^{19}F Nuclear Magnetic Resonance Studies of Aromatic Compounds. Part I. The Effect of Solvents on the Chemical Shift of Fluorine Nuclei in *para*-Substituted Fluorobenzenes, 4-Substituted 4'-Fluoro-*trans*-stilbenes, and 4-Substituted 3'-Fluoro-*trans*-stilbenes

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Solvent effects upon ^{19}F shielding in some aryl fluorides are examined. A criterion is established which, it is believed, enables solvents and reference to be chosen so that interactions other than those due to ' reaction fields ' are minimised. The reaction field model appears to work satisfactorily for 4-substituted 3'- and 4'-fluoro-*trans*-stilbenes, but breaks down for *para*-substituted fluorobenzenes.

THE effects of solvent variation upon nuclear shielding parameters have been much investigated.[1] It was concluded that the observed shielding constant of a nucleus in a molecule dissolved in a solvent can be considered as the sum of several contributions.[2] If σ_{obs} is the observed shielding constant then equation (1) follows,

$$\sigma_{obs} = \sigma_g + \sigma_B + \sigma_A + \sigma_W + \sigma_E + \sigma_C \qquad (1)$$

where σ_g is the shielding constant of a nucleus in an isolated molecule, σ_B is the contribution to shielding arising from the bulk magnetic susceptibility of the solvent, σ_W arises from any anisotropy in the solvent's magnetic susceptibility, and σ_W arises from van der Waals interactions between solute and solvent molecules. The term σ_E is important only for polar solute molecules, which polarise the surrounding medium and give rise to a reaction field in the solvent,[3] and σ_C is a contribution to shielding from specific molecular interaction or complex formation in solution. The chemical shift measured on a liquid sample is [σ_{obs}(sample) — σ_{obs}(reference)] and this will be equal to the difference [σ_g(sample) — σ_g(reference)] only when each of the terms in equation (1) is identical for both sample and reference. It is important that the observed shift difference should be as close as possible to the difference [σ_g(sample) — σ_g(reference)] if any real attempt is to be made to interpret chemical shifts in terms of fundamental molecular properties.

Emsley and Phillips[4] have investigated the effects of solvents upon ^{19}F shielding in a variety of aromatic fluorine-containing molecules. Where the solute and reference are present in the same solvent and closely resemble each other (both chemically and in terms of their physical dimensions), then the only term which is likely to cause the observed chemical shift to differ significantly from [σ_g(sample) — σ_g(reference)] arises from differences in σ_E. This term is important for polar molecules and arises because of induced polarisation of the surrounding medium; the ' reaction ' field thus set up polarises the electrons in the C–F bond and causes a contribution to the observed shielding. To a first approximation, σ_E may be expressed as being simply proportional to the magnitude of the induced field along the bond direction, as in equation (2), where A is the

$$\sigma_E = -AE_Z \qquad (2)$$

proportionality constant, and E_Z is the component of the reaction field along the bond in the direction C $\longrightarrow$ F.

The constant A is a measure of the ease of distortion of the electron distribution along the C–F bond direction, and for the CF bonds in CHF_3 has been shown[5] to have a value of $-(9{\cdot}9 \pm 3{\cdot}6) \times 10^{-12}$ e.s.u. It may be important in describing the nature of such a bond, but few attempts have been made to measure its value accurately. Emsley and Phillips[4] obtained values of A for C–F bonds in derivatives of pentafluoropyridine and pentafluorobenzene and in some *para*-substituted fluorobenzenes; the results in many cases however were made inaccurate by contributions to the solvent effect from the ill-defined σ_C term. A surprising observation made in this work is that the sign of A appears to be positive in some species but negative in others and may vary for different C–F bonds in the same molecule. The object of the present work was to make a more accurate evaluation of A for C–F bonds in some simple aromatic systems and to investigate the possible variation of its magnitude and sign with structure.

As part of a general study upon substituent effects on ^{19}F shielding in monofluorinated aromatic molecules, series of *para*-substituted fluorobenzenes, 4-substituted 4'-fluoro-*trans*-stilbenes, and 4-substituted 3'-fluoro-*trans*-stilbenes were available.[6] These molecules were chosen for the solvent effect study.

EXPERIMENTAL

Stilbene derivatives were synthesised according to the methods described in the following paper. Their purity was checked by spectroscopy and by analysis. *para*-Substituted fluorobenzenes were used as obtained from Koch–Light. Solvents were AnalaR grade for carbon tetrachloride and chloroform, and General Purpose Reagents in other cases.

Fluorine N.m.r. Spectra.—These were recorded on a

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[1] P. Laszlo, ' Progress in Nuclear Magnetic Resonance Spectroscopy,' vol. 3, ed. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon Press, Oxford, 1967.

[2] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.

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

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

[5] H. J. Bernstein and L. Petrakis, *J. Chem. Phys.*, 1963, **37**, 2731; 1963, **38**, 1562.

[6] I. R. Ager, L. Phillips, T. J. Tewson, and V. Wray, following paper.

Varian HA100 spectrometer operating at 94·1 MHz. Field-frequency locked conditions were used throughout, with extended lock and automatic phase compensation to enable spectral lines up to 20 kHz from the locking signal to be recorded in the absorption mode.[7] Chemical shifts were measured as the difference between the resonance frequency of the reference (internal hexafluorobenzene) and the sample by means of a frequency counter accurate to ±0·1 Hz. Chemical shifts were measured for a variety of solutions containing low concentrations of solute and the results extrapolated to infinite dilution; the 'infinite dilution chemical shifts' are considered to be accurate to within ±1·0 Hz or ±0·01 p.p.m. Values are in Table 1.

TABLE 1

^{19}F Chemical shifts (p.p.m. referred to C_6F_6 internal reference, negative shifts to low field) for some aromatic fluorine-containing compounds in a variety of solvents

X	n-C_6H_{14}	CCl_4	$CHCl_3$	$CHBr_3$	CH_2Cl_2	CH_2I_2	MeCN	$Me_2N{\cdot}CHO$
p-X-Fluorobenzenes								
NMe_2	−35·86							
NH_2	−35·94	−35·48	−35·01	−34·66		−34·26	−34·17	
OH	−38·46	−37·99	−36·68	−37·18		−36·83	−37·19	
OMe	−38·48	−38·00	−37·48	−37·06			−38·23	
Me	−44·61	−44·07	−43·14	−42·89		−42·70	−44·13	
H	−50·08	−49·51	−48·75	−48·41		−48·12	−49·56	−49·90
F	−43·18	−42·68	−42·16	−41·74		−41·51	−43·32	
Cl	−46·78	−46·31	−45·85	−45·46		−45·28	−46·99	
Br	−47·35	−46·89	−46·45	−46·05		−45·88	−47·52	
I	−48·32	−47·85	−47·39	−47·02		−46·90	−48·32	
NO_2	−58·87	−58·77	−59·70	−59·10		−58·72	−59·89	
$^{+}NMe_3$							−52·58	−51·73
4-X-3′-Fluoro-*trans*-stilbenes								
NH_2	−49·04	−48·51	−48·04	−47·62		−47·49	−49·06	
OH		−48·75	−48·18	−47·86		−47·68	−49·17	
OMe	−49·26	−48·71	−48·19	−47·83		−47·65	−49·21	
OEt	−49·26	−48·67	−48·15	−47·80		−47·62	−49·19	
Me	−49·38	−48·79	−48·21	−47·87		−47·72	−49·28	
H	−49·52	−48·89	−48·33	−47·96		−47·79	−49·31	
F	−49·65	−49·07	−48·40	−48·06			−49·34	
Cl	−49·79	−49·18	−48·50	−48·17		−48·01	−49·41	
Br	−49·80	−49·19	−48·53	−48·17		−48·00	−49·43	
I	−49·82	−49·18	−48·53	−48·20		−47·99	−49·44	
NO_2	−50·61	−49·76	−49·02	−48·69		−48·48	−49·67	
4-X-4′-Fluoro-*trans*-stilbenes								
NMe_2	−46·98							
NH_2	−47·27	−46·79			−46·43		−46·99	−47·42
Me	−48·21	−47·71			−47·30		−48·05	−48·24
H	−48·58	−48·09			−47·65		−48·37	−48·54
I	−49·34	−48·86			−48·20		−48·86	−49·00
NO_2	−50·96	−50·53			−49·65		−50·08	−50·26
$^{+}NMe_3$							−49·60	−49·60

Method of Calculation.—If each of the terms in equation (1) due to solvent interaction is the same for both solute and reference, with the exception of σ_E, then the chemical-shift difference between the two is given by equation (3). σ_E is

$$\Delta_{obs} = [\sigma_g(\text{sample}) - \sigma_g(\text{reference})] + [\sigma_E(\text{sample}) - \sigma_E(\text{reference})] \quad (3)$$

given approximately by equation (2), in which E_Z can be calculated by Diehl and Freeman's modification[8] of Buckingham's method[3] which considers only the contribution from molecular dipoles and uses the Onsager model for the reaction field. This gives for the reaction field E the expression (4) where μ is the dipole moment of the molecule; a, b, and c are the half-axes of an ellipsoidal cavity in the solvent sufficiently large to contain the molecule; n is the refractive index of the solute; ε is the dielectric coefficient of the solvent; and S_a is a shape factor given by equation (5). Expression of equation (3)

$$E = \frac{3\mu}{abc} S_a \frac{[1 + (n^2 - 1)S_a](\varepsilon - 1)}{\varepsilon + [n^2 S_a/(1 - S_a)]} \quad (4)$$

$$S_a = \frac{abc}{2}\int_0^\infty \frac{d\lambda}{(a^2 + \lambda)^{\frac{3}{2}}(b^2 + \lambda)^{\frac{1}{2}}(c^2 + \lambda)^{\frac{1}{2}}} \quad (5)$$

in terms of equation (4) leads to the conclusion that Δ_{obs} for any solute should be a linear function of $(\varepsilon - 1)/\{\varepsilon + [n^2 S_a/(1 - S_a)]\}$ if it is measured in a variety of solvents and the solvent effect is indeed due to the reaction field. The value of A can be determined from the slope of the correlation line.

For molecules of similar size and shape to hexafluorobenzene, the shape factor S_a has been evaluated[1] as 0·24 which leads to a useful form (6) of the dielectric function for such systems. For an elongated molecule such as *trans*-stilbene a different value of S_a is required and if an ellipsoidal cavity of dimensions $a = 7{\cdot}35$ Å, $b = 3{\cdot}55$ Å, and $c = 1{\cdot}85$ Å is assumed, S_a is found to be 0·116. For this case the dielectric function becomes (7).

$$\text{D.F.}_{(\text{benzenes})} = \frac{\varepsilon - 1}{\varepsilon + 0{\cdot}789} \quad (6)$$

$$\text{D.F.}_{(\text{stilbenes})} = \frac{\varepsilon - 1}{\varepsilon + 0{\cdot}329} \quad (7)$$

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

[8] P. Diehl and R. Freeman, *Mol. Phys.*, 1961, **4**, 39.

If Δ^{X}_{obs} is the substituent chemical shift for a molecule in which the substituent group is X (referred to the unsubstituted molecule, X = H), equation (3) can be written as (8). If A is constant, $A_H = A_X$; substitution of the

$$\Delta^{X}_{obs} = \Delta^{X}_{g} + \frac{3S_a[1 + (n^2 - 1)S_a](\text{D.F.})(A_H\mu_H - A_X\mu_X)}{abc} \quad (8)$$

appropriate values for n^2 (assumed constant, and given the value 2·5), S_a, and a, b, and c gives the expressions (9) and (10).

$$\Delta^{X}_{obs}(\text{stilbenes}) = 8{\cdot}4888 \times 10^3 A(\mu_H - \mu_X)(\text{D.F.}) + \Delta^{X}_{g} \quad (9)$$

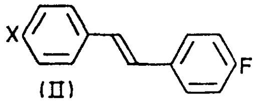
$$\Delta^{X}_{obs}(\text{benzenes}) = 3{\cdot}2428 \times 10^4 A(\mu_H - \mu_X)(\text{D.F.}) + \Delta^{X}_{g} \quad (10)$$

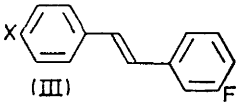
If the variation of Δ^{X}_{obs} with solvent (D.F.) is observed, then A can easily be evaluated from equations (9) and (10).

RESULTS AND DISCUSSION

A major problem which arose in the course of earlier work is the incomplete elimination of solvent contributions to the observed shifts other than σ_E; a high degree of scatter occurs in the plots of Δ_{obs} against D.F. if terms such as σ_W and σ_C are significant. It is apparent that some criterion must be established in order to identify solvents which are suitable for the present study, and for comparison purposes a 'reference' solvent in which all interactions are minimal should be chosen; an inert non-polar, non-polarisable solvent is required for this purpose, and n-hexane seems ideal.


(I)


(II)


(III)

It was decided to examine the series of molecules (I)—(III) in a variety of solvents, and to refer all chemical shifts to the member of each series in which X = H. These 'substituent chemical shifts' (s.c.s. = Δ) are most likely to be free from undesired solvent contributions due to the terms σ_B, σ_A, and σ_W but will certainly contain the σ_E term and possibly σ_C. It seems reasonable to suggest, however, that if the infinite dilution s.c.s. in a given solvent correlates linearly *with high precision* with the corresponding s.c.s. in n-hexane the solvent–solute system is also free from chemical-type interactions and σ_C is negligible. Seven organic solvents of widely varying polarity, in addition to n-hexane, were found which satisfy this criterion and these solvents were used.

TABLE 2

^{19}F Substituent chemical shifts (p.p.m. referred to X = H) for some aromatic fluorine-containing compounds in a variety of solvents. Positive s.c.s. are to high field of reference

X	n-C_6H_{14}	CCl_4	$CHCl_3$	$CHBr_3$	CH_2Cl_2	CH_2I_2	MeCN	$Me_2N{\cdot}CHO$
p-X-Fluorobenzenes								
NMe_2	14·22							
NH_2	14·14	14·03	13·74	13·75		13·86	15·39	
OH	11·62	11·52	12·07	11·23		11·29	12·37	
OMe	11·60	11·51	11·27	11·35			11·33	
Me	5·47	5·44	5·61	5·52		5·42	5·43	
H	0·00	0·00	0·00	0·00		0·00	0·00	0·00
F	6·90	6·83	6·59	6·67		6·61	6·24	
Cl	3·30	3·20	2·90	2·95		2·84	2·57	
Br	2·73	2·62	2·30	2·36		2·24	2·04	
I	1·76	1·66	1·36	1·36		1·22	1·24	
NO_2	−8·79	−9·26	−10·95	−10·69		−10·60	−10·33	
$^+NMe_3$							−3·02	−1·83
4-X-3′-Fluoro-*trans*-stilbenes								
NH_2	0·48	0·38	0·29	0·34		0·30	0·25	
OH		0·14	0·15	0·10		0·11	0·14	
OMe	0·26	0·18	0·14	0·13		0·14	0·10	
OEt	0·26	0·22	0·18	0·16		0·17	0·12	
Me	0·14	0·10	0·12	0·09		0·07	0·03	
H	0·00	0·00	0·00	0·00		0·00	0·00	
F	−0·13	−0·18	−0·07	−0·10			−0·03	
Cl	−0·27	−0·29	−0·17	−0·21		−0·22	−0·10	
Br	−0·28	−0·30	−0·20	−0·21		−0·21	−0·12	
I	−0·30	−0·29	−0·20	−0·24		−0·20	−0·13	
NO_2	−1·09	−0·87	−0·69	−0·73		−0·69	−0·36	
4-X-4′-Fluoro-*trans*-stilbenes								
NMe_2	1·60							
NH_2	1·31	1·30	1·13		1·22		1·38	1·12
Me	0·37	0·38	0·34		0·35		0·32	
H	0·00	0·00	0·00		0·00		0·00	0·00
I	−0·76	−0·77						
NO_2	−2·38	−2·44	−2·26		−2·00		−1·71	
$^+NMe_3$							−1·23	−1·06

Table 2 lists infinite dilution s.c.s. for the molecules under investigation in these solvents, and plots of $\Delta_{(\mathrm{solvent})}$ against $\Delta_{(\mathrm{hexane})}$ are linear and of high precision. The results are best considered in terms of the relationship $\Delta_{(\mathrm{solvent})} = m\Delta_{(\mathrm{hexane})} + C$ and Table 3 shows the results of applying a least-squares treatment to fit the data to this equation; the standard deviations and correlation coefficients show that the linear relationship is of high precision in all cases. The sensitivity of this method of detecting chemical interactions with solvent is apparent from the fact that in acetonitrile as solvent the two amino-substituted stilbenes show great deviation from the linear plot, and it is only when these compounds are eliminated from the results that a satisfactory degree of precision occurs. In order to calculate the values of A [equation (2)] the dielectric functions for the various solvents are plotted against the corresponding s.c.s. for a given compound and A is evaluated from the slope. Table 4 lists the dielectric functions of the various solvents for the two different types of molecule employed, and Table 5 shows a least-squares analysis of the linear correlations together with the calculated values of A. Most correlations are of an acceptably high standard, with the exception of those for *p*-fluorotoluene and 4-methyl-4′-fluoro-*trans*-stilbene in which the small observed solvent effects (owing to the small difference between dipole moments of the molecules and that of the unsubstituted molecule) lead to large errors. The data for *p*-fluoronitrobenzene also show considerable scatter.

TABLE 3

Comparison of s.c.s. in a variety of solvents with the corresponding s.c.s. in n-hexane by means of the relationship $\Delta_{(\mathrm{solvent})} = m\Delta_{(\mathrm{hexane})} + C$

Solvent	m	C	Standard deviation (p.p.m. in abscissa)	Correlation coefft.
p-X-Fluorobenzenes				
CCl_4	1·0114	0·9687	0·0982	0·9999
$CHCl_3$	1·0707	4·1428	0·4734	0·9976
$CHBr_3$	1·0492	3·4745	0·4094	0·9981
CH_2I_2	1·0547	3·9996	0·3677	0·9985
MeCN	1·0949	4·5657	0·4481	0·9980
4-X-3′-Fluoro-*trans*-stilbenes				
CCl_4	0·8159	−8·5159	0·0329	0·9954
$CHCl_3$	0·6341	−16·9307	0·0167	0·9980
$CHBr_3$	0·6738	−14·6077	0·0183	0·9979
CH_2I_2	0·6354	−16·3397	0·0170	0·9982
MeCN	0·3482	−32·0689	0·0186	0·9908
4-X-4′-Fluoro-*trans*-stilbenes				
CCl_4	1·1057	1·2443	0·0143	0·9999
$CHCl_3$	0·9137	−3·1912	0·0844	0·9972
CH_2Cl_2	0·8632	−5·6601	0·0384	0·9994
MeCN *	0·7305	−12·8445	0·0245	0·9995
$Me_2N{\cdot}CHO$	0·7563	−11·7323	0·0510	0·9985

* Excluding data for compounds in which X = NH_2.

TABLE 4

The dielectric function for fluorobenzenes and fluorostilbenes in a variety of solvents

Solvent	Dielectric constant	Dielectric function for fluorobenzenes	Dielectric function for fluorostilbenes
n-C_6H_{14}	1·890	0·332	0·401
CCl_4	2·238	0·409	0·482
$CHBr_3$	4·390	0·655	0·718
$CHCl_3$	4·806	0·680	0·741
CH_2I_2	5·320	0·707	0·764
CH_2Cl_2	9·080	0·819	0·859
$Me_2N{\cdot}CHO$	36·70	0·952	0·961
MeCN	37·50	0·953	0·965

If the results for these compounds are ignored, then it is apparent that the data for the stilbenes form a consistent set. In 4-X-3′-fluoro-*trans*-stilbenes, an average value of $A = (47{\cdot}5 \pm 4{\cdot}5) \times 10^{-12}$ e.s.u. can be calculated while for the 4-X-4′-fluoro-*trans*-stilbene the value is $35{\cdot}1 \pm 2{\cdot}0$ p.p.m. This difference is probably not real, for in order to calculate the field component along the C–F bond direction in the 4-X-3′-fluoro-derivatives it is necessary to assume that the bond is at an angle of 60° to the field direction which is presumed to be at an

TABLE 5

The correlation of dielectric function with s.c.s. and the calculated values of A [from equations (9) and (10)]

X	Slope of plot of D.F. against s.c.s.	Standard deviation (in abscissa)	Correlation coefft.	$\mu_X - \mu_H$ *	$10^{12}A$/c.s.u.
p-X-Fluorobenzenes					
NH_2	−0·9153	0·0562	0·9318	−1·17 †	−28·7 ± 4·9
OH	−0·9577	0·0399	0·9680	−0·96	−33·5 ± 7·0
OMe	−1·4039	0·1025	0·8599	−0·73	−30·0 ± 8·3
Me	−0·0524	0·2044	0·0170	−0·51	
F	−0·9430	0·0454	0·9750	+1·35	+24·2 ± 3·6
Cl	−0·8527	0·0130	0·9980	+2·32	+15·5 ± 1·3
Br	−0·8767	0·0229	0·9937	+1·87	+18·8 ± 2·0
I	−0·9305	0·0774	0·9256	+2·18	+15·1 ± 1·4
NO_2	−0·1966	0·1317	0·7650	+4·07	+38·5 ± 26·0
4-X-3′-Fluoro-*trans*-stilbenes					
NH_2	−2·0132	0·0535	0·9340	−2·06 ‡	+56·3 ± 5·5
OMe	−3·3803	0·0722	0·9227	−1·44	+48·2 ± 6·7
OEt	−4·0916	0·0417	0·9749	−1·65	+34·9 ± 4·2
Me	−4·3918	0·1050	0·8281	−0·47	+114·1 ± 48·5
F	3·5018	0·0909	0·8917	+1·49	+45·1 ± 6·1
Cl	2·7533	0·0708	0·9259	+1·71	+50·0 ± 5·9
Br	3·0835	0·0494	0·9647	+1·83	+41·7 ± 4·6
I	3·1431	0·0400	0·9769	+1·78	+42·1 ± 4·7
NO_2	0·8285	0·0451	0·9706	+4·63	+61·4 ± 3·3
4-X-4′-Fluoro-*trans*-stilbenes					
NH_2	−1·7231	0·1163	0·8444	−2·06	+33·1 ± 3·2
Me	−1·1772	0·1012	0·8899	−0·47	+34·9 ± 14·9
I	1·7358	0·0537	0·9702	+1·78	+35·6 ± 4·0
NO_2	0·6986	0·0805	0·9318	+4·63	+36·4 ± 1·6

* $\mu_X - \mu_H$ is the difference between dipole moments of the solute and reference. † From ref. 10. ‡ Calculated from the dipole moments of X-substituted-*trans*-stilbenes (ref. 9).

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[9] (*a*) K. B. Everard, L. Kumar, and L. E. Sutton, *J. Chem. Soc.*, 1951, 2807; (*b*) A. E. Lutskii, L. Ya Malkes, E. M. Obukhova, and A. I. Timchenko, *Zhur. fiz. Khim.*, 1963, **37**, 1076; (*c*) A. J. Boulton, G. M. Glover, M. Hely Hutchinson, A. R. Katritzky, D. J. Short, and L. E. Sutton, *J. Chem. Soc.* (*B*), 1966, 822.

[10] (*a*) A. L. McLellan, 'Tables of Experimental Dipole Moments,' W. H. Freeman, London, 1966; (*b*) D. C. Colinese, J. Hall, and D. A. Ibbotson, *J. Chem. Soc.*, 1962, 983; (*c*) M. J. Aroney, K. E. Calderbank, and R. J. W. LeFèvre, *J. Chem. Soc.* (*B*), 1969, 159; (*d*) M. D. Rudolph and M. Seiler, *Z. Naturforsch.*, 1965, **20**a, 1682.

angle of 60° to the central olefinic bond; a decrease in this, to 50°, will produce almost exact agreement between the two sets of data. No variation in the value of A with the nature of the distant substituent group is discernible.

The data for *p*-X-fluorobenzenes are somewhat different, for the value of A appears to depend upon the nature of the X substituent. For the compounds in which X is NH_2, OH, or OMe A has the value $-30{\cdot}5 \pm 2{\cdot}5$ p.p.m., while for those cases where X is F, Cl, Br, I, or NO_2 A ranges from $+15{\cdot}5 \times 10^{-12}$ e.s.u. for X = Cl to $+38{\cdot}5 \times 10^{-12}$ e.s.u. for X = NO_2.

Since A appears to vary with the nature of the substituent, then equation (10) is inappropriate and the more explicit form (11) must be used. When X = F,

$$\Delta^{X}_{\text{obs}}\ (\text{benzenes}) = 3{\cdot}2428 \times 10^{4}(A_{H}\mu_{H} - A_{X}\mu_{X})(\text{D.F.}) \quad (11)$$

$\mu_X = 0$; the data for *p*-difluorobenzene can thus be used to evaluate A_H, and from the slope listed in Table 5 a value of $+24{\cdot}2 \times 10^{-12}$ e.s.u. is obtained. This can be used in conjunction with the remaining data and the values of μ_X in Table 6 to evaluate A_X for the different situations; these values are in Table 6.

The variation in the calculated values of A indicates that the reaction field model breaks down for *para*-substituted fluorobenzenes, although it can be used successfully for the corresponding stilbenes. Apparently, the increased proximity of the two substituent groups makes the solvent polarisation take a more complex form (possibly owing to the increased contribution from molecular quadrupoles [3]), which is not well described by the present approximations.

TABLE 6

The apparent values of A for some *para*-substituted fluorobenzenes calculated from equation (11)

Substituent	μ/D	$10^{12}A$/e.s.u.
NH_2	$-2{\cdot}52$	$-26{\cdot}32 \pm 2{\cdot}08$
OH	$-2{\cdot}31$	$-28{\cdot}16 \pm 2{\cdot}42$
OMe	$-2{\cdot}08$	$-26{\cdot}26 \pm 2{\cdot}52$
H	$-1{\cdot}35$	$+24{\cdot}2 \pm 3{\cdot}58$
Cl	$+0{\cdot}97$	$+70{\cdot}95 \pm 14{\cdot}62$
Br	$+0{\cdot}52$	$+130{\cdot}46 \pm 50{\cdot}10$
I	$+0{\cdot}83$	$+79{\cdot}27 \pm 19{\cdot}02$
NO_2	$+2{\cdot}72$	$+69{\cdot}67 \pm 45$

* Average values obtained from ref. 10.

In Tables 5 and 6 the 'error' quoted for the estimated values of A are based upon an experimental uncertainty in the dipole moment of $\pm 0{\cdot}2$ D; in the case of *p*-fluoronitrobenzene the greatest error is in the slope of the correlation and this is the basis for the estimated error in A.

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