The Solvent Dependence of Fluorine Chemical Shifts. Part I

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The ^{19}F chemical shifts of a variety of organofluorine compounds (including the usual ^{19}F reference compounds) have been measured in a range of non-polar solvents. These allow elucidation of ^{19}F reference shifts from $CFCl_3$(int) in these solvents. The solvent dependence of the ^{19}F shifts in non-polar media is shown to be a product function of solute and solvent terms in the general case, and the experimental data are transformed into these solvent and solute numbers. The solvent numbers are discussed in the light of current theories of the van der Waals interaction, which are shown to require modification in order to fully explain the solvent shifts. The solvent sensitivity of the ^{19}F shift in any solute molecule (the solute number) is shown to be due to the extent of the electronic screening of the fluorine from the solvent by the other substituents in the solute molecule. A semi-empirical relationship is presented which quantitatively accounts for the observed results.

THE present knowledge concerning the effects of solvents on fluorine chemical shifts is extremely limited. Early studies by Glick and Ehrenson [1] and by Evans [2] on ^{19}F solvent shifts recognised that the van der Waals dispersion forces gave rise to the largest effects for this nucleus. The only other work of any magnitude has been carried out by Emsley and Phillips [3] and by Raynes and Raza.[4] However, all these studies together fall short of giving even a complete set of ^{19}F solvent shifts in as much as there has been no systematic survey of the shifts of ^{19}F reference compounds in normal solvents. As a consequence of this, precise data are not available as yet for the changes between ^{19}F reference scales in different solvents. These at present rely on the approximation of using one value, whatever the solvent, *e.g.* $CFCl_3 = C_6F_6 + 163$ p.p.m.[5] We shall show that the difference between these reference compounds can vary by *ca.* 3 p.p.m. even in non-polar solvents.

The effect of a solvent on the chemical shift of a nucleus is usually expressed by the relationship (1) [6]

$$\sigma_{\text{solvent}} = \sigma_b + \sigma_w + \sigma_E + \sigma_a \qquad (1)$$

where the contributions are σ_b the bulk susceptibility correction, σ_w the van der Waals shift, σ_E the total electric field effect, and σ_a the solvent anisotropy correction. It is σ_w the van der Waals shift that is the dominant term in ^{19}F solvent effects.[1,2] Theoretical treatments of σ_w have been given by several groups [7-10] but no satisfactory agreement has yet been found for fluorine shifts.

All these treatments are based on equation (2) where

$$\sigma_w = -B\langle E^2\rangle \qquad (2)$$

$\langle E^2\rangle$ is the time average square of the electric field at the nucleus considered produced by the fluctuating dipoles of the solvent molecules, and B is an empirical parameter.

A further factor which is regarded as significant is the position of the resonant nucleus within the solutes structure. This concept was termed the site factor,[10-12] and arises in the determination of $\langle E^2\rangle$ in equation (2).

Investigations of the B parameter have been performed for ^{19}F nuclei by Bernstein and his co-workers [13-15] from gas-phase solvent studies. In the case of liquids only Evans [2] and Raynes and Raza [4] have commented on possible causes for the observed differences in non-polar solvent effects on some fluoro-compounds.

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Recently it has been demonstrated from experimental results for proton solvent and gaseous ^{19}F chemical shifts that σ_W can be expressed as a product function of two terms, one characteristic of the solute, the other the solvent.[16,17] The theoretical consequences have yet to be thoroughly discussed.

We report here data for the ^{19}F chemical shifts of 19 types of fluorine resonances in a series of non-polar solvents and the gas phase as the first part of a general investigation of ^{19}F solvent shifts.* Included in the fluoro-compounds are a number of commonly used references so that the data can be used to correlate between reference scales for ^{19}F chemical shifts. Interpretation of the solvent effects allows quantitative investigation of the σ_W contribution to ^{19}F shifts and therefore also of the theory of the van der Waals interaction.

THEORY

Various formulations have been put forward to quantify the van der Waals contribution (σ_W) to solvent shifts.[7-10] They are generally based on the London formula applied to two non-polar molecules. The London energy of interaction (U_L) is given by equation (3) [18] where subscripts 1

$$U_L = -\frac{3\alpha_1\alpha_2 h}{2r^6}\left(\frac{\nu_1\nu_2}{\nu_1+\nu_2}\right) \qquad (3)$$

and 2 refer to solvent and solute respectively α is the polarizability, $h\nu$ is the excitation energy, and r is the distance between the centres of the solvent and solute.

The potential energy of a solute molecule in a static field E is [19] given by equation (4). Combining equations (3) and

$$U = -\tfrac{1}{2}\alpha_2 E^2 \qquad (4)$$

(4) gives the mean square electric field due to the attractive forces as (5). The chemical shift change of an atom in an

$$\langle E^2\rangle = \frac{3\alpha_1 h}{r^6}\left(\frac{\nu_1\nu_2}{\nu_1+\nu_2}\right) \qquad (5)$$

electric field was shown by Marshall and Pople [20] and by Stephen [21] to be proportional to the square of the electric field, to give equation (2).

Therefore the shift due to the dispersion forces is given by equation (6). Bothner-By [7] used a simplified version

$$\sigma_W = -\frac{3B\alpha_1 h}{r_6}\left(\frac{\nu_1\nu_2}{\nu_1+\nu_2}\right) \qquad (6)$$

of equation (6) using $\nu_1 \approx \nu_2$ which results in (7). Letting

$$\sigma_W = -3B\alpha_1 h\nu_1/2r^6 \qquad (7)$$

r equal the sum of the effective radii of the solvent and solute (r_1 and r_2) equation (6) becomes (8). Following

$$\sigma_W = -\frac{3B\alpha_1 h}{(r_1+r_2)^6}\left(\frac{\nu_1\nu_2}{\nu_1+\nu_2}\right) \qquad (8)$$

Bernstein [17] we use combining rules to separate this equation into product functions. Thus applying the relationships $\nu_1 + \nu_2 \approx 2(\nu_1\nu_2)^{\frac{1}{2}}$ and $r_1 + r_2 \approx 2(r_1r_2)^{\frac{1}{2}}$ to equation (8) we get (9) which gives the total shift as a product of a

$$\sigma_W = -\left(\frac{3Bh\nu_2^{\frac{1}{2}}}{2^7\, r_2^3}\right)_{\text{solute}} \times \left(\frac{\alpha_1\nu_1^{\frac{1}{2}}}{r_1^3}\right)_{\text{solvent}} \qquad (9)$$

solute and a solvent part without the assumption $\nu_1 = \nu_2$.

Howard *et al.*[8,22] used a continuum model treatment for the solvent and obtained a relationship (10) for σ_W, which was analogous to equation (6), where a_2 is the solute 'cavity'

$$\sigma_W = -\frac{3}{4}\frac{Bh}{a_2^3}\frac{(2n^2-2)}{(2n^2+1)}\left(\frac{\nu_1\nu_2}{\nu_1+\nu_2}\right) \qquad (10)$$

radius and n is the refractive index of the solvent.

The approximation $\nu_1 = \nu_2$ has been made for equation (10) by Weiner and Malinowski [16] and resulted in (11).

$$\sigma_W = \left(-\frac{3Bh}{4a_2^3}\right)_{\text{solute}} \times \left(\frac{n^2-1}{2n^2+1}\cdot\nu_1\right)_{\text{solvent}} \qquad (11)$$

However, the assumption $\nu_1 = \nu_2$ is strictly invalid as the basic treatment of Howard *et al.*[22] to give equation (10) is justifiable only if $\nu_1 \neq \nu_2$. The use of the combining rule for ν_1 and ν_2 above gives with equation (10), the relationship (12).

$$\sigma_W = -\left(\frac{3Bh}{4a_2^3}\nu_2^{\frac{1}{2}}\right)_{\text{solute}} \times \left(\frac{n^2+1}{2n^2+1}\cdot\nu_1^{\frac{1}{2}}\right)_{\text{solvent}} \qquad (12)$$

Thus the models used by Bothner-By [7] and Howard *et al.*[8,22] produce closely analogous results as given by equations (9) and (12) and both predict that the σ_W contribution is a product function of two terms.

EXPERIMENTAL

Solvent Shifts.—The ^{19}F chemical shifts were measured on a Varian A56/60 instrument by the sideband technique from an external reference compound held in a capillary tube. 1,1,2,2-Tetrachloro-1,2-difluoroethane was used as the external reference as its ^{19}F shift lies in the middle range of most fluoro-organic compounds and is suitable for giving sidebands up to ±6 kHz. Probe temperature was 39—42 °C. Solvents which would be gaseous at this temperature (n-C_5H_{12} and $CFCl_3$) were measured with a tight cap sealing the n.m.r. tube to prevent boiling. The gas C_4F_8 (b.p. −5 °C) was used as a liquid solvent by condensing it into an n.m.r. tube with the solute and sealing the tube. In this way it remained liquid at 40 °C.

All solutions contained between 1 and 2% solute mole fraction.

The gas-phase shifts were measured at probe temperature, using a Varian C.A.T. 1024 accessory in most instances. Fluoro-compounds which were gaseous at 40 °C (*i.e.* CF_2Br_2, CF_2BrCl, $CFCl_3$, CF_2Cl_2, *cis*- and *trans*-$CFCl{:}CFCl$, $CF_2{:}CCl_2$, $CF_3C{:}CCF_3$, and C_4F_8) were measured at pressures of 1—2 atmospheres. The remaining measurements for gas-phase shifts were taken at the liquid vapour pressure at 40 °C. Initial observation of the signal often required raising the probe temperature to increase the vapour pressure.

The shift was then measured on cooling to 40 °C. Very

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* The equivalent data for polar solvents will be given subsequently.

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rapid sample spinning was necessary and generally the signals obtained were between 5 and 40 Hz broad depending on the compound. No correction was made for the effects of pressure on the ^{19}F shifts but this is known to be small from work by Evans [2] (0·01 p.p.m. atm^{-1} for CF_4 gas).

The ^{19}F chemical shifts as measured directly from external $CFCl_2CFCl_2$ are given in Table 1. Most solvent shifts are reproducible to ± 2 Hz. The shifts of the α-, β-, and γ-fluorines of n-C_6F_{14} were measured to the centres of the multiplets. Gas-phase shifts are accurate to ± 8 Hz for the higher boiling compounds; and ± 4 Hz for the gases.

Bulk Susceptibilities.—As the shifts were measured using an external reference they had to be corrected to eliminate contributions from the bulk susceptibilities of the solvents (χ_v). Values of χ_v given in the literature are not of sufficient accuracy generally and also are not known for some of the solvents we used. This parameter is also temperature dependent due to its relation to liquid density and therefore it was desirable to obtain accurate values of χ_v at the probe temperature used for the solvents. To do this we employed the method used by Becconsall *et al.*[23] which relies on the difference in observed bulk susceptibility corrections depending on the magnetic field direction.

TABLE 1

Solute ^{19}F chemical shifts [a] in non-polar solvents

	Solvent								
	CCl_4	$CFCl_3$	C_7H_{16}	C_6H_{12}	C_6H_{14}	C_5H_{12}	C_6F_{14}	C_4F_8	Gas
CF_2Br_2	−4228·2	−4175·2	−4176·0	−4·1722	−4161·9	−4147·1	−4049·4	−4028·9	−3842
$CFCl_3$	−3851·0	−3791·5	−3789·3	−3786·0	−3774·0	−3758·2	−3646·8	−3652·2	−3425
CF_2BrCl	−3858·8	−3801·6	−3799·9	−3795·4	−3784·6	−3769·0	−3665·3	−3644·6	−3454
CF_2Cl_2	−3463·0	−3401·8	−3395·9	−3392·8	−3379·8	−3364·0	−3256·7	−3236·0	−3027
$CFCl_2CFCl_2$	−21·6	25·9	30·5	30·0	42·6	55·8	140·4	153·4	
CF_3CCl_3	791·8	848·3	859·0	859·0	874·1	890·6	982·4	997·4	1195
$CF_3C_6H_5$	−255·4	−187·6	−173·9	−167·7	−155·5	−136·6	−12·9	1·0	
$CF_3CHClBr$	474·0	544·9	557·8	559·4	575·4	593·8	707·0	723·8	
$C_6F_3Cl_3$	2507·2	2577·4	2575·4	2579·2	2593·2	2613·3	2750·9	2769·8	
C_6F_6	5314·2	5405·0	5409·2	5412·8	5431·2	5460·4	5622·8	5639·0	5915
cis-$CFCl{:}CFCl$	2059·2	2144·2	2144·0	2144·8	2166·6	2187·0	2338·6	2359·7	2598
trans-$CFCl{:}CFCl$	2890·9	2963·0	2962·2	2963·2	2981·8	3000·0	3128·3	3146·2	3362
$CF_2{:}CCl_2$	1126·7	1216·5	1225·5	1228·1	1245·8	1267·7	1418·6	1436·8	1682
$CF_3{\vdots}CCF_3$	−819·0	−747·0	−748·9	−735·0	−720·2	−702·5	−597·5	−577·4	−370
α n-C_6F_{14}	758·5	814·4	831·4	831·9	845·4	860·4	938·6	957·8	1155
β n-C_6F_{14}	3313	3355	3369	3368	3381	3393	3452	3466	3639
γ n-C_6F_{14}	3130	3169	3176	3178	3192	3200	3252	3263	
C_4F_8	3756·8	3826·0	3842·3	3847·4	3860·9	3884·4	3982·4	4001·4	4230·0
CF_4	−346·2	−258·7	−249·7	−243·9	−229·5	−208·7	−98·0	−73·8	

[a] In Hz upfield from $CFCl_2CFCl_2$(ext.) at 56·4 MHz.

TABLE 2

Solvent volumetric susceptibilities

	Volumetric susceptibilities [a] ($-\chi_v \times 10^6$ c.g.s.)
C_4F_8	0·564
n-C_6F_{14}	0·626
n-C_5H_{12}	0·558
n-C_6H_{14}	0·576
cyclo-C_6H_{12}	0·616
n-C_7H_{16}	0·600
$CFCl_3$	0·657
CCl_4	0·691
Me_4Si	0·538

[a] Relative to CCl_4 value from ref. 24.

For external referencing the relation used is (13) where

$$\chi_v - \chi_v^{ext} = \frac{1}{2\pi}(\nu_{obs}{}^{\perp} - \nu_{obs}{}^{\parallel}) \qquad (13)$$

χ_v and χ_v^{ext} are the bulk susceptibilities of the solvent and the external reference respectively; and $\nu_{obs}{}^{\perp}$ and $\nu_{obs}{}^{\parallel}$ are the shift differences between internal and external references for perpendicular and parallel magnetic field directions.

Thus the shift difference between internal and external tetramethylsilane was measured (ν_{obs}) in all the solvents used in this study on Varian A60 (perpendicular field direction) and Varian HR 220 MHz machines (parallel field direction) at 40 °C. The resulting values of $\chi_v - \chi_v^{ext}$ for the solvents give values of χ_v if one of the solvent values is known absolutely. We use the value of χ_v for CCl_4 ($-0{\cdot}691 \times 10^{-6}$ c.g.s.),[24] as the standard. Table 2 lists the values of χ_v obtained.

RESULTS

The correction for the bulk susceptibility of the solvent is given by equation (14). Strictly speaking the data

$$\sigma_b = 2\pi\chi_v/3 \qquad (14)$$

should be corrected also for the susceptibility of the external reference but this merely adds a constant increment to the shifts. Thus using the values of χ_v from Table 2 the ^{19}F chemical shifts in Table 1 were corrected for σ_b and the values obtained are given in Table 3. The chemical shifts in Table 3 are presented so that $CFCl_3$ solute in $CFCl_3$ solvent comes at zero and positive values are shifts to higher field. To enable solvent trends to be more easily distinguished a shift in p.p.m. has been subtracted from the total shift of each solute. This is expressed as an integer value and appears in parentheses by each solute in the Table.

Table 3 shows two important features. First the vertical columns represent the relative ^{19}F chemical shifts of the solutes in these solvents. As the bulk susceptibility correction is a constant for any vertical column (*i.e.* same solvent) the differences between values are equivalent to internally referenced shifts. Thus they may be used to give

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[24] G. W. Smith, General Motors Research Laboratories publication, GMR-317.

the shifts of these solutes relative to the standard fluorine reference compound $CFCl_3$ in the same solvent. All the commonly used reference compounds are included in the solutes, *i.e.* C_6F_6, CF_3CCl_3, $C_6F_3Cl_3$, and $CFCl_2CFCl_2$. This gives therefore the hitherto unknown correction factors between these reference scales and the $CFCl_3$ scale in a variety of commonly used non-polar solvents. This when combined with the comparable data for polar solvents (to be published subsequently) gives the complete conversion factors for all common reference compounds in all the common solvents.

TABLE 3

^{19}F chemical shifts [a] (p.p.m.) of reference compounds in common solvents, corrected for bulk susceptibility

		CCl_4	$CFCl_3$	C_7H_{16}	C_6H_{12}	C_6H_{14}	C_5H_{12}	C_6F_{14}	C_4F_8	Gas
CF_2Br_2	(−8·00)	0·33	1·20	1·06	1·16	1·26	1·49	3·36	3·59	5·73
$CFCl_3$	(0·00)	−0·98	0·00	−0·08	0·01	0·14	0·38	2·50	2·75	5·12
CF_2ClBr	(0·00)	−1·12	−0·18	−0·27	−0·16	−0·05	0·19	2·17	2·41	4·64
$CFCl_2CFCl_2$	(66·00)	0·91	1·69	1·65	1·67	1·81	2·01	3·65	3·75	5·65 [c]
sym-$C_6F_3Cl_3$	(111·00)	0·75	1·92	1·77	1·87	2·03	2·35	4·94	5·14	8·12 [c]
CF_2Cl_2	(5·00)	0·90	1·91	1·89	1·98	2·13	2·37	4·42	4·65	7·17
cis-$CFCl{:}CFCl$	(103·00)	0·81	2·25	2·12	2·17	2·47	2·79	5·62	5·87	8·91
trans-$CFCl{:}CFCl$	(118·00)	0·55	1·76	1·63	1·68	1·92	2·21	4·63	4·81	7·46
C_6F_6	(161·00)	0·52	2·06	2·01	2·11	2·35	2·83	5·86	6·01	9·73
CF_3CCl_3	(81·00)	0·34	1·27	1·34	1·37	1·35	1·81	3·58	3·71	6·04
$CF_2{:}CCl_2$	(87·00)	0·27	1·79	1·84	1·91	2·14	2·49	5·31	5·51	8·67
$C_6H_5CF_3$	(62·00)	0·77	1·90	2·02	2·17	2·30	2·60	4·93	5·05	7·68 [c]
$CF_3CHClBr$	(75·00)	0·70	1·89	2·00	2·06	2·26	2·55	4·70	4·86	7·38 [c]
$CF_3C{\vdots}CCF_3$	(52·00)	0·78	1·98	2·01	2·11	2·29	2·56	4·57	4·79	7·29
α C_6F_{14}	(80·00)	0·75	1·67	1·85	1·89	2·05	2·27	3·80	4·01	6·33
β C_6F_{14}	(126·00)	0·04	0·71	0·84	0·86	1·00	1·18	2·37	2·48	4·37
γ C_6F_{14}	(122·00)	0·79	1·41	1·42	1·49	1·65	1·76	2·82	2·88	4·73
C_4F_8	(133·00)	0·91	2·06	2·23	2·36	2·51	2·89	4·77	4·98	7·85
CF_4	(61·00)	0·16	1·64	1·68	1·82	1·99	2·32	4·42	4·72	7·76 [b]

[a] Relative to $CFCl_3$ in $CFCl_3$ (0·00). [b] Taken from ref. 4. [c] Calculated see text.

The second feature of interest in Table 3 is the horizontal values which show the effects of the solvents after eliminating σ_b. These effects are very large ranging from 5·40 for CF_2Br_2 up to 9·21 p.p.m. for C_6F_6 between the gas phase and CCl_4 solution. Following the work by Emsley and Phillips [3] it may reasonably be assumed that the contribution from the electric field effect is only small (<1 p.p.m. in these non-polar solvents). Similarly Weiner and Malinowski have shown from proton chemical shifts studied that the contribution from the anisotropy of the solvents is also small (<0·5 p.p.m.) [25] and therefore the observed variation in the different solvents is predominantly due to the contribution from the van der Waals interaction σ_w [equation (15)].

$$\sigma_{gas} - \sigma_{solvent} = - \sigma_w \qquad (15)$$

It has already been mentioned that σ_w has been interpreted as a product function of solute and solvent terms [16,17] and the theoretical justification has been given in an earlier section. Therefore it was of interest to break down the data into these constants.

These we have termed solvent (S^v) and solute (S^u) numbers following the nomenclature of Bernstein [17] [equation (16)].

$$\sigma_w = S^v \times S^u \qquad (16)$$

Solute and Solvent Numbers.—Using equation (16) the complete data in Table 3 may be broken down into solvent and solute numbers as follows. First a reference compound is required. Because of the anomalous behaviour of perfluoroalkanes (see later) we decided not to use CF_4 as used by Bernstein for gases,[17] but to use instead CF_3CCl_3 as the standard. For this compound $S^u = 1$; thus the solvent number of any solvent is simply defined as the shift of CF_3CCl_3 from the gas phase in that solvent.

The solute number (S^u) for any other solute is defined as the difference in the shift of this solute in any solvent from the gas-phase shift divided by the comparable shift for CF_3CCl_3.

In practise the complete data in Table 3 were analysed according to equation (16) by a least mean squares procedure to obtain the solvent and solute numbers given in Tables 4 and 5. A comparison of the calculated shifts according to equation (16) and the observed values is given in Table 6. The overall agreement between observed and calculated is

TABLE 4

Solvent numbers (S^v) and refractive indices for some non-polar solvents

No.	Solvent	S^v (p.p.m.) [a]	Refractive index [b]
(1)	Gas phase	0·00	1·00 (assumed)
(2)	C_4F_8	2·23	1·2303 [c]
(3)	n-C_6F_{14}	2·41	1·2515 [d]
(4)	n-C_5H_{12}	4·32	1·3579
(5)	n-C_6H_{14}	4·56	1·3749
(6)	cyclo-C_6H_{12}	4·72	1·4266
(7)	$CFCl_3$	4·74	1·3865 [e]
(8)	n-C_7H_{16}	4·79	1·3876
(9)	CCl_4	5·71	1·4664
(10)	$C(NO_2)_4$	3·60 [f]	1·4399
(11)	$SnEt_4$	4·70 [f]	1·4693 [g]
(12)	$SnMe_4$	5·12 [f]	1·4386 [g]
(13)	$SnCl_4$	6·13 [h]	1·512
(14)	n-C_7F_{16}	2·37 [i]	1·2618
(15)	n-$C_{16}H_{34}$	5·32 [i]	1·4345
(16)	$CHBr_3$	7·14 [i]	1·5976
(17)	$CBrCl_3$	6·26 [j]	1·5061
(18)	$CHBr_2Cl$	6·71 [j]	1·5482
(19)	CBr_2Cl_2	7·09 [j]	

[a] This work unless otherwise stated. [b] Taken from 'Handbook of Chemistry and Physics,' Chemical Rubber Company, Columbus, 49th edn. [c] Calculated from data by A. H. Fainberg and W. T. Miller, *J. Org. Chem.*, 1965, **30**, 864, using density quoted in Peninsular Catalog. [d] A. M. Lovelace, W. Postelnik, and D. A. Rausch, 'Aliphatic Fluorine Compounds', Reinhold, New York, 1958. [e] 'Langes Handbook of Chemistry,' McGraw-Hill, New York, 10th edn. [f] Calculated from ref. 4. [g] H. Korsching, *Z. Naturforsch.*, 1964, **1**, 219. [h] Calc. see text. [i] Calc. from ref. 2. [j] Calc. from ref. 1.

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[25] P. H. Weiner and E. R. Malinowski, *J. Phys. Chem.*, 1971, **75**, 1207.

TABLE 5

Solute numbers (S^u) for different classes of fluoro-compounds [a]

Alkanes		Alkenes		
(1) CF_2Br_2	0·97	(27) $CF_2{:}CCl_2$		1·43
(2) $CFCl_3$	1·08	(28) *cis*-$CFCl{:}CFCl$		1·40
(3) CF_2ClBr	1·02	(29) *trans*-$CFCl{:}CFCl$		1·21
(4) CF_2Cl_2	1·11			
(5) CF_3CCl_3	1·00			
(6) $CF_3C{\equiv}CCF_3$	1·11			
(7) $CFCl_2CFCl_2$	0·83			
(8) $CF_3C_6H_5$	1·21	Aromatics		
(9) $CF_3CHClBr$	1·17			
(10) α n-C_6F_{14}	1·00	(30) C_6F_6		1·62
(11) β	0·79	(31) *sym*-$C_6F_3Cl_3$		1·29
(12) γ	0·69	(32) *p*-$C_6F_4Cl_2$		1·44 [e]
(13) C_4F_8	1·23			
(14) CF_4	1·33	(33) C_6F_5H	*o*	1·28 [b]
(15) C_6F_{12}	0·94 [b]		*m*	1·53 [b]
(16) $C_5H_{11}F$	1·44 [c]		*p*	1·43 [b]
(17) α n-C_7F_{16}	0·92 [c]	(34) C_6F_5Cl	*o*	1·35 [b]
(18) β	0·71 [c]		*m*	1·62 [b]
(19) γ	0·60 [c]		*p*	1·62 [b]
(20) $CFBr_3$	0·59 [c]			
(21) Me_3CF	2·04 [c]	(35) *p*-FC_6H_4F		1·50 [f]
(22) CF_2BrCF_2Br	0·48 [d]			
(23) $CF_3CCl_2CCl_3$	0·90 [e]			
(24) $CCl_3CF_2CCl_3$	0·69 [e]			
(25) $\mathrm{C}\mathit{F}_2\mathrm{ClCFCl}_2$	0·89 [e]			
(26) $\mathrm{C}\mathit{F}\mathrm{Cl}_2\mathrm{CF}_2\mathrm{Cl}$	0·82 [e]			

[a] Values taken from Table 3 unless otherwise stated. [b] Calc. from ref. 3. [c] Calc. from ref. 2. [d] Calc. from ref. 1. [e] Calc. from further measurements. [f] Calc. from ref. 4.

very good for most compounds except in the case of the perfluoroalkanes which give a marked rise in the r.m.s. error (0·2—0·3 p.p.m.). Furthermore inspection of the individual values for the perfluoroalkanes shows that it is in the hydrocarbon solvents that consistent high field errors arise. These are shown in the boxed areas in Table 6. A graphical illustration of this is shown in Figure 1. The solvent shifts of two normal fluoro-compounds (CF_2Br_2 *vs.* $CFCl_3$) show a good linear correlation whereas those of C_4F_8 against $CFCl_3$ only correlate in non-hydrocarbon solvents. It is known that mixtures of perfluorocarbons and hydrocarbons show abnormal thermodynamic properties although the cause is not fully understood (see ref. 26 and for a recent review ref. 27). Therefore, this indicates that the anomalous shifts found for perfluorocarbons must arise from specific interactions.

TABLE 6

Observed and calculated (in parentheses) solvent shifts in p.p.m. from gas phase

	Solvent								
Solute	CCl_4	C_7H_{16}	$CFCl_3$	C_6H_{12}	C_6H_{14}	C_5H_{12}	C_6F_{14}	C_4F_8	R.m.s. error
R.m.s. error	*0·119*	*0·161*	*0·072*	*0·167*	*0·165*	*0·165*	*0·098*	*0·081*	
CF_2Br_2	5·40(5·54)	4·67(4·65)	4·53(4·60)	4·57(4·58)	4·47(4·42)	4·24(4·19)	2·37(2·34)	2·14(2·16)	*0·069*
$CFCl_3$	6·10(6·17)	5·20(5·17)	5·12(5·12)	5·11(5·10)	4·98(4·92)	4·74(4·67)	2·62(2·60)	2·37(2·41)	*0·050*
CF_2ClBr	5·76(5·82)	4·91(4·89)	4·82(4·84)	4·80(4·81)	4·69(4·65)	4·45(4·41)	2·47(2·46)	2·23(2·27)	*0·037*
CF_2Cl_2	6·27(6·34)	5·28(5·32)	5·26(5·26)	5·19(5·24)	5·04(5·06)	4·80(4·80)	2·75(2·68)	2·52(2·48)	*0·050*
cis-$CFCl{:}CFCl$	8·10(7·99)	6·79(6·71)	6·66(6·64)	6·74(6·61)	6·44(6·38)	6·12(6·05)	3·29(3·37)	3·04(3·12)	*0·090*
trans-$CFCl{:}CFCl$	6·91(6·91)	5·83(5·80)	5·70(5·74)	5·78(5·71)	5·54(5·52)	5·25(5·23)	2·83(2·92)	2·65(2·70)	*0·052*
C_6F_6	9·21(9·25)	7·72(7·76)	7·67(7·68)	7·62(7·65)	7·38(7·39)	6·90(7·00)	3·87(3·90)	3·72(3·61)	*0·062*
CF_3CCl_3	5·70(5·71)	4·70(4·79)	4·77(4·74)	4·67(4·72)	4·49(4·56)	4·23(4·32)	2·46(2·41)	2·33(2·23)	*0·075*
$CF_2{:}CCl_2$	8·40(8·17)	6·83(6·85)	6·88(6·78)	6·76(6·75)	6·53(6·52)	6·18(6·18)	3·36(3·45)	3·16(3·19)	*0·102*
$CF_3C\vdots CCF_3$	6·51(6·34)	5·28(5·32)	5·31(5·26)	5·18(5·24)	5·00(5·06)	4·73(4·80)	2·72(2·68)	2·50(2·48)	*0·082*
α n-C_6F_{14}	5·58(5·71)	4·48(4·79)	4·66(4·74)	4·44(4·72)	4·28(4·56)	4·06(4·32)	2·53(2·41)	2·32(2·23)	*0·207*
β	4·33(4·51)	3·53(3·78)	3·66(3·74)	3·51(3·73)	3·37(3·60)	3·19(3·41)	2·00(1·90)	1·89(1·76)	*0·200*
C_4F_8	6·94(7·02)	5·62(5·89)	5·79(5·83)	5·49(5·81)	5·34(5·61)	4·96(5·31)	3·08(2·96)	2·87(2·74)	*0·242*
CF_4	7·60(7·60)	6·08(6·37)	6·12(6·30)	5·94(6·28)	5·77(6·06)	5·44(5·75)	3·34(3·21)	3·04(2·97)	*0·247*

The overall results show therefore that the data in Table 3 do conform to a product function of two constants. Following from this we can calculate the solute numbers for the compounds for which the gas-phase shifts could not be measured and these are also included in Table 5. Further, from these the gas-phase shifts can be calculated and these are given in Table 3.

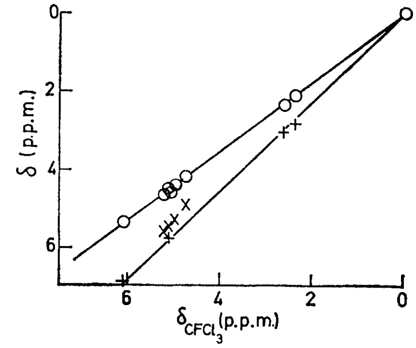

FIGURE 1 Solvent shifts (p.p.m. downfield from the gas phase) of CF_2Br_2 (○) and C_4F_8 (×, hydrocarbon solvents; +, all others) *versus* $CFCl_3$

Further solvent numbers may be deduced from previous studies on ^{19}F solvent shifts for several more non-polar solvents. The calculation of these solvent numbers requires some brief explanation. First in the solvent studies by Raynes and Raza [4] we found that only five of the ten non-polar solvents used behaved consistently. The criterion for normal behaviour was that graphs of the solvent shifts of SF_6, SiF_4, and C_6F_6 *versus* CF_4 should be straight lines. This was fulfilled by the solvents CCl_4, $SnMe_4$, $SnEt_4$, $C(NO_2)_4$, and the gas phase. Thus their solvent numbers were derived from the CF_4 shifts. A similar procedure was used for the data by Evans.[2] From his results we found consistent behaviour for the solutes $CF_3C_6H_5$, $CFCl_2CFCl_2$, $C_5H_{11}F$, and $CFMe_3$ in the solvents C_7F_{16}, C_7H_{16}, CCl_4, and $CHBr_3$. Therefore we obtained the solvent numbers for C_7F_{16} and $CHBr_3$. From the work by Glick and Ehrenson [1] we have calculated the solvent numbers for the solvents $CBrCl_3$, $CHBr_2Cl$, and CCl_2Br_2. Finally we

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[26] R. L. Scott, *J. Phys. Chem.*, 1958, **62**, 136.

[27] G. R. Patrick, *Chem. in Britain*, 1971, 154.

measured the shifts of C_4F_8 and CF_3CCl_3 in $SnCl_4$ (7·48 and 6·17 p.p.m. respectively from the gas phase) to obtain the average solvent numbers. These solvent numbers are presented in Table 4.

Additional solute numbers may be obtained in a similar manner.

In some instances the literature solvent shifts had to be corrected for bulk susceptibility using the values in Table 2. Also where shifts were quoted relative to an internal reference (*e.g.* C_6F_6) these were converted to the $CFCl_2CFCl_2$ scale using Table 1. It should be noted that in the case of perfluoroalkane solutes in hydrocarbon solvents the solute number must be determined relative to that of a known perfluoroalkane to reduce the error from any anomalous behaviour in hydrocarbon solvents.

The solute numbers obtained in this way are less accurate than those from Table 3 owing to the limited range of non-polar solvents used. It must also be noted that for compounds which exist in more than one rotational form, the solute number will vary due to the relative populations of the rotamers changing with solvent.[28] However, for all the substituted ethanes considered here (*i.e.* $CFCl_2CFCl_2$, CF_2BrCF_2Br, $CF_2ClCFCl_2$, and $C_5H_{11}F$) the change in rotamer population with phase or solvent is very small. Only for molecules for which the individual rotamers have very different dipole moments will there be an appreciable change in the rotamer populations with solvent [28] and these cases are excluded from consideration here precisely because of their polar nature.

All these solute numbers are given in Table 5.

DISCUSSION

(a) *Solvent Numbers.*—The solvent numbers obtained in Table 4 can now be used to investigate the theoretical treatments of the van der Waals term. As shown previously the solvent numbers should show a correlation with the solvent terms of equations (9) and (12), *i.e.* with $(\alpha_1\nu_1^{\frac{1}{2}}/r_1^3)_{\text{solvent}}$ from Bothner-By's treatment and with $[(n^2-1)\nu_1^{\frac{1}{2}}/(2n^2+1)]_{\text{solvent}}$ from that of Howard *et al.* The solvent polarizability α_1 is given by equation (17) [29]

$$\alpha_1 = (n^2-1)r_1^3/(n^2+2) \qquad (17)$$

and thus both treatments result in very similar solvent terms. Unfortunately calculation of the ν_1 values imposes some difficulty (see refs. 8 and 16 for a discussion) and therefore as an approximation we make the assumption suggested by Howard *et al.*[8] that ν_1 is constant for all solvents. The theoretical prediction is therefore that solvent number should correlate with a function of the solvent refractive index. Values of n for the solvents are included in Table 4. Very similar graphs are found for the plots of solvent number against either $(n^2-1)/(n^2+2)$ or $(n^2-1)/(2n^2+2)$ and therefore only the latter case has been illustrated. The results are shown in Figure 2 and the linear correlation obtained substantiates the theoretical treatments to some degree.

However, the observed linear correlation does not pass through the origin (*i.e.* the gas-phase point), as predicted theoretically. A similar anomaly was found by Laszlo *et al.*[30] for proton chemical shifts when the shifts of CH_4 were plotted against the same function of the refractive index of the solvents. These workers suggested that constant anisotropic contributions from the solvents caused the gas-phase point to deviate from the straight line. However, if anisotropy was the cause then there would be a constant deviation of the gas-phase point for all solutes. From our more general results the discrepancy has a constant solvent number (−2·55) but the magnitude of the observed effect for any solute is given by −2·55 × solute number. Thus the cause cannot be due to anisotropic contributions owing to its dependence on the solute.

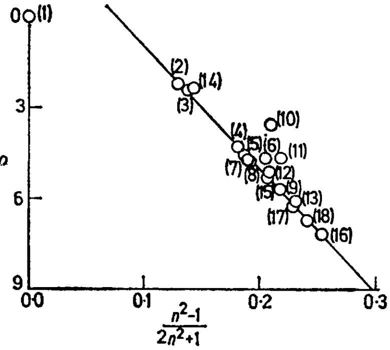

FIGURE 2 Solvent numbers (S^v) *versus* $(n^2-1)/(2n^2+1)$

A possible reason for the deviation of the gas phase is that the refractive index function is incorrect. In this connection it is of interest to note that a better result is obtained by plotting (n^2-1) against the solvent number (Figure 3).

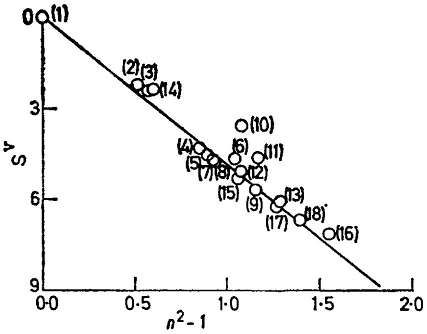

FIGURE 3 Solvent numbers (S^v) *versus* (n^2-1)

Here the gas-phase point is found to lie on the straight line and this suggests the deviation of the origin from the correlation of Figure 2 is due to the non-linearity of the graph. We conclude therefore that the approximations involved in deriving equations (9) and (12) may not be valid for describing the detailed van der Waals shifts of the solvents.

(b) *Solute Numbers.*—The solute numbers are a

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[28] R. J. Abraham, L. Cavalli, and K. G. R. Pachler, *Mol. Phys.*, 1966, **11**, 471.

[29] See for example, H. Frölich, 'Theory of Dielectrics,' Pergamon, Oxford, 1958, 2nd edn.

[30] P. Laszlo, A. Speert, and W. T. Raynes, *J. Chem. Phys.*, 1969, **51**, 1677.

measure of the susceptibility of the fluorine shift to the van der Waals dispersion forces of a non-polar solvent. Thus from equation (2) the solute numbers should reflect some dependence on the bond parameter *B*. However, in all investigations to date the parameter *B* for fluorine is defined by equation (2) and cannot be determined theoretically. It seems reasonable to assume that the susceptibility of the fluorine shift to the dispersion forces is a function of the C–F bond character. Therefore in our investigation of the solute numbers we will consider each class of fluoro-compound separately to minimise changes in the C–F bond character.

Fluoroalkanes.—It can be seen from Table 5 that the solute numbers for this type of compound cover the widest range of values going from CF_2BrCF_2Br (S^u = 0·48) up to Me_3CF (S^u = 2·04). Evans in an early study of ^{19}F solvent shifts came to two conclusions concerning the relative magnitude of solvent effects on solutes. He stated that the important factors affecting the solvent dependence were (a) the electron distribution around the fluorine and (b) the extent to which the fluorine is protected from the solvent by other atoms or groups in the molecule. Thus he accounted for the large solvent dependence of Me_3CF as being due to the high electron density on the fluorine relative to other compounds. For a fluorine protected from the solvent he quoted $CFBr_3$ (S^u = 0·59) as an example where the bromines sterically shield the fluorine. However, these arguments are inconsistent because on the basis of van der Waals radii bromine is as bulky as the methyl group.[31] Therefore on steric grounds alone the fluorine in Me_3CF should be shielded from the solvent to the same extent as in $CFBr_3$. This suggests that the difference between these solutes is due entirely to the electron density differences on the fluorine. Also as their solute numbers span the entire range of those observed the electron density should be the dominant contribution to the solute number. However, mere inspection of Table 5 demonstrates that this is not the case. For example the fluorine electron density in $C{\cdot}CF_2{\cdot}C$ (12) is certainly greater than in CF_4 (14), yet the solute number is much *less* (0·69 compared to 1·33).

This suggests a completely different approach to the problem.

If we consider the series of fluoromethanes CF_4, CF_2Cl_2, $CFCl_3$, CF_2ClBr, CF_2Br_2, and $CFBr_3$ the solute number decreases as the halogen size increases. However, as stated before Me_3CF does not have the same solute number as $CFBr_3$ although methyl and bromine are sterically of similar sizes. One difference between these groups is the number of electrons associated with them (equivalent to the atomic number *Z*). Thus the groups Me, F, Cl, and Br have electrons numbering 9, 9, 17, and 35 respectively and this approximately reflects the order of decrease of the solute numbers for the series of fluoromethanes. For example Me_3CF has 27 electrons in the substituent groups, $CFCl_3$ has 51, and $CFBr_3$ has 105, and their solute number are 2·04, 1·08, and 0·58 respectively.

This correlation of solute number with the total number of electrons in the substituent groups for fluoromethanes suggests that the solute number may be determined by the amount of electronic screening of the fluorine nucleus from the solvent electric field. Thus in certain orientations the effect of the oscillating solvent dipoles will be attenuated by the electron clouds of the substituents giving a reduced interaction with the fluorine. This mechanism explains the total observed range of solute number in fluoromethanes from 0·58 for $CFBr_3$ up to 2·04 for Me_3CF and this suggests that this is the dominant mechanism for these compounds. The solute numbers for fluoroethanes and higher order alkanes therefore should also reflect this dependence on the substituent atoms and the extension to these systems can be made if the distance (r) of the atoms to the fluorine nucleus is also taken into account. The effect of the substituent atom on the solute number will obviously lessen with increasing separation. If the shielding of the substituent is proportional to the solid angle subtended at the fluorine nucleus then the electronic screening will be proportional to the inverse square of the distance r. This suggests that a correlation should exist between solute number and the sum of the screening effects of the substituent atoms given by the relation $\sum_i Z_i/r_i^2$ where Z_i is the number of electrons in the ith atom, and r_i is the internuclear distance from the fluorine to the ith atom in Å.

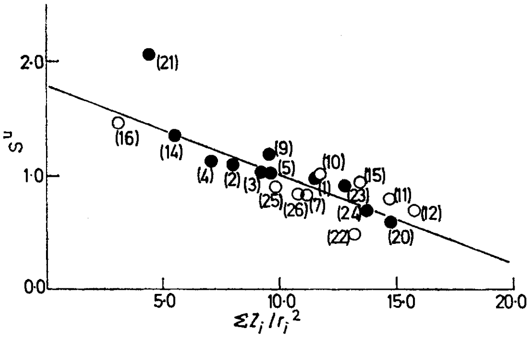

FIGURE 4 Solute numbers (S^u) *versus* the sum of the electronic screening term Z_i/r_i^2 for the fluoroalkane solutes of Table 5

Calculation of the Z_i/r_i^2 terms was made for each atom in the solute molecule but omitting the C–F fragment which is constant. Thus CF_4 has three geminal fluorine terms; whilst CF_3CCl_3 has two geminal fluorines, one geminal carbon, one vicinal *trans*, and two vicinal *gauche* chlorines.

The molecular geometries used to calculate r_i^2 were those given by Abraham and Parry.[32] The plot of solute number *versus* $\Sigma Z_i/r_i^2$ is shown in Figure 4.

The points marked by a filled circle in the Figure represent compounds with a rigid structure whilst the unfilled circles are for compounds having two or more conformations. This distinction is made because (a) as stated

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[31] B. L. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 4472.

[32] R. J. Abraham and K. Parry, *J. Chem. Soc.* (*B*), 1970, 539.

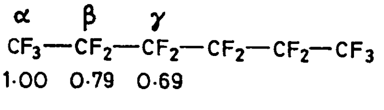
before the solute numbers for the latter are less accurate and (b) the value of $\Sigma Z_i/r_i^2$ in each rotamer varies. Therefore we have used the value of $\Sigma Z_i/r_i^2$ for the conformation that will be the most stable in non-polar solvents based on steric considerations.

The results in Figure 4 indicate that a reasonable correlation exists between solute number and the sum of the substituent effects. From this we infer that (a) our initial assumption to disregard the differences in electron density on the fluorine is reasonable (some of the scatter of the points in Figure 4 could of course be due to this) and (b) that the substituent's effect on the fluorine's susceptibility to solvent is not due merely to the steric size of the substituent shielding the fluorine from the solvent. This latter deduction now gives a new interpretation to the concept of the site factor of Rummens and his co-workers [10–12] which is given by equation (18)

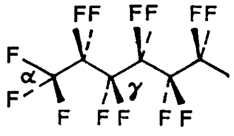
$$S_6 = (1 + q^2)/(1 - q^2)^4 \qquad (18)$$

where $q = d/r$, d being the distance of the fluorine to the centre of the molecule, and r the intermolecular solute–solvent distance. This was used to differentiate between the solvent effects on two types of ^1H resonances in the same molecule, *i.e.* $Si(CH_2CH_3)_4$. The observation that the methylene protons were less susceptible to solvent effects than the methyl was explained by the S_6 ratio of the two sites, *i.e.* CH_2 is closer to the centre and consequently further from the solvent. Our results lead to an alternative explanation in that the CH_2 protons are closer to the centre of the molecule experiencing a greater screening by the other atoms in the same molecule. We also note that this is a property only of the solute whereas the site factor concept results in different S_6 values for one solute in different solvents.[10] Thus the site factor is not compatible with the breakdown of the solvent effects into separate solute and solvent terms.

It is of interest therefore to investigate a compound having several types of fluorine in a molecule and to see how the observed and calculated ratio of solute numbers compare. Perfluoro-n-hexane has three types of fluorine and the observed solute numbers are shown. These



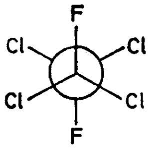
$$\begin{array}{cccccc} \alpha & \beta & \gamma & & & \\ CF_3 & —CF_2 & —CF_2 & —CF_2 & —CF_2 & —CF_3 \\ 1{\cdot}00 & 0{\cdot}79 & 0{\cdot}69 & & & \end{array}$$



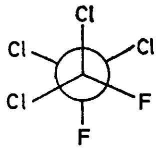
decrease on going to the centre of the molecule as expected. If we assume the planar zig-zag conformation as the most stable, which is reasonable in view of the low dielectric constant (ε 1·7) for the compound, we can sum the Z_i/r_i^2 contributions from every atom to each fluorine site.

The values obtained were 11·7 for α-CF_3 (average of three fluorines), 14·7 for β-CF_2, and 15·7 for γ-CF_2. The ratio of the reciprocals of these values 1·00 : 0·82 : 0·75 agrees very well with the ratio of the observed solute numbers, *i.e.* 1·00 : 0·79 : 0·69.

The possibility of measuring the solute number in the separate rotamers of a compound was also investigated. This can be done for $CFCl_2CFCl_2$ in solution on cooling to below 200 K, where the separate signals of the *trans* and *gauche* rotamers are observed.



trans



gauche

Newmark and Sederholm[33] have found the shift difference between the rotamers in $CFCl_3$ solution over a range of temperatures. We found the shift difference in n-pentane solution at 171·3 K to be 63 ± 1 Hz. Extrapolation of Newmark and Sederholm's data to 171·3 K gives a shift difference in $CFCl_3$ of 63·0 Hz. Thus we deduce that the solute numbers for the fluorines in both rotamers are very close. The value predicted from $\Sigma Z_i/r_i^2$ for the *gauche* : *trans* ratio of solute numbers is 1·04 : 1·00 which is in good agreement with that observed.

We conclude therefore that this, as yet, empirical relationship satisfactorily predicts the solute number of a fluorine in saturated systems. It has the advantage of reformulating the three previous concepts, *i.e.* the electron density on the fluorine, the steric shielding by groups, and the site factor, by one simple treatment which had hitherto not been considered, *i.e.* the screening by the substituent electron clouds.

Fluoroalkenes.—The three fluoroalkenes $CF_2{:}CCl_2$ (27), *cis*-$CFCl{:}CFCl$ (28), and *trans*-$CFCl{:}CFCl$ (29) were treated in a similar fashion to the fluoroalkanes, *i.e.* comparison of the solute numbers was made with the term $\Sigma Z_i/r_i^2$ from the atoms. The parameters used for calculating $\Sigma Z_i/r_i^2$ were taken from microwave data[34] for C_2Cl_4 and C_2F_4 and are: C=C 1·30, C–F 1·33, and C–Cl 1·72 Å; F–C–F = F–C–Cl = Cl–C–Cl = 114°. The values obtained are: (27) 5·7, (28) 5·9, and (29) 6·1 which approximately parallel the solute numbers giving the correct order. Also if these values are included in Figure 4 they would lie in the region around CF_4 which indicates that the double bond has little or no effect on the solute number in these compounds.

Aryl Fluorides.—The data in Table 5 for this class of fluorocarbon cover several series of compounds. These are chlorofluorobenzenes, pentafluorobenzenes, and *para*-substituted monofluorobenzenes.

If we consider the chlorofluorobenzenes the solute

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[34] 'Tables of Interatomic Distances and Configuration of Molecules and Ions,' The Chemical Society, London, 1958.

numbers range from 1·29 for *sym*-$C_6F_3Cl_3$ (31) up to 1·62 for C_6F_6 (30). Intermediate degrees of chlorine substitution result in values between these extremes. For example the *para*- and *meta*-positions in C_6F_5Cl (34) have solute numbers the same as C_6F_6, *i.e.* 1·62. The *ortho*-position however has a lower value of 1·35. Thus these results appear to indicate that the solute number correlates with the distance of separation of the chlorine from the fluorine as was the case in the fluoroalkanes and alkenes.

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