^{19}F Nuclear Magnetic Resonance Studies of Aromatic Compounds. Part II.† The ^{19}F Chemical Shifts in *meta*- and *para*-Substituted Fluorobenzenes, and 4-Substituted 3′- and 4′-Fluoro-*trans*-stilbenes

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A detailed study has been made of the effects of substituents, X, upon the shielding of ^{19}F nuclei in series of *meta* and *para*-X-fluorobenzenes, 4-X-4′-fluoro-*trans*-stilbenes, and 3′-fluoro-4-X-*trans*-stilbenes. The correlation of substituent chemical shifts for ^{19}F nuclei in fluoroaromatic compounds with reactivity parameters is examined, and a reassessment is made of the Taft and Swain and Lupton separation of polar substituent effects into field/inductive and resonance components.

THE study of substituent effects upon ^{19}F shielding in aromatic fluorine-containing molecules is of interest.[1-3] Many attempts have been made to interpret such effects in terms of local electron density changes caused by the ring substituents, by use of a variety of molecular orbital methods ranging from the simple Hückel MO theory to VESCF methods.[4] The approach underlying most of this work has been to assume that in *para*-substituted fluorobenzenes the interacting groups are sufficiently separated for σ bond effects to be negligible and to relate the observed shielding changes to π-electronic density variation upon the carbon atom α to fluorine. A growing amount of experimental evidence suggests however that even at such distances 'electric field' or σ-bond transmitted substituent effects may be important[5,6] and so it was decided to examine the possibility that changes in both σ and π terms contribute significantly to substituent effects upon the shielding of *para*-oriented fluorine nuclei in aromatic systems. The significance of both types of interaction has recently been shown for *ortho*-substituted fluorobenzenes,[3] and it was also decided to investigate the *meta*-substituted situation in the course of the present work.

The approach adopted here is to study first a related aromatic system in which the interacting groups are so

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† Part I, I. R. Ager and L. Phillips, preceding paper.

[1] J. W. Emsley and L. Phillips, *Mol. Phys.*, 1966, **11**, 437.

[2] J. W. Emsley and L. Phillips, *J. Chem. Soc.* (*B*), 1969, 434.

[3] L. Phillips and V. Wray, *J.C.S. Perkin II*, 1972, 223.

[4] J. W. Emsley and L. Phillips, 'Progress in Nuclear Magnetic Resonance Spectroscopy,' eds. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon Press, Oxford, vol. 7, 1971.

[5] L. Phillips and V. Wray, *J. Chem. Soc.* (*B*), 1971, 1618.

[6] G. L. Anderson and L. M. Stock, *J. Amer. Chem. Soc.*, 1968, **90**, 212.

far apart that σ-bond effects must be negligible. Series of 4-X-4′-fluoro-*trans*-stilbenes and 3-X-4′-fluoro-*trans*-stilbenes were prepared for this reason, in the hope that examination of their chemical shifts might give some information about the importance of π terms in analogous benzene derivatives.

EXPERIMENTAL

All compounds (Table 1) were identified and characterised by the use of i.r. u.v. and n.m.r. spectroscopy.

The *trans*-stilbenes were synthesised according to the methods described below.

*4-Fluoro-*trans*-stilbene* (I).—*p*-Fluorophenylacetic acid (1·5 g, 9·7 mmol), benzaldehyde (1·0 g, 9·4 mmol), trimethylamine (1·0 g, 10 mmol), and acetic anhydride (5·1 g, 50 mmol) were refluxed at 150—160 °C for 15 h. After cooling the product was poured into 20% hydrochloric acid (100 ml) and extracted with ether (2 × 50 ml). The combined ether extracts were washed with water and extracted with 5% sodium hydroxide solution (2 × 50 ml). The base extracts were acidified with concentrated hydrochloric acid and the precipitated α-(*p*-fluorophenyl)cinnamic acid was filtered off, washed with water, and dried under vacuum; yield 1·0 g (44%). This acid was decarboxylated by refluxing with quinoline (10 g, 77·5 mmol) and copper chromite (0·2 g) at 200—230 °C for 90 min. The product was allowed to cool, poured into 20% hydrochloric acid (100 ml), and extracted with ether (2 × 50 ml). The combined ether extracts were filtered, washed with 5% hydrochloric acid, water, dilute sodium hydrogen carbonate solution and water and dried ($MgSO_4$). The ether was removed under vacuum and the brown solid obtained was recrystallised from hexane to give pale pink *plates*; yield 128 mg (16%), m.p. 122—123 °C (lit.[7] 126 °C).

TABLE 1

M.p.s and quantitative elemental analysis

Compound	M.p./°C	Found (%)							Required (%)						
		C	H	N	F	Cl	Br	I	C	H	N	F	Cl	Br	I
(I)	122—123 [a]	84·8	5·41		9·64				84·84	5·35		9·60			
(II)	157—158 [b]	85·1	6·06		9·72				84·90	6·13		8·96			
(III)	153—154	53·4	3·6					36·7	51·90	3·10					39·20
(IV)	133—134 [c]	69·0	4·19	5·81	7·0				69·20	4·12	5·77	7·82			
(V)	196	78·85	5·16						78·5	5·18					
(VI)	84—86 [d]	69·1	4·26	5·90	7·80				69·2	4·12	5·77	7·82			
(VII)	70—72	84·8	5·38		9·90				84·6	5·56		9·60			
(VIII)	91—92	76·9	5·04		17·55				77·8	4·63		17·59			
(IX)	80—82	72·1	4·03		7·9	14·91			72·3	4·30		8·2	15·26		
(X)	84—86	61·1	3·82		7·05		28·1		60·7	3·61		6·85		28·8	
(XI)	131—133	69·3	4·16	5·88	7·76				69·2	4·12	5·77	7·82			
(XII)	169—170 [e]	77·8	5·77	6·50					78·9	5·64	6·56				
(XIII)	194—196	79·3	6·46	5·77	5·45				79·7	6·63	5·81	7·88			
(XIV)	196—197	52·8	4·89	3·40	4·25			33·9	53·3	4·96	3·66	4·96			33·2
(XV)	109—110	78·75	5·65	6·48	8·88				78·9	5·64	6·58	8·92			
(XVI)	128—128·5	78·8	5·76	6·43	8·96				78·9	5·64	6·58	8·92			
(XVII)	142	78·41	5·79						78·91	5·74					
(XVIII)	136 [f]														
(XIX)	130 [f]														
(XX)	139 [f]	72·13	4·37		7·93	15·05			72·23	4·33		8·17	15·26		
(XXI)	138 [f]														
(XXII)	43—44	78·98	5·54		8·33				78·94	5·70		8·33			
(XXIII)	99—101	83·7	6·20		8·97				84·9	6·13		8·96			
(XXIV)	157—159	78·5	5·11		9·7				78·5	5·14		8·9			
(XXV)	108—110	77·2	5·71		8·94				79·0	5·71		8·34			
(XXVI)	110—112	77·9	6·20		9·0				79·3	6·20		7·86			
(XXVII)	*g*														
(XXVIII)	*g*														
(XXIX)	218—219	38·4	4·79	4·83	6·76			45·1	38·4	4·63	4·98	6·85			45·2

[a] Ref. 7 gives m.p. 126 °C. [b] Ref. 8 gives m.p. 159 °C. [c] R. A. Andersen, H. Enomoto, E. C. Miller, and J. A. Miller, *Cancer Res.*, 1964, **24**, 128, give m.p. 133—134 °C. [d] R. G. Pews and N. D. Ojha, *J. Amer. Chem. Soc.*, 1969, **91**, 5769, give m.p. 82 °C. [e] Ref. 8 gives m.p. 164 °C. [f] Analysis not available. [g] See text.

4-Methyl-4′-fluoro- (II), *4-iodo-4′-fluoro-* (III), *4-nitro-4′-fluoro-* (IV), *4-hydroxy-4′-fluoro-* (V), *3-nitro-4′-fluoro-* (VI), *3-fluoro-* (VII), *3,4′-difluoro-* (VIII), *4-chloro-3′-fluoro-* (IX), *4-bromo-3′-fluoro-* (X), and *4-nitro-3′-fluoro-*trans-*stilbene* (XI) were prepared by the method described for (I) and purified by column chromatography.

*4-Amino-4′-fluoro-*trans-*stilbene* (XII).—4-Nitro-4′-fluoro-*trans*-stilbene (IV) (500 mg, 2·1 mmol) was warmed with ethanol (25 ml) and 5% palladium on charcoal (25 mg) until refluxing commenced, whereupon 100% hydrazine hydrate (1 ml, 1·03 g, 20·6 mmol) was added and the mixture was refluxed for a further 2 min. The product was allowed to cool, the catalyst was filtered off, and the solvent was removed under vacuum to leave a pale yellow solid. This was recrystallised from hexane–chloroform to give an off-white crystalline *solid*; yield 205 mg (47%, m.p. 169—170 °C (lit.,[8] 164 °C).

*4-Dimethylamino-4′-fluoro-*trans-*stilbene* (XIII).—*p*-Dimethylaminobenzaldehyde (1·5 g, 10·1 mmol) and *p*-fluorophenylacetic acid (1·5 g, 9·7 mmol) were refluxed in piperidine (1 ml, 0·86 g, 10·1 mmol) at 160 °C for 16 h. The product was allowed to cool, dissolved in methylene dichloride, and carefully neutralised to litmus by shaking with very dilute hydrochloric acid. The organic layer was separated, washed with water, dilute potassium

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[7] L. Ya Malkes, A. I. Timchenko, and L. L. Nagornaya, *Zhur. obshchei Khim.*, 1962, **32**, 893.

[8] T. J. Tewson, 3rd Year Research Report, Imperial College, 1967.

carbonate solution, and water and dried ($MgSO_4$), and the solvent removed to give a brown solid. The product was boiled with acetone–ethanol to remove excess of starting material, filtered hot, and washed with ethanol. The pale yellow crystals were recrystallised from chloroform to give very pale green *flakes*; yield 650 mg (27%), m.p. 194—196 °C. 4-*Trimethylammono*-4′-*fluoro*-trans-*stilbene iodide* (XIV) was prepared by quaternisation of (XIII) with methyl iodide. 4-*Amino*-3′-*fluoro*- (XV) and 3-*amino*-4′-*fluoro*-trans-*stilbene* (XVI) were prepared by the method described for (XII).

4-*Methoxy*-4′-*fluoro*-trans-*stilbene* (XVII).—4-Hydroxy-4′-fluoro-*trans*-stilbene (V) (40 mg, 0·2 mmol) was dissolved in dilute aqueous sodium hydroxide and dimethyl sulphate (2 ml, 2·65 g, 21 mmol) was added. After stirring for 12 h the solution was boiled briefly and allowed to cool, and the *product* was filtered off; this was recrystallised from ethanol and purified by vacuum sublimation; yield 30 mg (70%), m.p. 142 °C. 4-*Ethoxy*-4′-*fluoro*-trans-*stilbene* (XVIII) was prepared by a similar method to (XVII) with diethyl sulphate instead of dimethyl sulphate.

4,4′-*Difluoro*-trans-*stilbene* (XIX).—The Grignard reagent from *p*-fluorobenzyl chloride (1·0 g, 6·9 mmol) and magnesium (170 mg, 6·9 mmol) was prepared in diethyl ether, and *p*-fluorobenzaldehyde (1·0 g, 8 mmol) in ether was slowly added with stirring. The mixture was refluxed for 2 h and worked up with saturated ammonium chloride solution. The ether layer was separated, washed twice with water and dried ($MgSO_4$), and the solvent was removed to give crude 1,2-bis-*p*-fluorophenylethanol, a yellow oil. The alcohol was dehydrated by refluxing in benzene with phosphoric oxide (1·5 g, 10 mmol) for 15 min. The benzene was removed under reduced pressure, the excess of phosphoric oxide decomposed with water, and the product dissolved in aqueous potassium hydroxide. The product was extracted with ether, washed three times with water and dried ($MgSO_4$) and the solvent removed to give a yellow oil. The oil was purified by column chromatography (grade III alumina, 25% benzene in light petroleum) and recrystallised from light petroleum (b.p. 40—60 °C) to give a white crystalline *solid*; yield 200 mg (10%), m.p. 130 °C. 4-*Chloro*-4′-*fluoro*- (XX), 4-*bromo*-4′-*fluoro*- (XXI), 4-*fluoro*-3′-*methoxy*- (XXII), and 4-*methyl*-3′-*fluoro*-trans-*stilbene* (XXIII) were prepared in an analogous way to (XIX).

4-*Hydroxy*-3′-*fluoro*-trans-*stilbene* (XXIV).—*m*-Fluorophenylacetic acid (1·5 g, 9·7 mmol), *p*-hydroxybenzaldehyde (1·2 g, 9·8 mmol), and piperidine (1 ml, 0·86 g, 10·1 mmol) were refluxed at 160—170 °C for 3 h. The red gum formed was dissolved in acetone, poured into excess of dilute hydrochloric acid (400 ml), extracted with chloroform (3 × 50 ml) and dried ($MgSO_4$), and the solvent was removed to give a brown oil. This oil was purified by column chromatography (grade III alumina, 50% methanol in chloroform), decolourised with charcoal, and recrystallised from ethanol–water to give a colourless *solid*; yield 337 mg (16%), m.p. 157—159 °C. 4-*Methoxy*-3′-*fluoro*- (XXV) and 4-*ethoxy*-3′-*fluoro*-trans-*stilbene* (XXVI) were prepared from (XXIV) by reaction with dimethyl sulphate and diethyl sulphate respectively.

4-*Iodo*-3′-*fluoro*-trans-*stilbene* (XXVII).—4-Amino-3′-fluoro-*trans*-stilbene (XV) (150 mg, 0·7 mmol) was dissolved in 33% hydrochloric acid (3 ml) and diazotised with sodium nitrite solution (0·7 g, 10 mmol in 5 ml of water). The diazo-salt was treated with potassium iodide (1·7 g, 10·8 mmol in 2 ml of water), the solution was basified with sodium hydroxide solution, and the product was extracted with ether. The ether extract was washed with sodium thiosulphate solution and water and dried (Na_2SO_4) and the solvent removed to give an orange solid. This product was purified by column chromatography (grade III alumina, benzene) and recrystallised from methanol–water to give pale yellow crystals; yield 61 mg (27%). The ^{1}H n.m.r. indicated that the material was not pure, owing to partial reduction of the double bond, but further purification was not attempted.

NN-*Dimethyl*-p-*fluoroaniline* (XXVIII).—*p*-Fluoroaniline (2·2 g, 19·8 mmol), 40% formaldehyde solution (3·0 g, 40 mmol), and 5% palladium on charcoal were added to methanol (25 ml) and the mixture shaken under hydrogen at room temperature and atmospheric pressure for 15 h during which *ca.* 900 ml of hydrogen were taken up. The catalyst was filtered off, the solvent removed under reduced pressure, and the product redissolved in ether. The ether solution was washed twice with water and dried ($MgSO_4$) and the ether removed to leave an orange *oil*; yield 2·1 g (75%).

p-*Trimethylammoniofluorobenzene Iodide* (XXIX).—NN-Dimethyl-*p*-fluoroaniline ((XXII) 0·7 g, 5 mmol) was quaternised with methyl iodide in the usual manner. The product was recrystallised from methanol to give a colourless crystalline *solid*; yield 0·6 g (43%), m.p. 218—219 °C.

meta *and* para-*Substituted Fluorobenzenes*.—These were obtained from Koch–Light and used without further purification.

N.m.r. Spectra.—These were recorded with a Varian HA100 sprctrometer operating under field-frequency locked conditions with extended lock and phase compensation[9] to enable spectral lines up to 20 kHz from reference to be recorded in absorption mode. The chemical shifts were measured as the difference between the resonance frequency of the reference (internal hexafluorobenzene) and that of the sample by means of a frequency counter accurate to ±0·1 Hz. The shift of each compound was recorded for a number of different low concentrations, usually dissolved in n-hexane, and the results extrapolated to infinite dilution. Table 2 lists ^{19}F chemical shifts recorded in this way.

TABLE 2

Observed ^{19}F chemical shifts for a variety of aryl fluorides. Positive shifts (p.p.m.) are to high field of internal hexafluorobenzene, recorded for infinitely dilute solutions in n-hexane or chloroform unless otherwise indicated

	4-X-Fluorobenzenes	*trans*-Stilbenes			
		4-X-4′-F			
		Hexane	$CHCl_3$	3-X-4′-F	4-X-3′-F
NMe_2	−35·86	−46·98			
NH_2	−35·94	−47·27	−46·45	−47·77	−49·04
OH	−38·46		−46·86		−48·75 [a]
OMe	−38·48		−46·96	−48·10	−49·26
Me	−44·61	−48·21	−47·24		−49·38
H	−50·08	−48·58	−47·58	−48·09	−49·52
F	−43·18		−47·72	−48·91	−49·65
Cl	−46·78		−48·08		−49·79
Br	−47·35		−48·16		−49·80
I	−48·32	−49·34			−49·82
NO_2	−58·87	−50·96	−49·84	−49·97	−50·61
NMe_3^+	−51·73 [b]	−50·26 [b]			

[a] CCl_4 solvent. [b] Dimethylformamide solvent.

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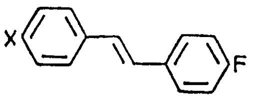
[9] P. N. Jenkins and L. Phillips, *J. Phys.* (*E*), 1971, **4**, 530.

Molecular Orbital Calculations.—It seems reasonable to assume that if the group X, in a series of 4-X-4′-fluoro-*trans*-stilbenes is changed then the accompanying variation in the shielding of the ^{19}F nucleus will parallel changes in the π-electron density at the carbon atom α to fluorine;[4] perturbation of the σ- electronic framework will be negligible in the region of the fluorine. It should be possible to calculate the π electron density variation at this carbon in terms of MO theory and check the exactness of the correlation, but because of the large size of the stilbene molecules it was impracticable to carry out sophisticated MO calculations during the present work.



(1)

It seems unlikely that advanced MO methods such as the all valence electron VESCF method used by Emsley[10,11] offer very significant improvement over simple Hückel MO calculations (HMO) for the estimation of relative electron densities at positions *para* to substituents in a series of such molecules, although of course they are very significantly better for other positions in the ring and for calculating electronic distributions and both π and σ energy levels.

It was decided to adopt the semiempirical HMO method for this study. In common with more sophisticated LCAO–MO theories, this method predicts that the π electron densities upon the carbon atom bonded to fluorine (and upon the fluorine atom itself) in the series of 4-X-4′-fluoro-*trans*-stilbenes are linearly related to those in 4-X-fluorobenzene [equation (1)].

$$\delta\pi_{(C-F)}(\text{benzene}) = k\delta\pi_{(C-F)}(\text{stilbene}) \qquad (1)$$

The value of k is independent of the coulomb (α) and exchange (β) integrals chosen for the substituents X and F, but depends solely upon the approximations made concerning the equality of α values for the carbon atoms and β value for the C–C bonds constituting the π MO framework.

TABLE 3

Relative π electron charge densities upon the carbon atom bonded to fluorine in 4-X-fluorobenzenes and 4-X-4′-F-*trans*-stilbenes. The values of α_X $(=\alpha_0 + h_X\beta_0)$ and $\beta_{CX}(=k_{CX}\beta_0)$ and $\alpha_{C1}(=\alpha_0 + h_1\beta_0)$ are arbitrary

α_X	β_{CX}	α_{C1}	4-X-Fluoro-benzenes	4-X-4′-F-*trans*-stilbenes
1·03	1·00		0·0699	0·0097
1·32	1·00		0·0597	0·0080
1·85	0·90		0·0383	0·0048
2·10	0·90		0·0346	0·0043
2·50	0·70		0·0183	0·0022
			0·0000	0·0000
2·20	0·80	0·42	−0·0133	−0·0014
1·50	0·50	0·50	−0·0329	−0·0037
1·30	0·40	0·50	−0·0371	−0·0042
1·00	0·30	0·50	−0·0404	−0·0046
3·50	0·50	0·90	−0·0776	−0·0091
5·00	0·50	1·43	−0·1207	−0·0144

Table 3 lists the π electron density at C-4 in a series of 1-substituted 4-fluorobenzenes, an arbitrary set of parameters being used for α(X) and β(C–X). The parameters are defined in the usual way, namely $\alpha_X = \alpha_O + h_X\beta_0$ and $\beta_{C-X} = k_{CX}\beta_0$; in some cases, the C-1 (bonded to X) is given a non-standard value of α, $\alpha_1 = \alpha_0 + h_1\beta_0$ (A.I.P.). With the same set of parameters, the π-electron densities at the C-4′ in 4-X-4′-fluoro-*trans*-stilbenes were calculated (full conjugation being assumed), and relative values are listed in Table 3. A plot of the two sets of calculated values is linear, and shown in Figure 1 to yield a value for k of 8·072 (calculated by least squares) [*i.e.*, equation (2)].

$$\delta\pi_{(C-F)}(\text{4-X-fluorobenzenes}) = 8{\cdot}072\delta\pi_{(C-F)}(\text{4-X-4}'\text{-fluoro-}trans\text{-stilbenes}) \qquad (2)$$

If the s.c.s. in the stilbene series are solely controlled by π electronic changes, then the effective π contributions to the s.c.s. in the *para*-X-fluorobenzenes can easily be calculated; they should be 8·072 times larger than the corresponding s.c.s. in 4-X-4′-fluoro-*trans*-stibene and are calculated and shown in Table 4. Ideally, allowance should be made for the fact that the stilbenes may not be completely planar and there will be some steric inhibition

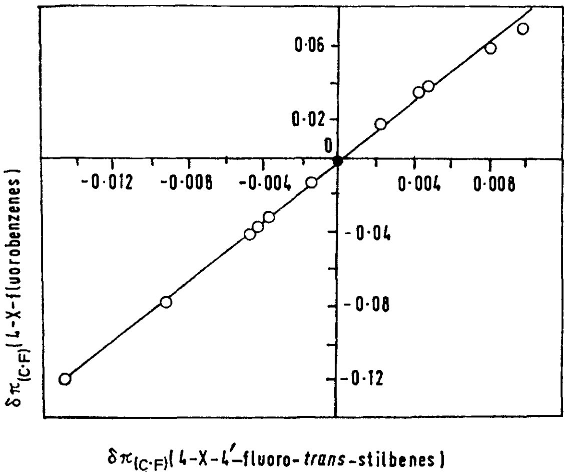


FIGURE 1 Relative π-electron densities upon the C atom bonded to F in 4-X-fluorobenzenes, plotted against the corresponding values in 4-X-4-F-*trans*-stilbenes

TABLE 4

Calculated π electron s.c.s. for *p*-X-fluorobenzenes

X	Calc.[a]	Obs.[a]	(Obs. − calc.)	σ_I
NMe_2	12·92	14·22	1·30	
NH_2	10·57	14·14	3·57	0·10
OH	6·38	11·62	5·24	0·25
OMe	5·73	11·60	5·87	0·23
Me	2·93	5·47	2·48	−0·05
H	0·00	0·00	0·00	0·00
F	−1·94	6·90	8·84	0·50
Cl	−5·01	3·30	8·31	0·47
Br	−5·57	2·73	8·30	0·45
I	−6·14	1·76	7·90	0·38
NMe_3^+	−12·03	−1·03	11·00	
NO_2	−19·21	−8·79	10·42	0·63

[a] Solution in n-hexane, p.p.m. to high field positive. Calculated from data for solution in dimethylformamide by means of the precise solvent–solvent relationships discussed in the preceding paper.

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[10] J. W. Emsley, *J. Chem. Soc.* (*A*), 1968, 2018.

[11] D. T. Clarke and J. W. Emsley, *J. Chem. Soc.* (*A*), 1968, 2523.

of conjugation; recent calculations by Pople *et al.* however indicate that in the sterically similar molecule styrene a coplanar arrangement can be maintained by relaxing of bond angles without introducing a dihedral angle beteeen the ' olefinic ' bond and the ring, in which case full π conjugation would persist.[12] If, in fact, there was a dihedral angle of say 15° between each ring and the olefinic bond to which they are conjugated, this would allow for *ca.* 85% conjugation and the calculated π s.c.s. contributions in Table 4 would be *ca.* 15% too small.

In order to check the validity of this approach, it was decided to calculate the π contribution to ^{19}F s.c.s. in 4-X-4′-fluorobiphenyls where the substituent effects should also be predominantly *via* the π system. In this situation, the appropriate constant k is evaluated to be 1·378 [*i.e.*, equation (3)], and the results (shown in Table 5) are in close agreement with the experimentally observed s.c.s.

TABLE 5

Calculated π electron s.c.s. and experimentally observed values for 4-X-4′-fluorobiphenyl

X	Calc.[a]	Obs.[b] (15)
NH_2	1·81	2·34 [c]
F	−0·33	−0·14 [d]
Br	−0·95	−0·78 [d]
I	−1·05	−0·90 [d]
NO_2	−3·28	−2·74 [d]

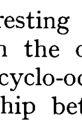
[a] Solution in n-hexane, p.p.m. to high field positive. [b] M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, 1966, **88**, 3318. [c] Solution in dimethylformamide. [d] Solution in benzene.

$$\delta\pi_{\text{s.c.s.}}(\text{4-X-4}'\text{-fluorobiphenyl}) = 1{\cdot}378\,\delta\pi_{\text{s.c.s.}}(\text{4-X-4}'\text{-fluoro-}\textit{trans}\text{-stilbene}) \quad (3)$$

The problem of steric inhibition to conjugation should again be considered, and the biphenyls are likely to be less conjugated than the stilbenes; the calculated values in Table 5 may therefore be somewhat too large and a correction would lead to even closer general agreement with experiment.

RESULTS AND DISCUSSION

para-*Substituent Effects.*—In the series of *para*-X-fluorobenzenes, a comparison of the calculated s.c.s. with experimentally observed values shows very poor agreement as expected, and Table 4 also gives the differences between these quantities. It is obvious that all groups are more shielding towards fluorine than can be accounted for by the π electron contribution, and that the extra shielding contributions are in some way a function of the polar nature of the C–X bond.



(2)

It would be interesting to compare observed and calculated s.c.s. with the observed s.c.s. in series of 1-fluoro-4-X-[2,2,2]bicyclo-octanes (2) in which the geometrical relationship between F and X is similar to that for benzenes but the groups are separated by a wholly σ-bonded framework. There are few compounds available in this series, but when X is fluorine or methoxycarbonyl the ^{19}F nucleus is more shielded than when H = X, which is in qualitative agreement with the above results.[6] A large number of such derivatives in which F is replaced by CO_2H have been prepared, however, and their acid dissociation constants used to define Taft's σ_I parameter as a measure of the polar effects of the groups X.[13] It would therefore be reasonable to expect the ^{19}F shielding in the corresponding fluoro-derivatives to correlate linearly with the σ_I value and by analogy it is valid to examine the correlation between the (obs. — calc.) s.c.s. values in Table 5 and σ_I. This is shown in Figure 2 and it is surprisingly good with a correlation coefficient of 0·9654. This could be taken as evidence that the calculational procedure outlined earlier has indeed separated a π electronic contribution to shielding from a ' polar ' contribution.

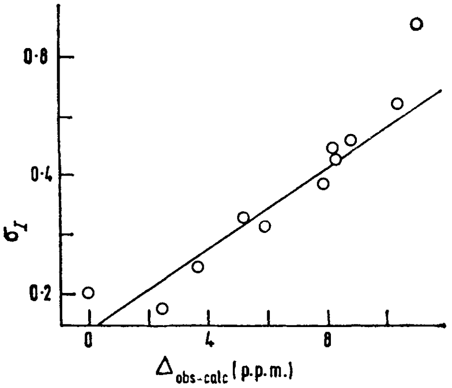


FIGURE 2 Plot of $\Delta_{\text{obs}-\text{calc}}$ against σ_I

However, there are some conceptual difficulties; the present empirical treatment, based upon ^{19}F chemical-shift data in the series of 4-X-4′-fluoro-*trans*-stilbenes, leads to the conclusion that halogen substituents cause a *decrease* (relative to X = H) in the π-electron density upon the *para*-position in the series $X{\cdot}C_6H_4{\cdot}F$-*p*. This is contrary to what is predicted by even the most sophisticated of modern MO theories,[10,12] and must therefore be regarded with suspicion. It was pointed out to us by a Referee that the reason for this may lie in the fact that the s.c.s. for the halogens in the stilbene series are very small (F = —0·24, Cl = —0·62, Br = —0·69, I = —0·76); if they are not entirely due to π effects, then any uncertainty will be multiplied on translating the data to the benzene series and an ' uncertainty ' as small as +0·5 p.p.m. in the stilbene data would account for the discrepancy of the sign between predicted and observed shifts. We are unable to suggest what the origin of the suggested ' non-π ' contribution to s.c.s. in the stilbenes could be however, since we have taken trouble to eliminate intramolecular

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

[13] H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, 1964, **86**, 5188.

effects and solvent effects [by recording spectra at ' infinite dilution ' in non-polar solvents (see preceding paper)]. Any discrepancy which *does* exist however, must also occur *in the same sense* for a very wide range of binuclear aromatic molecules (see following paper) varying from biphenyls to *trans,trans*-diphenylbutadienes, since substituent effects in all of these show parallel behaviour to the stilbene results. We are unable to offer further comment upon this dichotomy.

meta-*Substituent Effects*.—The ^{19}F chemical shifts of the series of 4-X-3′-F-*trans*-stilbenes and 3-X-4′-F-*trans*-stilbenes depend in a parallel fashion to those in the 4-X-4′-F-*trans*-stilbenes upon the nature of X. It seems likely that even for this relative orientation of the substituents F and X (which is exactly analogous to the *meta*-orientation in *meta*-X-fluorobenzenes) π electronic changes must control the substituent effects; it is impossible to carry out meaningful calculations of π electron density changes for such an arrangement either by the HMO method or by many much more sophisticated techniques. If it is assumed that the same proportionality holds for the relationship between carbon π electron densities and ^{19}F nuclear shielding as for the 4,4′ arrangement of F and X, then the linear correlation between the two sets of chemical shifts enables estimates to be made of the values of the relative changes for the 3,4′ arrangement. The same ratio, 2·57, must hold between the calculated π contribution to s.c.s. in *p*-X-fluorobenzene (Table 4) and the corresponding ' calculated ' values for *m*-X-fluorobenzenes, and Table 6 lists values of s.c.s. contributions in *m*-X-fluorobenzenes and compares them with observed s.c.s. The results show a surprising degree of agreement and indicate that in many cases the *meta*-s.c.s. can be accounted for wholly by the π contribution. This is in complete disagreement with previous conclusions, such as those of Taft *et al.*[14] which assume that the *meta*-s.c.s. are almost wholly dependent upon the inductive effect of the group X and that π-electronic effects are negligible.

TABLE 6

Comparison of the calculated π contribution to s.c.s. for *m*-X-fluorobenzenes with the experimentally observed s.c.s.

X	s.c.s.(calc.)/ p.p.m.	s.c.s.(obs.)/p.p.m. *a*	*b*
NH_2	4·11	0·2	3·64
OH	2·48	−0·9	3·22
OMe	2·22	1·05	2·21
Me	1·16	1·21	2·24
H	0·00	0·00	0·00
F	−0·75	−2·97	0·22
Cl	−1·94	−2·01	−0·56
Br	−2·16	−2·32	−1·16
I	−2·38	−2·36	−2·46
NO_2	−7·47	−3·45	−3·20

[a] S.c.s. calculated from data for *meta*-substituted monofluorobenzenes. [b] S.c.s. calculated from data for monosubstituted perfluorobenzenes.

Correlation of ^{19}F *s.c.s. with Reactivity Parameters*.—Many linear correlations have been observed between the various structure–reactivity parameters such as those of Hammett[15] or Taft[16] and n.m.r. substituent chemical shifts (s.c.s.) and (to a lesser extent) coupling constants.[4] The reactivity parameters are derived from kinetic or equilibrium data and therefore concern molecules not only in the ground state but also in an excited or ' transition ' state. It is not obvious why there should be linear correlations with purely ground-state properties such as n.m.r. data, but Emsley and Phillips[4] have examined this question using an approach based upon that suggested by Ehrenson.[17] They concluded that there are grounds for believing that experimental Hammett σ values[15] should be related to differences in electronic energy between ground and transition states produced by substitution; a direct relationship with localised electron density changes, such as are supposed to affect nuclear shielding[18] is not obvious however. Most methods of calculating electron density and energy changes caused by substituent variation do give an approximately linear relationship between the two however,[19-21] so it is valid to expect a relationship between the Hammett σ parameters and corresponding ^{19}F s.c.s.

Gutowsky *et al.*[22] observed a correlation of ^{19}F n.m.r. chemical shift data with the Hammett σ_p and σ_m values, for shifts in *para*- and *meta*-substituted monofluorobenzenes respectively. This work was extended[23] to the prediction of σ values for substituents for which this parameter was not known. Taft,[24] using Gutowsky's data, improved the correlation using σ_I and σ_R parameters;[16] σ_I and σ_R are derived from the Hammett σ_p value by the relationship (4). σ_I Is regarded as a

$$\sigma_p = \sigma_I + \sigma_R \qquad (4)$$

measure of the effect of the substituent group arising from its power to attract or repel electrons either through space or *via* the σ bonds of the benzene system, while σ_R is regarded as a measure of the ability of a substituent to attract or repel electrons through resonance interaction (*p*–π overlap) with the π molecular orbitals of benzene. Independent measurements of σ_I are possible but not of σ_R. He observed that *para*-^{19}F substituent chemical shifts, Δ_p (*i.e.*, the chemical shifts of fluorine in *para*-X-fluorobenzenes referred to the member of the series in which X = H), can be

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[14] R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, *J. Chem. Phys.*, 1963, **38**, 380.

[15] L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96; *Trans. Faraday Soc.*, 1938, **34**, 156.

[16] R. W. Taft, ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1966.

[17] S. Ehrenson, *Progr. Phys. Org. Chem.*, 1964, **2**, 195.

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

[19] C. A. Coulson, *Proc. Phys. Soc.*, 1952, *A*, **65**, 933.

[20] L. Goodman and H. Shull, *J. Chem. Phys.*, 1955, **23**, 33.

[21] G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, 1967, **8**, 165.

[22] H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Amer. Chem. Soc.*, 1952, **74**, 4809.

[23] L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, 1953, **57**, 481.

[24] R. W. Taft, *J. Amer. Chem. Soc.*, 1957, **79**, 1045.

calculated with a fair degree of precision by equation (5)

$$\Delta_p = -5\cdot83\sigma_I - 18\cdot8\sigma_R + 0\cdot8 \qquad (5)$$

while the corresponding *meta*-s.c.s. are given by equation (6).

$$\Delta_m = -5\cdot83\sigma_I + 0\cdot2 \qquad (6)$$

It was decided to examine the validity of the Taft separation of σ_p into σ_R and σ_I in the light of the results discussed above. It was suggested above that in 4-fluoro-4′-X-, 4-fluoro-3′X-, and 3-fluoro-4′-X-*trans*-stilbenes the observed substituent chemical shifts may be due to the changing perturbation of the π electron system on changing the group X. If Taft's values of σ_R are a measure of this interaction with the system, then a linear correlation with the observed s.c.s. should be obtained. The correlation is non-existent however, as shown in Figure 3, which indicates that σ_R is not in fact a measure of the resonance effect of a group or that the observed s.c.s. are not directly related to such resonance effects.

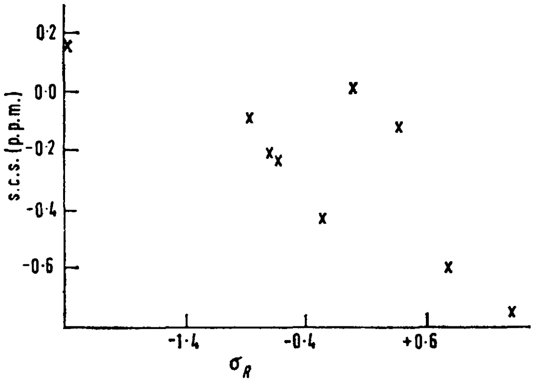

FIGURE 3 Plot of s.c.s. of 4-fluoro-4′-X-*trans*-stilbenes against σ_R

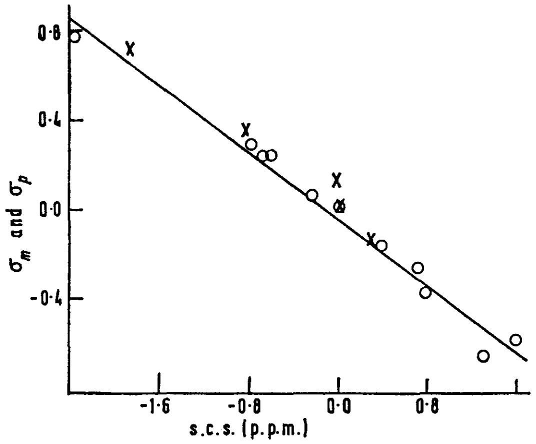

FIGURE 4 Plot of s.c.s. of 4-fluoro-4′-X-*trans*-stilbene (○) and 4-fluoro-3′-X-*trans*-stilbene (×) against the Hammett substituent constant

Very precisely linear correlations do, however, exist between these data and the appropriate Hammett σ parameter. Thus the s.c.s. for the series of 4-fluoro-4′-X-*trans*-stilbenes (A) and 3-fluoro-4′-X-*trans*-stilbenes (B, in which the fluorophenylvinyl group is *para* to X) both correlate linearly with σ_p, while those for the 4-fluoro-3′-X-*trans*-stilbenes (C, in which the fluorophenylvinyl group is *meta* to X) correlate linearly with σ_m. The data for (A) and (C) may be incorporated upon the same graph since both correlations have the same slope (or ρ value) and the relationship described as (7). The data fit this expression with a correlation

$$\Delta_{\mathrm{A(C)}} = 2\cdot6766\ \sigma_{p(m)} \qquad (7)$$

coefficient of 0·9917, and a plot of s.c.s. against σ_m or σ_p is shown in Figure 4. The data for series (B) can be expressed by the relationship (8) with a correlation

$$\Delta_{\mathrm{B}} = 1\cdot1238\sigma_p \qquad (8)$$

coefficient of 0·9760 and the appropriate plot is shown in Figure 5.

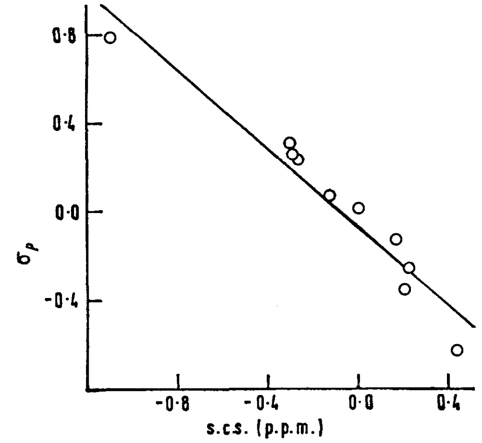

FIGURE 5 Plot of s.c.s. of 3-fluoro-4′-X-*trans*-stilbene against the Hammett substituent constant σ_p

The high precision of these correlations indicates that σ_p may be a much better measure of the net π interaction between groups X and the aromatic ring than is σ_R. An analysis of the s.c.s. in *p*-fluorobenzenes may now be made by use of σ_p and σ_I parameters. An explicit (9) relationship can be derived and used to calculate s.c.s. to a higher degree of precision (r.m.s. error ±1·52 p.p.m.) than the Taft relationship (r.m.s. ±1·95 p.p.m.) [equation (5)]. Values calculated by

$$\Delta_p = -21\cdot0567\ \sigma_p + 15\cdot7480\ \sigma_I \qquad (9)$$

this equation are compared with those obtained from the Taft equation and experiment in Table 7.

Apparently the separation of σ_p into σ_R and σ_I is unnecessary in order to interpret the shielding data. Indeed, it seems to be a quite artificial separation since σ_R is not obtainable by any independent measurement (whereas σ_p and σ_I both can be [25]) and appears solely as a consequence of Taft's treatment of the chemical

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[25] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

shift data, a conclusion that is in accord with some recent observations of Dewar *et al.*[26]

TABLE 7

A comparison of s.c.s. for *p*-X-fluorobenzenes calculated by equation (9) and by equation (5) with experimentally observed values

X	Δ_p(calc.) [equation (9)]	Δ_p(calc.) [Taft, equation (5)]	Δ_p(obs.)
NH_2	15·47	14·51	14·14
OH	11·52	10·81	11·62
OMe	9·27	8·86	11·60
Me	2·79	3·53	5·47
H	0·00	0·80	0·00
F	6·57	6·15	6·90
Cl	2·62	2·57	3·30
Br	2·20	3·32	2·73
I	0·17	0·46	1·76
NO_2	−6·46	−5·69	−8·79

By analogy with the treatment given above (p. 1984), it should be possible to relate the s.c.s. in *meta*-substitured fluorobenzenes to σ_p and the appropriate equation is (10).

$$\Delta_m = -8{\cdot}85\sigma_p \qquad (10)$$

Table 8 lists values calculated by this equation and compares them with experiment and with those calculated by Taft's relationship [equation (6)]. With the exception of two substituents ($X = NH_2$ and NO_2) the agreement with experiment is of the same order of precision as that obtained by Taft, and even the disagreement for these two substituents is not sufficiently high to enable a sharp differentiation to be made between the two. The results are interesting: Taft's equation has been interpreted as showing that σ bond inductive effects are all-important in determining *meta*-s.c.s. while equation (10) and the earlier discussion concerning σ_p indicates that resonance interactions are of major importance compared with inductive!

TABLE 8

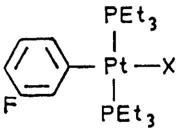
A comparison of s.c.s. for *m*-X-fluorobenzenes calculated by equation (10) and by equation (6) with experimentally observed values

X	Δ_m(calc.) [equation (10)]	Δ_m(calc.) [Taft, equation (6)]	Δ_m(obs.)	
			a	*b*
NH_2	5·84	−0·78	0·2	3·64
OH	3·19	−1·66	−0·9	3·22
OMe	2·37	−1·54	1·05	2·21
Me	1·50	0·09	1·21	2·24
H	0·00	0·20	0·00	0·00
F	−0·55	−3·12	−2·97	0·22
Cl	−2·01	−2·94	−2·01	−0·56
Br	−2·05	−2·82	−2·32	−1·16
I	−2·44	−2·42	−2·36	−2·46
NO_2	−6·89	−3·87	−3·45	−3·20

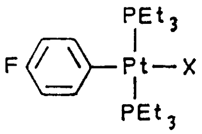
[a,b] See footnotes to Table 6.

The success of relationships (5), (6), (9), and (10) in predicting ^{19}F s.c.s. demonstrates the inadvisability of using such an empirical analysis in order to obtain information about the transmission of electronic interactions in aromatic systems. Taft's results and those of the present work are probably equally valid as judged by their success in calculating s.c.s., but each leads to a directly opposing interpretation in terms of modes of electronic interactions. It may be that the present work offers the more realistic assessment however, for the stilbene data for both *para*- and *meta*-like orientation of substituents most probably arise wholly from π-resonance interactions.

It has been fairly common practice [27] to assume that *meta*-^{19}F chemical shifts arise solely from σ-electron transmitted effects. Parshall, for example,[28] has considered some organoplatinum complexes of the type



(3)



(4)

(3) and (4). For these he assumes that the ^{19}F shielding parameters measure the ability of the fluorophenyl group to compete with the ligand X for π-electron density on the central Pt atom. He assumes that the shielding of the *meta*-^{19}F nucleus varies with the σ-donor character of X as transmitted by the Pt atom, while the *para*-^{19}F shielding varies with both this and the π-acceptor nature. The difference in the two shielding parameters for a given substituent, X, is taken as a 'π-bond criterion of X to compete with the *p*-fluorophenyl group for electron density in the Pt d_{xy} orbital.' It is assumed that the d_π–P_π interactions occur between the aromatic π and the Pt $5d_{xy}$ orbitals with which vacant orbitals on the ligand are also interacting. The concept rests upon the postulate that the transmission of the electronic effect to the *meta*-position is solely *via* the σ-framework, and this seems to be untenable.

The Separation of Reactivity Parameters into Field (or Inductive) and Resonance Effects.—It was mentioned that perhaps the first attempt at analysing reactivity parameters in terms of various types of electronic effects was that of Taft.[16] The whole question of separability has been the subject of much work and review,[25,29] and the most complete analysis has been that of Swain and Lupton.[29] This work has demonstrated the futility of the attempts of many workers to interpret the correlations of experimental kinetic and equilibrium data with an abundance (*ca.* 40) of substituent parameters, by showing that all such parameters can in turn be analysed in terms of a general two-parameter equation (11) involving a field-cum-

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[26] M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Amer. Chem. Soc.*, 1971, **93**, 4187.

[27] R. W. Taft, *J. Phys. Chem.*, 1960, **64**, 1805; R. W. Taft and J. W. Rakshys, *J. Amer. Chem. Soc.*, 1965, **87**, 4387; R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709, 3146.

[28] G. W. Parshall *J. Amer. Chem. Soc.*, 1964, **86**, 5367; 1966, **88**, 704.

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

inductive part, F, and a resonance (or π interaction) part, R. The values of F are, in fact, refined σ_I values

$$\sigma = fF + rR \qquad (11)$$

based upon observations of the dissociation constants of 4-substituted bicyclo[2,2,2]octanecarboxylic acids; the values of R are based upon the assumption that in the case of 4-trimethylammoniobenzoic acid cation, p-$Me_3N^+{\cdot}C_6H_4{\cdot}CO_2H$ the dissociation constant of the carboxylic acid is solely determined by the F interaction of the Me_3N^+ group and its 'resonance' contribution, R, is zero.

TABLE 9

The analysis of reactivity constants in terms of σ_p and F by use of the equation $\sigma = f'F + r'\sigma_p$

Reaction [a] series No.	Substituent constant	n [b]	f'	r'	$\%\sigma_p$ [c]	$\%R$ [c]
1	σ_m	42	0·45	0·27	27	22
2	σ_p	42	0·00	1·00	100	53
3	σ_p	18	−0·10	1·56	90	56
4	$\sigma_p{}^+$	23	−0·37	1·52	73	66
5	σ'	14	1·03	−0·01	1	1
6	σ'	5	0·64	0·03	3	3
7	σ''	5	0·50	0·00	0	0
8	$\sigma_m{}^+$	20	0·24	0·34	47	33
9	σ_3	5	0·34	0·34	38	29
10	σ_4	9	−0·11	1·24	88	57
11	σ_5	9	0·18	0·38	57	38
12	σ_6	8	0·10	0·38	70	43
13	σ_7	7	0·05	0·38	83	48
14	σ_o	13	0·29	0·61	57	37
15	$\sigma^I{}_m$	5	0·51	0·41	34	26
16	$\sigma^I{}_p$	6	−0·39	1·73	74	65
17	$\sigma^Q{}_m$	8	0·45	0·38	35	26
18	$\sigma^F{}_m$	15	−3·85	0·08	1	1
19	$\sigma^F{}_p$	15	4·40	−19·40	73	65
20	$\sigma^c{}_p$	14	3·41	−12·50	70	68
21	σ_R	14	−65·84	112·00	52	96
22	I	11	9·07	0·88	6	5
23	$\sigma^n{}_p$	16	0·10	0·75	82	47
24	$\sigma^o{}_m$	13	0·44	0·29	29	23
25	$\sigma^o{}_p$	13	0·21	0·70	67	42
26	σ^*	21	1·30	0·14	6	6
27	σ^*	7	0·93	1·81	55	37
28	σ^*	6	2·89	−0·01	0	0
29	σ^*	7	0·70	−0·17	13	15
30	σ^*	4	0·77	−0·43	26	33
31	σ^*	9	−0·01	1·11	98	53
32	$\sigma^I{}_m$	25	0·60	0·00	0	0
33	$\sigma^R{}_o$	13	−0·22	0·36	51	92
34	$\sigma^R{}_o$	12	−0·42	0·63	48	84
35		11	0·20	0·61	66	41
36	F_{Dewar}	41	0·78	0·47	27	22
37	M	41	−2·70	5·27	55	93
38	F'	41	0·71	0·63	36	27
39	M'	41	−3·52	6·86	55	93
40	$\sigma_p{}^+$	42	−0·48	1·65	68	70
41	F	42	1·00	0·00	0	0
42	R	42	−0·56	1·00	53	100
43	σ_p, σ_m	42	−0·45	0·73	50	92

[a] Reaction series number corresponds to that in Table II of the work of Swain and Lupton.[29] [b] n Is the number of substituents upon which the correlation is bdsed. [c] Calculated by the method given in reference 29.

The work described above must cast some doubt upon the choice of origin for the R values, for the substituent effect of the group Me_3N^+ upon ^{19}F shielding in 4-fluoro-4′-trimethylammonio-*trans*-stilbene is large (−1·49 p.p.m.) and probably arises from an interaction with the π system (*i.e.*, an R type interaction). The linearity of the correlations with σ_p (and σ_m) clearly indicates that σ_p values are a more valid measure of π interactions than other parameters, and so we suggest that a more meaningful way of utilising the method of Swain and Lupton is to analyse all substituent parameters in terms of F and σ_p which are listed in Table 1 of ref. 29. This can be done *without altering in any way* the precision of the correlations obtained by these workers but greatly altering the interpretations which should be placed upon the various substituent parameters. Table 9 lists the substituent constants considered by Swain and Lupton, and analyses them in terms of equation (12). Also listed are the percentage σ_p con-

$$\sigma = f'F + r'\sigma_p \qquad (12)$$

tributions to the various parameters,[29] and they are compared with the corresponding percentage R calculated by Swain and Lupton. It should again be emphasised that the difference between the two sets of parameters arises from the basis for the definition of the π or resonance contribution; Swain and Lupton assume without experimental evidence, that the group Me_3N^+ exerts no such effect ($R = 0$) while we have given experimental evidence which suggests that this is not so but that σ_p is a valid experimental measure of such interactions for all substituents. The choice of F values is the same in both treatments, and the results lead to correlations with experimental data of the same high precision.

The Hammett σ_p value of a substituent may be taken as a measure of the net interaction between it and the aromatic π system by all mechanisms which redistribute π-electron density. This encompasses both the I_π effect of Murrell[30] (the C.T. term in the recent treatment of substituent effects by Godfrey[31]] and the more traditional mesomeric or resonance interaction (the F_{OR} term of Godfrey[31]). It is noteworthy that the use of this parameter predicts that groups such as $-NR_2$, $-OR$, or $-SR$ will be π-electron donating (or repelling) compared with hydrogen and that the halogens will be π-electron accepting (or attracting) with fluorine the least effective. This is exactly the order given by Godfrey[31] but not by Swain and Lupton who preserve the more traditional idea that all groups such as $-NR_2$, $-OR$, $-SR$, and halogen which possess a lone pair of π-symmetry are π-electron donors, while few groups (*e.g.*, $-NO_2$) are π-electron acceptors.

We thank the S.R.C. for a maintenance grant (to I. R. A.).

[1/1870 *Received*, 13*th October*, 1971]

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[30] J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963.

[31] M. Godfrey, *J. Chem. Soc.* (*B*), 1971, 1534.