175. *Solvent Shifts of Fluorine Nuclear Magnetic Resonance Spectra.*

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The solvent shifts of the fluorine nuclear magnetic resonance lines of a number of organic fluorine compounds are recorded and discussed. Appreciable shifts are observed with change in pressure of a gaseous fluorine compound, and with change in temperature of a liquid compound. Intramolecular van der Waals forces may be important in determining fluorine shifts.

THE fluorine resonances of organic fluorine compounds show [1] large solvent shifts, which are too great to be attributed to changes in the volume susceptibilities of the solvents. These anomalous shifts may be due to an increase in the paramagnetic shielding term of the electrons in the vicinity of the fluorine nucleus, caused by the polarizable solvent molecules. Recently Glick and Ehrenson [2] published similar results, and more data are now presented.

Experimental

The solvents were purified by standard procedures. Two or more dilute solutions of each fluorine compound were studied, and the results extrapolated to infinite dilution. A capillary containing the pure fluorine compound, or a strong solution of it, was normally used as an external reference. Carbon tetrafluoride was studied at pressures up to 30 atm., obtained by condensing a known volume of gas in the standard Pyrex nuclear magnetic resonance tubes (3 mm. internal diameter, 5 mm. external diameter). These tubes have successfully withstood pressures of 60 atm. The external reference was a capillary of benzotrifluoride, and the results were extrapolated to zero pressure.

Measurements were made at 40 Mc. on a Varian V4300B spectrometer. The data at temperatures other than room temperature (21° ± 1°) were obtained with a Varian Model V-4340 variable temperature probe. The accuracy of the results is normally about ±0·02 p.p.m. The solutions were air-saturated, except those of carbon tetrafluoride.

Results and Discussion

The solvent shifts observed for a number of organic fluorine compounds are given in Table 1, heptane being normally taken as the standard. Values are also given for the shifts corrected for the bulk diamagnetic shielding of the solvent. The theoretical expression [3] $\Delta H/H = (2\pi/3)\Delta\kappa$ was used, where $\Delta\kappa$ is the difference in volume susceptibilities. Higher numerical factors ($\sim$2·60) have been found for proton resonances.[4] Nevertheless, it seems preferable to use the theoretical factor of $2\pi/3$ (=2·09) for fluorine resonances, since the deviations from the theoretical factor for proton resonances may be due to medium effects similar to, but much smaller than, those found with fluorine resonances. In any case, the use of an empirical factor of 2·60 for fluorine resonances would not affect the corrected values very greatly.

It can be seen that, although the solvent shifts of fluorine compounds vary greatly in relative magnitude, the solvent dependence is roughly similar in all cases. Only one gas (carbon tetrafluoride) was studied, but the solvents probably produce an anomalous shift of all the fluorine resonances to lower fields, as compared with those for isolated molecules in the gas phase. This effect is greatest with methylene iodide, and least with the perfluoro-hydrocarbons. Carbon disulphide and benzene are anomalous; for example, carbon disulphide produces a very large shift of the fluorine resonance of pentyl fluoride,

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[1] Evans, *Proc. Chem. Soc.*, 1958, 115.

[2] Glick and Ehrenson, *J. Phys. Chem.*, 1958, **62**, 1599.

[3] Dickinson, *Phys. Rev.*, 1951, **81**, 717.

[4] Bothner-By and Glick, *J. Chem. Phys.*, 1957, **26**, 1647.

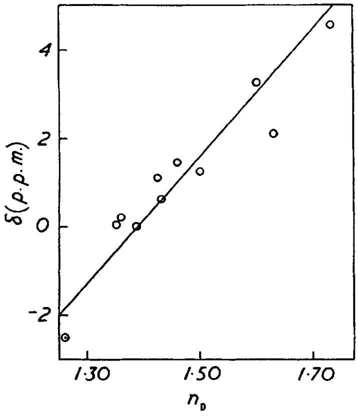
TABLE 1. *Solvent shifts δ (p.p.m.) to lower applied fields of the fluorine resonances in compounds at infinite dilution in several solvents.*

	Compound									
	$C_6H_5{\cdot}CF_3$		$CCl_2F{\cdot}CCl_2F$		$C_5H_{11}F$		$(CH_3)_3CF$		CF_4	
Solvent	δ	δ (corr.)	δ	δ (corr.)	δ	δ (corr.)	δ	δ (corr.)	δ	δ (corr.)
CH_2I_2	5·78	4·57	3·52	2·31	7·33	6·12	$8{\cdot}5_3$	$7{\cdot}3_2$	11·85	9·88
$CHBr_3$	4·03	3·26	2·71	1·94	4·53	3·76	5·95	5·18		
CS_2	2·32	2·11	1·47	1·26	5·35	5·14	3·88	3·66		
CCl_4	1·70	1·47	1·05	0·82	1·88	1·64	2·55	2·32	9·24	7·78
CH_2Cl_2	1·42	1·11	0·43	0·11						
C_6H_6	1·31	1·24	0·03	−0·05	1·24	1·17				
$C_{16}H_{34}$	0·77	0·64								
$C_2H_5{\cdot}OH$	0·17	0·20								
C_7H_{16}	0	0	0	0	0	0	0	0	7·30	6·06
$(C_2H_5)_2O$	−0·08	+0·04	−0·78	−0·66						
$C_6F_{11}{\cdot}CF_3$									5·10	3·75
C_7F_{16}	−2·45	−2·61	−1·76	−1·92	−3·00	−3·16				
Vapour									0	0

Shifts to lower applied fields of perfluoroheptane in going from pure liquid to infinite dilution in carbon tetrachloride.

$CF_3{\cdot}$		β-CF_2:		γ-CF_2:	
δ	δ (corr.)	δ	δ (corr.)	δ	δ (corr.)
3·13	3·06	2·42	2·35	2·05	1·98

but a comparatively much smaller shift of the fluorine resonance of tetrachloro-1,2-difluoroethane. It is perhaps significant that the molecules of carbon disulphide and benzene are the most anisotropic of those studied, and the extent to which the outer electrons on the fluorine atoms interact with the solvent could depend considerably on the preferred relative orientations of the molecules of the fluorine compound and of the solvent, which will in turn be sensitive to the molecular geometry of the fluorine compound.



The solvent shifts, δ (p.p.m. to lower applied fields, relative to a heptane solution), of the fluorine resonance of benzotrifluoride, plotted against the refractive indices, n_D, of the solvents.

Since chemical shifts of fluorine resonances in different fluorine compounds probably arise largely from changes in the paramagnetic shielding term,[5] it seems likely that the solvent shifts to lower applied fields are due to an increase in this term. This increase can arise from a decrease of 1—2% in the average energy ΔE between the ground state of the molecule and those excited states which contribute to the paramagnetic shielding term. This decrease is mainly brought about by the dispersion forces between the fluorine compound and the solvent. Polar forces do not seem to be very important in the systems studied, although no detailed study of the effect of polar solvents was attempted.

[5] Saika and Slichter, *J. Chem. Phys.*, 1954, **22**, 26.

Alternatively, the dispersion forces (and possibly also the repulsive forces) can be regarded as reducing the free precession of the electrons round the fluorine nucleus.

Glick and Ehrenson [2] have reported a correlation between the (corrected) solvent shifts and the (molar) polarizabilities of the solvents. Although it is likely that the polarizability will be an important factor in determining the shifts, other factors, and, in particular, the size of the solvent molecules, will also be important. Thus, to take an extreme example, the polarizability of hexadecane (313×10^{-25} cm.^{3}) is more than twice that of heptane (136×10^{-25} cm.^{3}) but the solvent shifts of the fluorine resonance of benzotrifluoride are not very different (Table 1). A close correlation between solvent shifts and polarizabilities would only be expected for solvent molecules of similar molecular volume, or for molecules where the polarizability and molecular volume are roughly related (as is the case for the halogenomethanes studied by Glick and Ehrenson [2]). Further, the polarizability of a solvent is virtually independent of temperature, whereas the solvent shifts are appreciably temperature dependent (see below). A relation which is reasonably successful for a wide range of different solvents is that between the (corrected) solvent shifts and the refractive index of the solvent (see Figure). It is unlikely that great theoretical significance attaches to this relation, except for the fact that the refractive index is approximately equal to a function of the polarizability of the solvent molecules divided by the molecular volume.

The temperature dependence of the fluorine resonance of benzotrifluoride was studied over the temperature range —29° to 159°, carbon tetrafluoride being used at 13 or 26 atm. pressure as external reference (Table 2). To a good approximation, these values vary linearly with the temperature. A shift to higher applied fields of $1{\cdot}06 \times 10^{-2}$ p.p.m. per degree increase in temperature was obtained. The calculated shift due to the change in volume susceptibility is only $1{\cdot}61 \times 10^{-3}$ p.p.m. per degree (averaged over the temperature range 20—80°), and the anomalous shift of $9{\cdot}0 \times 10^{-3}$ p.p.m. per degree can be attributed largely to the increase in the average distance between the molecules as the temperature is raised (as indicated by the thermal expansion of the liquid).

TABLE 2. *Solvent shifts δ (p.p.m. relative to heptane solutions) of the fluorine resonances in compounds at infinite dilution in bromoform and carbon tetrachloride.*

	$CHBr_3$		CCl_4			$CHBr_3$		CCl_4	
Compound	δ	δ (corr.)	δ	δ (corr.)	Compound	δ	δ (corr.)	δ	δ (corr.)
$(CH_3)_3CF$	5·95	5·18	2·55	2·32	$C_6H_5{\cdot}CF_3$	4·03	3·26	1·70	1·47
$CF_2{:}CCl_2$	4·87	4·10	2·01	1·78	CCl_3F	2·83	2·06	1·30	1·07
CF_4	4·55	3·82	1·95	1·72	$(CCl_2F)_2$	2·71	1·94	1·05	0·82
$C_5H_{11}F$	4·53	3·76	1·88	1·64	CBr_3F	1·57	0·80	0·81	0·58
$(C_6H_5)_3CF$	4·03	3·26	1·70	1·47					

It was also found that the position of the fluorine resonance in gaseous carbon tetrafluoride is noticeably dependent upon the pressure. A shift to lower applied fields of $1{\cdot}15 \pm 0{\cdot}15 \times 10^{-2}$ p.p.m./atm. was observed with increase in the pressure of the carbon tetrafluoride.

An important point concerns the effect of changes in the fluorine compound on the solvent shifts. Some additional results are given in Table 2 for two solvents only, carbon tetrachloride and bromoform, in addition to the standard, heptane. The tabulated shifts run closely parallel, which indicates that these values are, in fact, a good measure of the ease with which the fluorine resonances are affected by a (roughly isotropic) solvent. In the absence of any additional data no definite conclusions can be drawn. However, two factors which should be important in determining the solvent dependence of the

TABLE 3. *Effect of temperature on the fluorine resonance of liquid benzotrifluoride.*

Temp.	—29°	21°	65°	113°	135°	159°
Relative shifts to higher applied fields (p.p.m.)	—0·49	(0)	+0·46	0·99	1·26	1·50

fluorine resonance in a compound are (1) the electron distribution around the fluorine atom and (2) the extent to which the fluorine atom is protected from the solvent by other atoms or groups in the molecule. With the exception of the fluorine atom in triphenylmethyl fluoride, where appreciable steric interference from the phenyl groups will be present, the fluorine atom in t-butyl fluoride will probably have the highest electron density, and hence be most easily polarized. The largest solvent shifts are, in fact, observed with this compound. Similarly the shift from the gas phase to carbon tetrachloride solution is greater for silicon tetrafluoride (12·80 ± 0·15 p.p.m.) than for carbon tetrafluoride (9·24 ± 0·08 p.p.m.). Tribromofluoromethane shows the smallest solvent shifts. In this compound the fluorine atom will be considerably shielded by the bulky bromine atoms.

Filipovich and Tiers [6] have suggested that reliable chemical shifts for fluorine compounds can be obtained by the use of trichlorofluoromethane as a solvent. The data are extrapolated to infinite dilution, and the fluorine resonance of the solvent molecule is used as an internal standard. Although this is a useful procedure, its fundamental accuracy should not be overestimated. A measure of the accuracy of any method involving solution measurements is presumably given by how closely the observed shifts correspond to those which would be obtained for isolated molecules in the gas. For an infinitely dilute solution of a fluorine compound in trichlorofluoromethane, the difference between the gas shift (relative to gaseous trichlorofluoromethane) and the measured shift will be equal to the difference between the solvent shifts (gas — trichlorofluoromethane) of the fluorine compound and trichlorofluoromethane itself. Since, as discussed above, the solvent shifts of different fluorine compounds differ greatly, this difference will be neither zero nor constant, and may vary by as much as several parts per million. Fortunately, since the observed spread of fluorine resonances is so wide, this will not normally be very serious, and a more rigorous extrapolation procedure involving the use of several different solvents, such as that suggested by Glick and Ehrenson,[2] will not normally be necessary.

Intramolecular interactions, similar to the intermolecular ones described above, will also be involved between a fluorine atom and other adjacent atoms or groups in the same molecule. Where these internal van der Waals forces are important, the fluorine resonance(s) should occur at lower applied fields than would be expected from purely electronic factors, such as electronegativity. Examples of the operation of this effect may be the fluorine derivatives measured by Tiers,[7] the *o*-halogeno-fluorobenzenes,[8] and halogenated methanes such as trichlorofluoromethane and tribromofluoromethane. In the first case, bulky groups such as trichloromethyl and iodomethyl produced shifts of the fluorine resonance of an adjacent difluoromethylene group to lower applied fields as compared to that in the fully fluorinated compound. Tiers [7] postulated a " repulsion unshielding " effect due to steric interactions to account for this, but did not elaborate further.

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[6] Filipovich and Tiers, *J. Phys. Chem.*, 1959, **63**, 761.
[7] Tiers, *J. Amer. Chem. Soc.*, 1956, **78**, 2914.
[8] Gutowsky, McCall, McGarvey, and Meyer, *J. Amer. Chem. Soc.*, 1952, **74**, 4809.