594. *High-resolution Nuclear Magnetic Resonance Spectroscopy of Pentafluorosulphur Compounds. Part II.*[1] *Complex Nuclear Magnetic Systems.*

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The fluorine-19 nuclear magnetic resonance spectrum of pentafluorosulphur hypofluorite was examined as an example of the AB_4X nuclear magnetic system with a relatively small value for the chemical shift between the A and B nuclei. Both the magnitudes and the relative signs of the fluorine–fluorine coupling constants were obtained. The spectra of bispentafluorosulphur peroxide and disulphur decafluoride were also examined.

We reported previously[1] the fluorine-19 nuclear magnetic resonance spectra of some pentafluorosulphur compounds containing the AB_4 nuclear magnetic system,[2] and a new compound $SF_5{\cdot}O{\cdot}SO_2F$ containing the AB_4X system. The AB_4 part of the latter was treated as a simple AB_4 system with each line split by the appropriate coupling constant, J_{BX} for the B lines and J_{AX} for the A lines. This was valid only because $J_{AX} - J_{BX}$ was considerably less than the chemical shift δ_{AB}, between the A and B nuclei. Furthermore, the X band was symmetrical and no information about the relative signs of J_{AX}, J_{BX}, and J_{AB} could be obtained. Here we report the nuclear magnetic resonance spectrum, and its analysis as an AB_4X system, of pentafluorosulphur hypofluorite for which the above simplification is not valid and the X band is unsymmetrical, giving information about the relative signs of the coupling constants.[3,4]

Experimental.—The spectra were obtained at 40 Mc./sec. by using a Varian Associates V4300A spectrometer and 12 in. electromagnet with flux stabilisation, sample spinning, and a Varian V4365 field-homogeneity control unit. The compounds were dissolved in trichlorofluoromethane and sealed under vacuum in Pyrex tubes of 5 mm. outside diameter. The concentrations obtained were ~60% by volume for the hypofluorite and peroxide, and ~55% for the disulphur decafluoride. The separations between the lines were measured by using sidebands of the compounds themselves, generated by a Muirhead–Wigan D695A decade oscillator.

The AB_4X *Nuclear Magnetic System.*—The wave functions in which the spin of the X nucleus is $+\frac{1}{2}$ (designated the X_α functions) do not mix with those in which the spin of X is $-\frac{1}{2}$ (the

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[1] Harris and Packer, *J.*, 1961, 4736.

[2] Pople, Schneider, and Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959.

[3] Bak, Shoolery, and Williams, *J. Mol. Spectroscopy*, 1958, **2**, 525.

[4] Banwell and Sheppard, *Proc. Roy. Soc.*, 1961, *A*, **263**, 136.

X_β functions), this being a general property of A_nB_mX systems.[2,5,6] Consequently the AB_4 part of the spectrum of such a system can be calculated as two independent overlapping AB_4 systems, with the effective unperturbed resonances of the A and B nuclei at $\nu_A + \frac{1}{2}J_{AX}$ and $\nu_B + \frac{1}{2}J_{BX}$ respectively for the X_α state and at $\nu_A - \frac{1}{2}J_{AX}$ and $\nu_B - \frac{1}{2}J_{BX}$ for the X_β state; ν denotes the Larmor frequency of the nucleus indicated. These two AB_4 systems can be calculated as before [2,7] and J_{AX} and J_{BX} obtained from the difference in the effective unperturbed resonance positions. The value of J_{AX} is particularly simple to obtain since it is equal to the separation between the DS lines [1,7,8] arising from the X_α and the X_β state.

TABLE 1.

The diagonal elements of the matrix representation of the Hamiltonian for the AB_4X nuclear magnetic system in the X_α state.

AB_4 [a] spin state	I_Z of AB_4	Wave function no.[b]	Diagonal element	Sub-matrix
$D^{-\frac{1}{2}}S^0$	$-\frac{1}{2}$	1	$\frac{1}{2}\nu_X - \frac{1}{2}\nu_A - \frac{1}{4}J_{AX}$	
$D^{\frac{1}{2}}S^0$	$\frac{1}{2}$	2	$\frac{1}{2}\nu_X + \frac{1}{2}\nu_A + \frac{1}{4}J_{AX}$	
$D^{-\frac{1}{2}}T^{-1}$	$-\frac{3}{2}$	3	$\frac{1}{2}\nu_X - \frac{1}{2}\nu_A - \nu_B - \frac{1}{4}J_{AX} - \frac{1}{2}J_{BX} + \frac{1}{2}J_{AB}$	
$D^{\frac{1}{2}}T^{-1}$	$-\frac{1}{2}$	4	$\frac{1}{2}\nu_X + \frac{1}{2}\nu_A - \nu_B + \frac{1}{4}J_{AX} - \frac{1}{2}J_{BX} - \frac{1}{2}J_{AB}$	K
$D^{-\frac{1}{2}}T^0$	$-\frac{1}{2}$	5	$\frac{1}{2}\nu_X - \frac{1}{2}\nu_A - \frac{1}{4}J_{AX}$	
$C^{\frac{1}{2}}T^0$	$\frac{1}{2}$	6	$\frac{1}{2}\nu_X + \frac{1}{2}\nu_A + \frac{1}{4}J_{AX}$	L
$D^{-\frac{1}{2}}T^1$	$\frac{1}{2}$	7	$\frac{1}{2}\nu_X - \frac{1}{2}\nu_A + \nu_B - \frac{1}{4}J_{AX} + \frac{1}{2}J_{BX} - \frac{1}{2}J_{AB}$	
$D^{\frac{1}{2}}T^1$	$\frac{3}{2}$	8	$\frac{1}{2}\nu_X + \frac{1}{2}\nu_A + \nu_B + \frac{1}{4}J_{AX} + \frac{1}{2}J_{BX} + \frac{1}{2}J_{AB}$	
$D^{-\frac{1}{2}}Qt^{-2}$	$-\frac{5}{2}$	9	$\frac{1}{2}\nu_X - \frac{1}{2}\nu_A - 2\nu_B - \frac{1}{4}J_{AX} - J_{BX} + J_{AB}$	
$D^{\frac{1}{2}}Qt^{-2}$	$-\frac{3}{2}$	10	$\frac{1}{2}\nu_X + \frac{1}{2}\nu_A - 2\nu_B + \frac{1}{4}J_{AX} - J_{BX} - J_{AB}$	M
$D^{-\frac{1}{2}}Qt^{-1}$	$-\frac{3}{2}$	11	$\frac{1}{2}\nu_X - \frac{1}{2}\nu_A - \nu_B - \frac{1}{4}J_{AX} - \frac{1}{2}J_{BX} + \frac{1}{2}J_{AB}$	
$D^{\frac{1}{2}}Qt^{-1}$	$-\frac{1}{2}$	12	$\frac{1}{2}\nu_X + \frac{1}{2}\nu_A - \nu_B + \frac{1}{4}J_{AX} - \frac{1}{2}J_{BX} - \frac{1}{2}J_{AB}$	N
$D^{-\frac{1}{2}}Qt^0$	$-\frac{1}{2}$	13	$\frac{1}{2}\nu_X - \frac{1}{2}\nu_A - \frac{1}{4}J_{AX}$	
$D^{\frac{1}{2}}Qt^0$	$\frac{1}{2}$	14	$\frac{1}{2}\nu_X + \frac{1}{2}\nu_A + \frac{1}{4}J_{AX}$	P
$D^{-\frac{1}{2}}Qt^1$	$\frac{1}{2}$	15	$\frac{1}{2}\nu_X - \frac{1}{2}\nu_A + \nu_B - \frac{1}{4}J_{AX} + \frac{1}{2}J_{BX} - \frac{1}{2}J_{AB}$	
$D^{\frac{1}{2}}Qt^1$	$\frac{3}{2}$	16	$\frac{1}{2}\nu_X + \frac{1}{2}\nu_A + \nu_B + \frac{1}{4}J_{AX} + \frac{1}{2}J_{BX} + \frac{1}{2}J_{AB}$	Q
$D^{-\frac{1}{2}}Qt^2$	$\frac{3}{2}$	17	$\frac{1}{2}\nu_X - \frac{1}{2}\nu_A + 2\nu_B - \frac{1}{4}J_{AX} + J_{BX} - J_{AB}$	
$D^{\frac{1}{2}}Qt^2$	$\frac{5}{2}$	18	$\frac{1}{2}\nu_X + \frac{1}{2}\nu_A + 2\nu_B + \frac{1}{4}J_{AX} + J_{BX} + J_{AB}$	

[a] See references 1, 7, and 8. [b] The numbering here is the same as that of the X lines arising from transitions to these energy levels, when diagonalised, from the corresponding X_β levels, assuming R positive.

TABLE 2.

The symmetrical X lines.

Spin state	Line positions, E_X	Degeneracy,[a] p, of the spin state	Line numbers[b]
DS	$\pm\frac{1}{2}J_{AX}$	2	1 & 2
DT	$\pm(\frac{1}{2}J_{AX} + J_{BX})$	3	3 & 8
DQt	$\pm(\frac{1}{2}J_{AX} + 2J_{BX})$	1	9 & 18

TABLE 3.

Parameters used for the unsymmetrical X lines.

Spin state	Sub-matrix	Off-diagonal parameter, q	n	Line numbers[b]
DT	K	$2^{-\frac{1}{2}}$	1	4 & 5
DT	L	$2^{-\frac{1}{2}}$	-1	6 & 7
DQt	M	1	3	10 & 11
DQt	N	$3^{\frac{1}{2}} . 2^{-\frac{1}{2}}$	1	12 & 13
DQt	P	$3^{\frac{1}{2}} . 2^{-\frac{1}{2}}$	-1	14 & 15
DQt	Q	1	-3	16 & 17

[a] The relative intensities, Z_X, of the symmetrical lines are given directly by p. [b] The number of the line with a plus sign in the expression for line position is given first, R being assumed positive.

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[5] Pople and Diehl, *Mol. Phys.*, 1960, **3**, 547.

[6] Pople and Schaeffer, *Mol. Phys.*, 1960, **3**, 557.

[7] Chapman, to be published.

[8] Whitman, Onsager, Saunders, and Dubb, *J. Chem. Phys.*, 1960, **32**, 67.

The X end of the spectrum, however, requires a complete analysis of the AB_4X system. The matrix representation for the X_α state is given in Table 1. The corresponding matrix for the X_β state is obtained by changing the signs of all the ν_X, J_{AX}, and J_{BX} terms. Off-diagonal elements are given by qJ_{AB} (the values of q are in Table 3). The X lines arising from those basic functions (1, 2, 3, 8, 9, and 18) which are already eigenfunctions, are symmetrical in position and intensity about the Larmor frequency, ν_X, of the X nucleus, and are given in Table 2. In this Table, as elsewhere in this paper, line positions denoted by E_X are given relative to ν_X; they are positive for a high field shift. Line intensities, denoted by Z_X, are given relative to the intensity of a single DS line [1,7,8] at the AB_4 end as 2. It can be seen that the separation of lines 1 and 2 gives J_{AX} directly, while J_{BX} is equal to the line separations 1—3, 2—8, 3—9, and 8—18.

The lines not given in Table 2 are unsymmetrical about ν_X, as can be seen by diagonalising the appropriate sub-matrices. The following general formulæ are obtained:

$$E_X = \tfrac{1}{2}nJ_{BX} \pm \tfrac{1}{4}\delta_{AB}\{[(2 - R' - nR)^2 + 16q^2R^2]^{\frac{1}{2}} - [(2 + R' - nR)^2 + 16q^2R^2]^{\frac{1}{2}}\} \quad . \quad (1)$$

$$Z_X = p\cos^2(\theta_\alpha - \theta_\beta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $R = J_{AB}/\delta_{AB}$, $R' = (J_{AX} - J_{BX})/\delta_{AB}$, p is the degeneracy of the spin state, and θ_α and θ_β are corresponding angles for the X_α and X_β states given by $\tan 2\theta_\alpha = 4qR/(2 + R' - nR)$ and $\tan 2\theta_\beta = 4qR/(2 - R' - nR)$. The parameters q and n are given in Table 3, whilst p is given in Table 2.

The positions of combination lines in the X region are given by equation (1) with the single alteration of a plus sign between the square-root terms. Their intensity is $p\ \sin^2(\theta_\alpha - \theta_\beta)$. A sufficient condition for the intensity of the strongest combination line to be less than 0·1 is that $|(J_{AX} - J_{BX})/J_{AB}| < 0{\cdot}4$. If this is fulfilled, combination lines can be neglected, and the intensity of the unsymmetrical lines is given simply by the degeneracy factor p. If $|nR \mp R'| \ll 2$ for $n = \pm 1, \pm 3$, equation (1) reduces to the symmetrical form:

$$E_X = \tfrac{1}{2}nJ_{BX} \pm \tfrac{1}{2}(J_{AX} - J_{BX})$$

This was the case for $SF_5{\cdot}O{\cdot}SO_2F$.[1]

δ_{AB} is defined throughout this paper as the chemical shift of the B nuclei from the A nucleus; it is positive if B is to high field of A. It is possible to determine from the symmetrical lines the relative signs of J_{AX} and J_{BX}. The effect of a change in the relative signs of R and R' is to invert the whole X pattern about ν_X,[3,4] so that the sign of J_{AB} relative to J_{AX} and J_{BX} can also be readily determined. The actual numbering of the lines in the spectrum depends on the sign of R. To avoid confusion, we have adopted the convention of numbering on the assumption that R is always positive, that is we have taken J_{AB} to be the same sign as δ_{AB}. Since it is normally impossible to determine the absolute sign of J_{AB}, this is quite legitimate, and very convenient in practice.

The Spectrum of Pentafluorosulphur Hypofluorite, $SF_5{\cdot}OF$.—This molecule is an example of an AB_4X nuclear magnetic system where $R > 1$ and $R' \sim \frac{1}{4}$. Consequently it cannot be analysed in the simplified way that proved sufficient for $SF_5{\cdot}O{\cdot}SO_2F$.[1] Its spectrum has been reported by Dudley *et al.*[9] They observed an unsymmetrical sextet for the fluorine on oxygen, and suggested that this might be due to restricted rotation. The asymmetry, which we have also observed (Fig. 1a; the band, however, is considerably more complex than a sextet) is in reality, as we have shown, a natural consequence of the AB_4X system. Dudley and his co-workers [9] did not succeed in resolving the AB_4 end beyond a doublet, and suggested that all five fluorine nuclei were equivalent. Our results show a complex spectrum (Fig. 2a) and are only compatible with an AB_4 group such as is found in other pentafluorosulphur compounds.[1,20]

Analysis of the Spectrum.—(*a*) *The* X-*band.* The symmetrical lines are easily picked out as shown in Fig. 1. The central pair of DS lines are not visibly split, showing that J_{AX} is small. The splittings between the mean position of this pair of lines and the symmetrical DT lines [1,8] are less than the separations of the latter from the symmetrical DQt lines, showing that J_{AX} and J_{BX} are actually of opposite sign. The values obtained are numerically $|J_{AX}| = 0{\cdot}6 \pm 0{\cdot}2$ c./sec. and $|J_{BX}| = 18{\cdot}3 \pm 0{\cdot}1$ c./sec. J_{AB} was taken to be 155 c./sec. and δ_{AB} as $+73{\cdot}6$ c./sec. (see below), so that $R = 2{\cdot}106$ and $R' = 0{\cdot}2562$. The fully calculated spectrum

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[9] Dudley, Shoolery, and Cady, *J. Amer. Chem. Soc.*, 1956, **78**, 568.

is shown in Fig. 1b. The unsymmetrical lines show that J_{BX} and J_{AB} are of the same sign. Since $|(J_{AX} - J_{BX})/J_{AB}| = 0{\cdot}1217$, the combination lines could not be observed (see above).

(*b*) *The* AB_4 *band.* The spectrum only covers 100 c./sec. so it is assumed that $R > 1$. In this case lines 2, 5, 8, 10, 13, 17, 21, and 24 [1,7] and all combination lines are far from the main band and too weak to observe (later calculation showed that the strongest of them has only one eighth of the intensity of one of the DS lines). Also the largest gap in the spectrum should be that between the DS lines and the nearest line 3 (for J_{AX} small). Consequently the DS lines were identified as in Fig. 2b. The resolution was not good enough to split them, as was the case at the X end of the spectrum. Since the centre of the two DS lines is at ν_A, the B resonance can be seen to occur to high field of the A resonance (Fig. 2), and δ_{AB} is positive in our convention. A possible assignment of the other lines was assumed (Fig. 2b), the two independent AB_4 spectra being labelled U and V, the U spectrum being that in which the effective unperturbed resonance positions are $\nu_A - \frac{1}{2}|J_{AX}|$ and $\nu_B + \frac{1}{2}|J_{BX}|$. It is impossible to determine which spectrum corresponds to the X_α state, since this depends on the absolute sign of the coupling constants. The centres of the B resonances of U and V were taken to be at the average position of the corresponding lines 4 and 7 as before. The separation of these centres gave $J_{BX} = 18{\cdot}2$ c./sec.,* in good agreement with the X spectrum. The distance from the centres to the DS lines gave the effective chemical shift between the A and B nuclei of the two AB_4 spectra as $\delta_u = 83{\cdot}0$ c./sec. and $\delta_v = 64{\cdot}2$ c./sec., when corrected for $J_{AX} = -0{\cdot}6$ c./sec.* Thus $\delta_{AB} = +73{\cdot}6$ c./sec. Because lines 2, 5, and 8 were too weak to observe, we

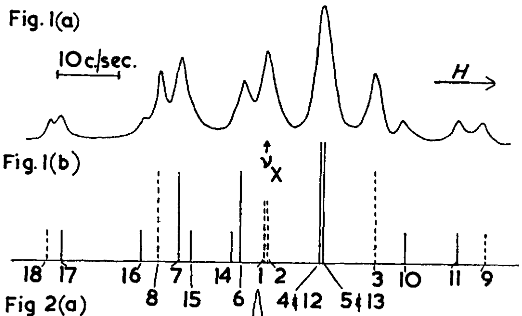

FIG. 1. (a) The observed and (b) the calculated spectrum of the hypofluorite fluorine nucleus in pentafluorosulphur hypofluorite.

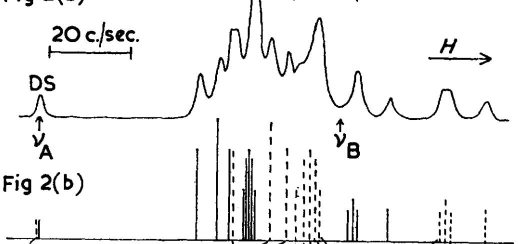

FIG. 2. (a) The observed and (b) the calculated spectrum of the pentafluorosulphur fluorine nuclei in pentafluorosulphur hypofluorite.

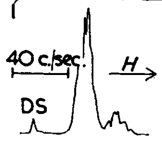

Fig. 3

FIG. 3. The spectrum of bispentafluorosulphur peroxide.

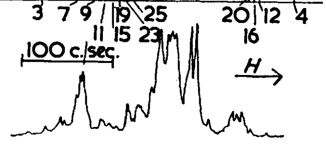

Fig. 4

FIG. 4. The spectrum of disulphur decafluoride.

The full lines in Fig. 1(b) are those of the lines unsymmetrical about ν_X; the dashes indicate symmetrical lines. The full lines in Fig. 2(b) are those of the V spectrum, the dashes show lines of the U spectrum. The numbering of the lines in the V spectrum is in exactly the same order as that of the U lines. Line 1 is the DS line, lines 3,4,7,9 are DT lines, the rest are DQt lines. Note that line 11, in origin an A line, has crossed over lines 7 and 9, in origin B lines. The numbering of lines in Fig. 1(b) is as in the text, R being assumed positive. The intensity scale of Fig. 2 is not the same as that of Fig. 1.

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* The sign given is that relative to J_{AB}.

could not obtain J_{AB} directly from any equations which did not involve square-root terms, and the errors incurred in the use of more complex equations were too great to give a good value for J_{AB}. We, therefore, assumed J_{AB} = 155 c./sec. from our previous results for pentafluorosulphur compounds,[1,10] and took R_u = 1·867 and R_v = 2·414. This gave a good fit to the spectrum (Fig. 2). Further calculations showed that this value of J_{AB} is probably correct to ±10 c./sec. The calculated and observed positions of DT lines in both the AB_4 and X parts of the spectrum are given in Table 4.

TABLE 4.

Calculated and observed line positions of DT lines in the spectrum of SF_5·OF.

In AB_4 spectrum						In X spectrum		
Line	Calc.[a]	Obs.[a, d]	Line	Calc.[b]	Obs.[b, d]	Line	Calc.[c]	Obs.[c, e]
3_U	−34·86	−35·1	3_V	−25·68	−25·5	4_X	8·96	9·16
4_U	26·23	26·2	4_V	20·74	20·7	5_X	9·30	
7_U	−26·23	−26·2	7_V	−20·74	−20·7	6_X	−3·78	−3·76
9_U	−21·81	−22·0	9_V	−17·65	−17·7	7_X	−14·47	−14·59

[a] From $\nu_B + \frac{1}{2} | J_{BX} |$ in c./sec. [b] From $\nu_B - \frac{1}{2} | J_{BX} |$ in c./sec. [c] From ν_X in c./sec. [d] Average error over 8 measurements, 0·25 c./sec. [e] Average error over 12 measurements, 0·15 c./sec.

*The Spectra of Bispentafluorosulphur Peroxide and Disulphur Decafluoride.**—Both of these molecules contain an $AB_4B'_4A'$ nuclear magnetic system.[2] Merrill and Cady [11] have reported the fluorine-19 nuclear magnetic resonance spectrum of bispentafluorosulphur peroxide as being a single line with evidence of some fine structure. We find that the spectra of both of these molecules (Figs. 3 and 4) are complex because of a small value of δ_{AB}. However, there should be a single DSSD line at ν_A. We have not attempted the analysis of the spectrum of disulphur decafluoride, but that for the peroxide is much simpler (Fig. 3), probably because the long-range couplings are smaller and it approximates to a simple AB_4 system. We have analysed it on this basis. The single DS line can be seen to low field, separated from the main band by the largest gap in the spectrum as for pentafluorosulphur hypofluorite. A rough assignment of the other lines was made and located, giving $\delta_{AB} \sim +50$ c./sec. A calculation with $R = 3$ (assuming $J_{AB} \sim 150$ c./sec) gave a rough fit to the spectrum, deviations probably being due to the long-range couplings, although it was not possible to obtain values for any of these. The chemical shift values from trichlorofluoromethane are −573 p.p.m. for the A nuclei and −56·0 p.p.m.† for the B nuclei.

For disulphur decafluoride the spectrum (Fig. 4) covers ~200 c./sec. and probably $R \sim 1$ or slightly less. It is uncertain whether δ_{AB} is positive or negative. The resonances occur over the range −51·5 to −56·5 p.p.m.† from trichlorofluoromethane (in the same region as sulphur hexafluoride).

DISCUSSION

Chemical Shifts.—The resonance of the hypofluorite fluorine nucleus in pentafluorosulphur hypofluorite occurs at very low field (−188·8 † p.p.m. from trichlorofluoromethane), in the same region as fluorine fluorosulphonate, as Dudley *et al.*[9] pointed out. The axial fluorine of the pentafluorosulphur group has a chemical shift of −55·6 † p.p.m. from trichlorofluoromethane, whereas the equatorial fluorines are at −53·8 † p.p.m. There is an impurity line (shown to be so by reduction in intensity after fractional distillation) at −57·3 p.p.m. from trichlorofluoromethane to low field of ν_A, almost certainly due to sulphur hexafluoride which gives a single resonance at −57·0 p.p.m. It can be seen from these and previous results [1,10] that there is no obvious correlation between the chemical

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* Since the publication by Merrill, Williamson, Cady, and Eggus (*Inorg. Chem.*, 1962, **1**, 215) of the fluorine-19 nuclear magnetic resonance spectrum of disulphur decafluoride, we have noticed that our sample contains some bispentafluorosulphur peroxide as impurity, as shown by the group of peaks to low field of the main group in Fig. 4 (cf. also Fig. 3).

† Average error 0·5 p.p.m.

[10] Muller, Lauterbur, and Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1043.

[11] Merrill and Cady, *J. Amer. Chem. Soc.*, 1961, **83**, 298.

shifts, δ_{AB}, in SF_5Y compounds and the size and electronegativity of Y, or between the chemical shifts of the A and B nuclei respectively from sulphur hexafluoride. However, it is perhaps instructive that by far the largest value of δ_{AB} was found in pentafluorosulphur chloride, the only molecule studied where Y is neither oxygen nor highly fluorinated (as in $F_5S{\cdot}SF_5$ and $F_5S{\cdot}CF_2{\cdot}CF_3$ [10]).

Coupling Constants.—Very little is known about the dependence of fluorine–fluorine coupling constants on stereochemistry, and analogies with proton–proton values are not good. In particular, an alternation in the magnitude of the coupling constant as the number of bonds separating the fluorine nuclei increases has been noticed by several workers.[12-14] The value of the coupling constant in the system F–C–C–F is low, usually 0—20 c./sec.,[14,15] and appears to be smaller for the more highly fluorinated molecules. For those of the type $CF_3{\cdot}CF_2{\cdot}Y$, the coupling is generally less than 2 c./sec. This compares with a geminal coupling constant in a difluoromethylene group of 150—300 c./sec.[13,15] Petrakis and Sederholm [14] report a value of $\leqslant 1$ c./sec. for the F–C–N–F coupling constant in perfluoro(propylamine). We have found that the F–C–P–F coupling constant in fluorobistrifluoromethylphosphine is 3·5 c./sec., while for the F–C–S–F system in trifluoromethanesulphonyl fluoride it is 18·5 c./sec. However, no measurements of relative signs of fluorine couplings in saturated molecules have been published so far. It has also been suggested that close proximity of fluorine nuclei tends to increase the coupling between them.[14] The values we have obtained for the molecules $F_5S{\cdot}O{\cdot}SO_2F$ and $F_5S{\cdot}O{\cdot}F$ therefore tend to confirm the above views. In each case the coupling of the X fluorine to the equatorial fluorines of the SF_5 group is much greater than that to the axial fluorine, where the nuclei are much further apart and in fact are shielded by the four equatorial fluorine nuclei. The magnitudes of the coupling constants are 7·2 c./sec. and 0·9 c./sec. for $F_5S{\cdot}O{\cdot}SO_2F$ where the nuclei are separated by four bonds, and 18·2 c./sec. and 0·6 c./sec. for $F_5S{\cdot}O{\cdot}F$ where they are three bonds apart. This indicates a considerable dependence of coupling on stereochemistry. Moreover, in $F_5S{\cdot}O{\cdot}F$, as shown above, J_{BX} is of the same sign as J_{AB}, whereas J_{AX} is of the opposite sign. This may be explained as a superposition of a through-the-bonds term and a direct through-space term of opposite sign when the separation is three bonds. The former may well alternate in sign and probably falls off rapidly in magnitude as the number of bonds separating the fluorine nuclei increases (as in the case of proton–proton couplings).

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[12] Saika and Gutowsky, *J. Amer. Chem. Soc.*, 1956, **74**, 4818.
[13] Crapo and Sederholm, *J. Chem. Phys.*, 1960, **33**, 1583.
[14] Petrakis and Sederholm, *J. Chem. Phys.*, 1961, **35**, 1243.
[15] Lee and Sutcliffe, *Trans. Faraday Soc.*, 1959, **55**, 880.