the changing ' structural type ' of the group Z which links the rings and four different sets of values j for substituents i apply. The work implies that if an equation such as (1) can be shown to describe a set of data adequately, there is a causal relationship in existence. The coefficients $\rho_I{}^j$ and $\rho_R{}^j$ are taken to be a measure of the effectiveness of the linking group Z in transmitting substituent effects by the ' polar mechanism ' and ' resonance mechanism ' respectively, and Taft *et al.* list the values for best fits to equation (1) for their experimental data (together with their ratio $\lambda = \rho_R/\rho_I$) in Table V of their paper.[2]

In all cases studied, whether the bridge is saturated, unsaturated, or charged the ratio $\rho_R{}^j : \rho_I{}^j$ for every series is quite close to unity [0·97 ± 0·13 (r.m.s.) for 21 sets of data comprising 18 series] even though the values of ρ may vary by more than 20-fold. If the causal relationship implied by equation (1) is accepted, this implies that the group Z, irrespective of its structure, is able to transmit both σ and π electronic substituent effects (over a distance of 10 or 11 bonds) with equal efficiency and that these effects are equally important over such large distances. All MO calculations on aromatic systems however, irrespective of their complexity,[17–19] suggest that attenuation of substituent effects upon electronic distribution in orbitals of σ symmetry is much more rapid than in orbitals of π symmetry. It is most unreasonable to suggest that the two should have comparable effects over such large distances upon ^{19}F shielding (and presumably upon other experimental measurements of substituent effects), and for this reason it is necessary to postulate several different types of interaction between the substituent and the π system which follow the σ_I order rather than σ_R; we shall see later that these are probably artefacts caused by the method of analysis and have no physical significance.

We commented above that in all the series studied by Taft, the values of ρ_I and ρ_R are in an essentially constant ratio to each other of approximately unity. This suggests that, to a degree of approximation which will certainly describe the trends at least, the data could be analysed in terms of equation (2). Originally, σ_R

$$\text{S.C.S.}\ (i,j) = k_j(\sigma_I + \sigma_R) \qquad (2)$$

was defined as the difference between σ_p and σ_I,[20] *i.e.* $\sigma_R{}^i = \sigma_p{}^i - \sigma_I{}^i$ and so equation (2) is simply equivalent to (3). We showed previously[1] that ^{19}F S.C.S. in 4-fluoro-4′-X-*trans*-stilbenes were very precisely related to $\sigma_p{}^i$ in a linear fashion, and so equation (3) is entirely equivalent to the method of analysis adopted by us previously[1] and earlier in the present work, *i.e.* the data

$$\text{S.C.S.}\ (i,j) = k_j\sigma_p{}^i \qquad (3)$$

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[17] J. W. Emsley, *J. Chem. Soc.* (*A*), 1968, 2735.

[18] G. R. Howe, *J. Chem. Soc.* (*B*), 1971, 984.

[19] W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496.

[20] J. D. Roberts and W. T. Moreland, *J. Amer. Chem. Soc.*, 1953, **75**, 2167.

given by Taft *et al.* should be linearly related to the S.C.S. in the series of stilbenes.

Table 7 lists the slopes of linear correlation of Taft's experimental data with the S.C.S. of the corresponding series of *trans*-fluorostilbenes obtained previously by us;[1,2] also listed are correlation coefficients, standard deviations, and ' fit parameters f ' (defined by Taft *et al.* as the ratio of the standard deviation to the r.m.s. of the data points, but of limited statistical significance except for comparative purposes between similar treatments of similar sets of data). These latter parameters are also listed for the Dual Substituent Parameter treatment.[2]

The first point to observe is the result of correlating our stilbene data with those of Taft *et al.*; the correlation coefficient of 0·9952 and 'f' value of 0·10 demonstrate the experimental error between the two sets of data and set a limit upon the best correlations that can reasonably be expected. Taft *et al.* regard a value of $f = 0{\cdot}10$ as a limiting criterion of high significance, but in order to accommodate the probable experimental errors between the data sets we take a value of $f \leqslant 0{\cdot}20$ (corresponding to a correlation coefficient of *ca.* 0·98) as representing a highly significant correlation. The data for 12 different series (14 sets of data) lie within this very high level of significance and only six series (seven data sets) lie outside; even in those sets for which the correlation is not so precise, however, the linear relationships describe the trend very adequately, with correlation coefficients of between 0·92 and 0·98. (The sole exception is that in which $Z = \overset{-}{C}{=}N$, which Taft also finds to be anomalous.)

The only series of the type in which Z is uncharged [*i.e.* Z = saturated or unsaturated linkage, either ' $\sigma_R{}^0$ ' or ' σ_R(BA) ' type according to Taft *et al.*[2]] which lies outside the ' very highly significant ' range is that in which $Z = C(OH)CF_3$ for which there are two sets of data available (one for solutions in CH_2Cl_2, the other for benzene solutions). This alcohol would be expected to be significantly acidic however, and the varying degrees of dissociation which would occur as a result of substituent variation together with the failure to extrapolate results to infinite dilution could easily account for the observed scatter in the linear correlation; the correlation coefficients (0·9745 for CH_2Cl_2 solutions, 0·9674 for C_6H_6 solutions) show that the linear relationship is, in fact, a fair description of the observed trend.

Of the postively charged series (Taft's $\sigma_R{}^+$ types), two ($Z = CH{=}\overset{+}{N}H$ and $\overset{+}{N}H{=}CH$) must be regarded as showing perfectly satisfactory behaviour (correlation co-

TABLE 7

A comparison of the Dual Substituent Parameter treatment of the data of Taft *et al.*,[2] with a single parameter analysis for p-$FC_6H_4{\cdot}Z{\cdot}C_6H_4X$-$p$

						Dual Substituent Parameter treatment	
Z	Solvent	Slope	Standard deviation	Correlation coefficient	f	Standard deviation	f
CH_2	CH_2Cl_2	0·41	0·05	0·9921	0·12	0·08	0·06
CHPh	CH_2Cl_2	0·40	0·06	0·9912	0·12	0·03	0·08
CHOH	CH_2Cl_2	0·49	0·06	0·9915	0·13	0·05	0·09
CHOH	C_6H_6	0·52	0·07	0·9933	0·11	0·07	0·11
C(OH)Me	CH_2Cl_2	0·56	0·07	0·9943	0·10	0·04	0·09
C(OH)Ph	CH_2Cl_2	0·43	0·05	0·9912	0·13	0·07	0·10
$C(OH)CF_3$	CH_2Cl_2	0·47	0·10	0·9745	0·22	0·04	0·09
$C(OH)CF_3$	C_6H_6	0·48	0·12	0·9674	0·25	0·03	0·07
CH=N	C_6H_6	0·86	0·03	0·9995	0·10	0·04	0·08
N=CH	C_6H_6	0·88	0·07	0·9979	0·07	0·09	0·07
$\diagdown{=}\diagdown$	C_6H_6	0·95	0·11	0·9952	0·10	0·08	0·07
C=O	CH_2Cl_2	1·04	0·22	0·9845	0·18	0·12	0·09
C=NH	$CHCl_3$	1·22	0·17	0·9896	0·14	0·08	0·07
$\diagdown N{=}N\diagdown$	C_6H_6	1·21	0·07	0·9968	0·08	0·04	0·04
$CH{=}\overset{+}{N}H$	FSO_3H	1·66	0·17	0·9959	0·09	0·13	0·05
$\overset{+}{N}H{=}CH$	FSO_3H	1·46	0·35	0·9759	0·22	0·16	0·08
$\overset{+}{C}{-}CH_3$	FSO_3H	18·53	4·30	0·9515	0·24	0·62	0·03
$\overset{+}{C}H$	FSO_3H	18·31	6·76	0·9259	0·31	1·37	0·06
$\overset{+}{C}F_3$	FSO_3H	25·21	6·91	0·9375	0·32	1·28	0·05
$\overset{-}{C}C_6H_5$	Me_2SO	4·25	1·35	0·9649	0·26	0·36	0·06
$\overset{-}{C}{=}N$	Me_2SO	1·02	0·77	0·7655	0·59	1·47	0·38

efficients 0·9959 and 0·9759 respectively) while three have correlation coefficients of <0·98. The use of fluorosulphonic acid as a solvent must, however, cause great ' solvent effects ', especially when substituents such as OMe and NMe_2 are included in the six or so compounds studied; these must surely be significantly (if not completely) protonated under the experimental conditions. Probably the largest contributory factor to the observed imprecision (correlation coefficients of 0·9515 for Z = $\overset{+}{C}$Me, 0·9259 for Z = $\overset{+}{C}$H, and 0·9375 for Z = $\overset{+}{C}CF_3$) arises from this cause. It is surely significant that neither of the series which does show highly precise correlations in this medium (Z = CH=$\overset{+}{N}$H, $\overset{+}{N}$H=CH) has an *NN*-dimethyl substituted member!

The two negatively charged series, Z = $\overset{-}{C}C_6H_5$, $\overset{-}{C}$=N, both show significant deviation but the former set of data (correlation coefficient 0·9649) must be regarded as satisfactory in the light of the probable solvent effects in dimethyl sulphoxide solution; the latter series does appear to be anomalous, as it is in Taft's treatment of the data.

We feel that the success and generality of the correlations of these data with substituent effects upon ^{19}F shielding in the stilbene series probably indicates a common origin for all the substituent effects studied, *i.e.* a perturbation of the π system which follows the simple Hammett σ_p order. A Dual Substituent Parameter treatment (which actually uses three variable parameters σ_R^{ij}, ρ_I^j, ρ_R^j) can give *statistically* more significant results as Taft has shown; this is not surprising because of the large number of in-built degrees of freedom of choice, but it is probably wrong to infer that this tells us anything about the ' mechanism ' of transmission of substituent effects in these series.

It seems probable that the correlations which have very large slopes (or *T* values in our nomenclature), namely those for the series in which Z = $\overset{+}{C}$Me, $\overset{+}{C}$H, $\overset{+}{C}CF_3$, and $\overset{-}{C}C_6H_6$, do so because the proportionality constant, *k*, relating shielding changes to π electron density variation is unusually large and *not* because these π electron density changes are themselves large. *k* Depends in part upon the inverse of an average excitation energy, ΔE, and this will be smaller in charged species because of easier accessibility of excited states. As pointed out earlier, small values of ΔE are more likely to show a significant dependence upon the substituent group X than are large values and variation in ΔE (and hence *k*) throughout a series may be a contributing factor to the relative imprecision of the correlations for these species.

It is relevant, now, to turn to some more recent work in which a Dual Substituent Parameter approach has been utilised to interpret n.m.r. shielding data. Hamer *et al.*[21,22] utilise the *F* (field) and *R* (resonance) parameters of the Swain–Lupton [23] equation (4) and have

$$\text{S.C.S.} = fF + rR \qquad (4)$$

analysed in this manner the substituent effects upon ^{1}H and ^{13}C shielding in the side chains of 4-substituted styrenes,[21] α-methylstyrenes,[22] and α-t-butylstyrenes.[22] They give an excellent and well reasoned analysis of the origin of these effects in terms of through-space field interactions (Buckingham's approach [24]) and through-bond electronic effects which are supported by CNDO/2 calculations of charge density distributions. The ' through-bond effects ' are analysed in terms of ' resonance ' and ' π polarisation ', and Hamer *et al.* conclude that when all these factors are considered together the use of *F* and *R* parameters in equation (4) gives satisfactory results and the values of the weighting factors *f* and *r* are very reasonable and completely accounted for.

The ' resonance effect ' is characterised by a transfer of charge from the substituent to the aromatic system, and the parameter *R* is taken to be a measure of this. The ' π polarisation effects ' however do not involve charge transfer and Hamer *et al.* describe them as being a ' type of π inductive effect '. There are two distinct types, one of which occurs when there is no conjugation between the phenyl ring and the vinyl π system (dihedral angle approaching 90°) and results in the two groups being independently polarised (presumably by the substituent acting through space); when conjugation is important there is an additional polarisation of the entire conjugated π system which in turn causes polarisation of the σ MOs at distances which are considered to be too great from the substituent to allow for the normal σ inductive effect. This latter is Taft's ' resonance polar effect ',[2,25,26] and the conclusions reached by Hamer *et al.* are very similar to those of Taft *et al.*[2] which were discussed above.

Previously [8] we showed that it was possible to give an exactly equivalent treatment of data which correlate with a two-parameter equation involving *F* and *R* by using σ_I and σ_p, which have the advantage of being experimentally determinable by direct methods. We interpret σ_p as being a measure of the ability of a substituent group to perturb a π system by *all* mechanisms, including mesomeric and π inductive interactions, and hence ^{19}F S.C.S. in the many series of dinuclear aromatic compounds discussed here and previously correlate very well with σ_p. ^{19}F S.C.S. in *para*-substituted fluorobenzenes do not correlate with σ_p however, but they do so with a Dual Substituent Parameter equation involving σ_p and σ_I.[8] It seems probable that, in π conjugated and related systems, a ' cross-over point ' may occur beyond

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[21] G. K. Hamer, I. R. Peat, and W. F. Reynolds, *Canad. J. Chem.*, 1973, **51**, 897.

[22] G. K. Hamer, I. R. Peat, and W. F. Reynolds, *Canad. J. Chem.*, 1973, **51**, 915.

[23] C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, 1968, **90**, 4328.

[24] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.

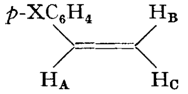
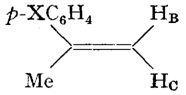
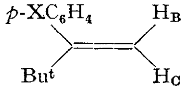
[25] R. W. Taft, ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, pp. 570, 578.

[26] R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, 1970, **92**, 7007.

which (in terms of the separation between X and F) correlation with a ' π only ' parameter, namely σ_p, will occur; at closer distances, correlation with a Dual Substituent Parameter equation involving σ_p and σ_I will describe the data better.

TABLE 8

Correlation of ^1H and ^{13}C S.C.S. of the side-chain nuclei in styrene derivatives, with ^{19}F S.C.S. in 4-fluoro-*trans*-stilbenes

	Slope	Standard deviation	Correlation coefficient
			
δ(A)	−0·05	0·03	0·8566
δ(B)	−0·11	0·02	0·9748
δ(C)	−0·13	0·01	0·9940
δ(B − C)	0·02	0·01	0·8096
C(α)	0·45	0·30	0·8465
C(β)	−2·21	0·23	0·9952
			
δ(B)	−0·07	0·02	0·9575
δ(C)	−0·10	0·01	0·9944
δ(B − C)	0·03	0·01	0·9011
C(α)	0·25	0·36	0·6206
C(β)	−1·77	0·20	0·9948
			
δ(B)	−0·03	0·006	0·9806
δ(C)	−0·04	0·007	0·9901
δ(B − C)	0·02	0·001	0·9975
C(α)	0·41	0·27	0·8494
C(β)	−0·48	0·17	0·9476

Substituent effects upon ^{13}C and ^1H n.m.r. shielding in aromatic compounds often show very similar trends to ^{19}F shielding[27] so it is valid to examine the data of Hamer *et al.* in this way. Table 8 shows the results of correlating the ^1H and ^{13}C chemical shifts of the side-chain nuclei in the three series of styrene derivatives with the *para* ^{19}F S.C.S. in our fluorinated *trans*-stilbenes. The trend is very clear; carbon atoms and hydrogen nuclei which are α to the ring have chemical shifts which ***do not*** correlate significantly with the ^{19}F S.C.S. (or therefore, with σ_p); in all three series of styrenes however, the shielding of the β carbon atoms and protons correlate linearly (with very high correlation coefficients) with the stilbene ^{19}F S.C.S. The β hydrogen atom *cis* to the ring shows a slightly lower correlation coefficient than that which is *trans*, presumably due to the slight effect of changing the diamagnetic susceptibility of the ring upon substituent variation.[21,22] In all, we use 11 of the available data points since this represents the limit of the stilbene data presently available; it is particularly encouraging however to note that all the halogen substituents are included even though these are excluded as ' anomolous substituents ' in the treatment of Hamer.

The shielding data for the α protons and carbon atoms are successfully analysed in terms of F and R parameters[21,22] and hence presumably also in terms of σ_I and σ_p;[8] we do not wish to offer the alternative treatment here however, since the argument would be of a semantic nature. Suffice it to say that we agree with Hamer *et al.* that *both* σ and π type interactions are important, in accord with our analysis of substituent effects upon ^{19}F S.C.S. of the similarly situated fluorine nucleus in *para*-substituted fluorobenzene.[8]

We conclude that the superiority of Dual Substituent Parameter treatments of shielding data over a single parameter analysis, as judged by statistical criteria, should not be used as a reason for proposing unusual mechanisms for the transmission of substituent effects. A single parameter treatment (*i.e.* correlation with ^{19}F S.C.S. in 4-substituted 4′-fluoro-*trans*-stilbenes and hence with σ_p) works very well for all 4,4′-disubstituted linked dinuclear aromatic compounds so far examined, and also for ^{13}C and ^1H S.C.S. of nuclei which are β to a ring system.

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