ELECTRON SPIN RESONANCE STUDIES OF HIGHLY-FLUORINATED AROMATIC RADICAL IONS

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by

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and St. Leonard, St. Andrews.

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Dr. C. Thomson since 1st October 1965, the date of my admission as a research student.

I hereby certify that Walter John MacCulloch has spent eleven terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research.

ABSTRACT

The new oxidative technique, $SbCl_5-SO_2$, has been used to prepare and record the E.S.R. spectra of the radical cations of octafluoronaphthalene; 2H-heptafluoronaphthalene; 2,6H-hexafluoronaphthalene; 2,3,7H-pentafluoronaphthalene; 2,3,6,7H-tetrafluoronaphthalene (dimer cation); 5,6,7,8H-tetrafluoronaphthalene and is described in detail. Unlike perfluorinated anions which could not be detected by E.S.R., those highly-fluorinated radical cations are stable at room temperature for several hours. The fluorine hyperfine splittings are much larger than those observed for fluorinated anions and the spectra display pronounced linewidth and intensity anomalies. The spectrum of 2H-heptafluoronaphthalene could not be analysed. The fluorine hyperfine splittings have been used in conjunction with McLachlan spin density calculations of ρ_C,ρ_F[1] to determine the magnitudes of the spin polarisation parameters Q_{eff} (26), Q^F_{CF} and $Q^F_{F(FC)}$ (25) for radical cations by performing least squares fits to those equations. The values obtained are much larger than the corresponding values for fluorinated anions (p.132) and attempts are made to show how this arises.

[1] Footnote:

In this thesis the notation A,B ≡ A and B (where A and B are numbers or quantities) is extensively used.

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CONTENTS

CHAPTER I : INTRODUCTION

A. General

The investigation of the electronic structure of radical ions by E.S.R. Spectroscopy is now well established and has been reviewed in detail.[1-5] In addition, Annual Reviews of Physical Chemistry and Annual Reports of the Chemical Society, both since 1954, provide a yearly account of progress in the field. This thesis is concerned with E.S.R. studies of radical ions in solution and there follows a brief summary of the relevant theory; more detailed accounts are given in references 2 and 3.

1. Hyperfine Interactions in Solution and Q^{H}_{CH}

The Zeeman Hamiltonian for the interaction of the unpaired electron of radical ions in solution with a strong magnetic field, H, is

$$\hat{H}_0 = g\beta H\hat{S}_z \qquad (1)$$

where $\hat{S}_z$ is the z-component of the electron spin angular momentum operator; g, the g value, is the isotropic component of the g tensor and β is the Bohr magneton. The eigenvalues of this Hamiltonian are $E_1 = \frac{1}{2}g\beta H$ and $E_2 = -\frac{1}{2}g\beta H$ and their difference, $\Delta E = g\beta H$. If the system is allowed to absorb radiation of fixed microwave frequency ν, resonance occurs at a value of H where

$$h\nu = \Delta E = g\beta H \qquad (2)$$

In the majority of radicals a series of hyperfine absorption lines and not a single line are, however, obtained as the unpaired electron also interacts with any magnetic nuclei present in the radical. Those lines appear at slightly different field values when H is varied through resonance. The Hamiltonian, $\hat{H}_1$ for this interaction is the sum of the anisotropic dipolar interaction Hamiltonian, $\hat{H}_1'$ and the isotropic contact interaction[6] term, $\hat{H}_1''$. In the strong field approximation

$$\hat{H}_1' = \sum_n g\beta g_N\beta_N \left[\frac{\hat{S}_z . \hat{I}_{nz}}{|r-r_n|^3} - \frac{3(\hat{S}_z . \vec{r})(\hat{I}_{nz} . \vec{r})}{|r-r_n|^5} \right] \qquad (3)$$

where g_N, β_N are the nuclear g value and nuclear magneton respectively and the sum is over all magnetic nuclei, n. $\hat{I}_{nz}$ is the z-component of the nuclear spin angular momentum operator and $\vec{r}, \vec{r}_n$ the position vectors of the unpaired electron and nucleus, n. Weissman[7] has shown that the rapid tumbling in solution causes $\hat{H}_1'$ to vanish leaving only

$$\hat{H}_1'' = 8\pi/3 \; g\beta g_N\beta_N \sum_n S_z . \hat{I}_{nz} \delta(\vec{r}-\vec{r}_n)$$

$$= \sum_n a_n \hat{S}_z . \hat{I}_{nz} \qquad (4)$$

where $\delta(\vec{r}-\vec{r}_n)$ is the Dirac delta function for the distance between the unpaired electron and nucleus n and a_n is the isotropic hyperfine splitting of this nucleus.

The total effective Hamiltonian is thus

$$\hat{H} = \hat{H}_0 + \hat{H}_1''$$

$$= g\beta H\hat{S}_z + \sum_n a_n \hat{S}_z . \hat{I}_{nz} \qquad (5)$$

As $\hat{H}_1''$ is much smaller than $\hat{H}_0$, the hyperfine energy levels can be regarded as small perturbations of E_1, E_2 and the eigenvalues of $\hat{H}$ found from first order perturbation theory. If Ψ is the total molecular electronic wave function, the hyperfine energy levels, E_n', are to a first order given by

$$\sum_n E_n' = \langle\Psi|\hat{H}|\Psi\rangle \tag{6}$$

$$= \langle\Psi|\hat{H}_0|\Psi\rangle + \langle\Psi|\sum_n a_n \hat{S}_z \cdot \hat{I}_{nz}|\Psi\rangle$$

$$\text{and } E_n' = \langle\Psi|\hat{H}_0|\Psi\rangle + \langle\Psi|a_n \hat{S}_z \cdot \hat{I}_{nz}|\Psi\rangle \tag{7}$$

It is seen from (7) that interaction of the unpaired electron with a single nucleus n causes both E_1, E_2 to split into $(2I_n + 1)$ hyperfine levels. The selection rules for transitions between those levels are $\Delta m_s = \pm 1$, $\Delta m_{In} = 0$ where $m_s = \pm\frac{1}{2}$, $m_{In} = +I_n, +(I_n - 1) \cdots 0 \cdots -I_n$ are the eigenvalues of $\hat{S}_z, \hat{I}_{nz}$ respectively and I_n is the spin quantum number of nucleus, n. $(2I_n + 1)$ hyperfine lines, separated by a_n, are therefore obtained by interaction with a single nucleus.

A radical ion may contain numbers N_A, N_B, N_C etc. of symmetrically equivalent nuclei of type A,B,C with nuclear quantum numbers I_A, I_B, I_C respectively. If $a_A > a_B > a_C$, each of the $(2N_A I_A + 1)$ hyperfine lines obtained by interaction with type A is further split into $(2N_B I_B + 1)$ lines by interaction with nuclei of type B etc. Complete analysis of such an E.S.R. spectrum gives all hyperfine splitting constants a_A, a_B, a_C, etc.

The isotropic hyperfine splitting, a_n, from nucleus n is related to the wave function Ψ by the expression[6]

$$a_n = 8\pi/3\, g\beta g_N\beta_N |\Psi(0)|_n^2$$
$$= 8\pi/3\, g\beta g_N\beta_N \rho_n \qquad (8)$$

$|\Psi(0)|_n$ is the value of Ψ at the nucleus and ρ_n, the unpaired spin density at nucleus n, is defined as

$$\rho_n = \langle\Psi|\sum_k \delta(\vec{r}_k - \vec{r}_n)\hat{S}_{kz}|\Psi\rangle / S_z \qquad (9)$$

where the summation is over all the electrons. $\hat{S}_{kz}$ is the z-component of the spin angular momentum operator of electron k and S_z, the z-component of the total spin angular momentum for the radical.

This thesis is concerned with π-electron radical ions where the unpaired electron moves in a π orbital with nodes at the nuclei. Many molecular calculations on such planar π systems assume the σ-π separability approximation, i.e. that

$$\Psi = \Theta[\Psi_\sigma \Psi_\pi] \qquad (10)$$

where Ψ_σ and Ψ_π are functions of only σ and only π- electron co-ordinates respectively and Θ is the antisymmetrization operator with respect to σ-π interchange.[8] Within this approximation, all nuclei in a π radical ion lie in the nodal plane of Ψ_π and therefore ρ_n and a_n(8) must both equal zero. Thus the very existence of hyperfine interactions indicates some departure from σ-π separability. Hence, in order to relate theory with experiment, some relationship between a_n and Ψ_π must be developed.

A relationship of this kind for aromatic protons was established by McConnell[9-11] who theoretically examined the hyperfine interaction in a C–H fragment. He postulated an exchange polarisation of the electrons in the C–H σ bonding orbital by the unpaired π–electron on the carbon atom leading to net unpaired spin density at the proton. He made allowance for this effect by admixing into the ground state wave function a small amount of the excited doublet valence bond function where both σ electrons in the C–H bond have parallel spins. The use of first order perturbation theory resulted in the approximate relationship

$$a_H = {}^{-1}\!/(1-S_o^4)\left[\frac{\langle h\pi|\pi h\rangle - \langle s\pi|\pi s\rangle}{\Delta E}\right] a_H^H \rho_C$$
$$= Q\rho_C = Q \qquad (11)$$

where a_H, a_H^H are the isotropic hyperfine splittings of the proton and a free hydrogen atom respectively and ρ_C, the unpaired spin density on the carbon atom, is taken to be unity for a C–H fragment. Q, the spin polarisation parameter, is a constant for the C–H fragment and is defined by the terms within the brackets. The quantities

$$\langle h\pi|\pi h\rangle = \iint h(1)\pi(2)|{}^{e^2}\!/r_{12}|\pi(1)h(2)d\tau_1 d\tau_2$$
$$\text{and } \langle s\pi|\pi s\rangle = \iint s(1)\pi(2)|{}^{e^2}\!/r_{12}|\pi(1)s(2)d\tau_1 d\tau_2 \qquad (12)$$

are exchange integrals involving orbitals π, h and s where π, h are the carbon $2p_\pi$ and hybrid orbitals respectively and s is the hydrogen 1s orbital. S_o is the overlap integral between h and s and ΔE is the difference in energy between the bonding and antibonding configurations. Molecular orbital treatments gave essentially identical results. The theory was also extended to polyatomic π–electron radicals[11] where $\rho_C < 1$ resulting in the

McConnell relationship

$$a_i^H = Q_{CH}^H \rho_i \qquad (13)$$

where a_i^H, the hyperfine splitting from the proton attached to carbon atom i varies linearly with the π-electron spin density, ρ_i, on that atom. The superscript on the spin polarisation parameter, Q_{CH}^H, refers to the nucleus (here a proton) giving rise to the splitting and the subscript refers to spin polarisation in the C–H σ bond by unpaired π spin density on the associated carbon atom.

The introduction of (13) made possible detailed comparisons of 'experimental' values of ρ_i with those calculated from various types of π-electron approximations (see chapter III,B). The validity of those approximations to describe the ground states of π-electron radicals could therefore be estimated. The magnitude of Q_{CH}^H had first to be established, however, and numerous attempts to do so theoretically have resulted in values from –20 to –30 gauss e.g. Jarrett[12] has evaluated all the terms in equation (11) and obtained Q_{CH}^H = –28 gauss. For some radicals ρ_i is determined by symmetry or can be reliably estimated as in the benzene negative ion[13] where Q_{CH}^H = –22.5 gauss or in the methyl radical[14] where Q_{CH}^H = –23.03gauss. Similar considerations, however, for other radicals give quite different values e.g. the cyclooctatetraene anion[15] (Q_{CH}^H = –25.68) or the butadiene anion[16] (Q_{CH}^H = –20.81). Thus, although (13) is approximately valid, Q_{CH}^H does vary from one radical species to another.

The pairing theorem[17] predicts that the radical cations and anions of even-alternant hydrocarbons should have the same values of ρ_i, but the proton hyperfine splittings of the former are found to be larger than the corresponding splittings of the latter. This could arise either from a breakdown of the pairing theorem or from variation of Q^H_{CH} with excess charge. Bolton and Fraenkel's work[18] on proton and C^{13} hyperfine splittings in the cation and anion of anthracene, however, established the validity of the pairing theorem and led to the conclusion that variations in the splittings must arise from variations in Q^H_{CH}. For the cation and anion of anthracene the best values of Q^H_{CH} are -29, -25 gauss respectively and similar values have been found for the radical ions of other even-alternant hydrocarbons. Colpa and Bolton[19] have extended the McConnell relationship (13) to account for those excess charge effects. Their molecular orbital treatment, based on second order perturbation theory, resulted in the equation

$$a^H_i = \left[Q^H_{CH}(0) + K^H_{CH}\xi_i\right]\rho_i \qquad (14)$$

where $Q^H_{CH}(0)$ is the value of Q^H_{CH} for the neutral C-H fragment and K^H_{CH} is a theoretical constant which is negative in sign. The term ξ_i is the excess π charge density on the ith carbon atom and is given by the expression

$$\xi_i = 1 - q_i \qquad (15)$$

where q_i is the total π-electron density on atom i. Thus ξ_i is positive for cations and negative for anions. Values of $Q^H_{CH} = -27$ gauss and $K^H_{CH} = -12$ gauss best accomodate a wide range of experimental data.

Giacometti et alia[20] maintained, however, that the direct effect of excess charge is too small to account for the variations, but have obtained an equation similar to (14) by including the effect of nearest-neighbour $2p_\pi$ interactions with the C-H fragment.

Bolton[21] later presented a calculation of the exchange integrals in (11) including the effect of the excess charge in changing the orbital screening exponents of the carbon atom. The results predicted an equation of the form of (14) with a negative value of K_{CH}^{H}. In addition, Vincow has prepared the radical cation of benzene in the solid state and, by comparison of the hyperfine splitting with that of the benzene negative ion, found the Colpa-Bolton theory to be in best agreement with experiment.

The magnitude of Q_{CH}^{H} (13) has often been established by comparing experimental hyperfine splittings with spin densities calculated from the various types of π-electron approximation. This procedure is of limited use if the resulting value of Q_{CH}^{H} is then used to compare 'experimental' and theoretical spin densities for other species in the manner previously discussed. Several attempts have been made to solve this problem by calculation of Q_{CH}^{H} [9,11,12,23,24] and most of those have used first order perturbation theory, a notable exception being the work of Higuchi[24] who extended the calculation to higher orders. Vincow et alia[25] have recently presented molecular orbital calculations of Q_{CH}^{H} which improve on those previous attempts by eliminating some of their cruder approximations and have also extended the calculations to higher orders in perturbation theory. This work is now discussed.

Q^H_{CH} was calculated by considering configuration interaction between a ground state configuration

$$\Psi_0 = |1s_c \bar{1s}_c h_2 \bar{h}_3 \phi_B \bar{\phi}_B \pi| \qquad (16)$$

and excited configurations

$$\Psi_1 = 1/\sqrt{2} \left[|1s_c \bar{1s}_c h_2 \bar{h}_3 \phi_B \bar{\phi}_A \pi| - |1s_c \bar{1s}_c h_2 \bar{h}_3 \bar{\phi}_B \phi_A \pi| \right]$$
$$\text{and } \Psi_2 = 1/\sqrt{6} \left[|1s_c \bar{1s}_c h_2 \bar{h}_3 \phi_B \bar{\phi}_A \pi| + |1s_c \bar{1s}_c h_2 \bar{h}_3 \bar{\phi}_B \phi_A \pi| - 2|1s_c \bar{1s}_c h_2 \bar{h}_3 \phi_B \phi_A \bar{\pi}| \right] \qquad (17)$$

Ψ_1, Ψ_2 correspond to a one-electron excitation from ϕ_B to ϕ_A where ϕ_B, ϕ_A are respectively the bonding and anti-bonding molecular orbitals for the C-H fragment. The other terms are as follows: $1s_c$ is the 1s atomic orbital on carbon, h_2 and h_3 are sp^2 hybrid orbitals on carbon and π is the $2p_z$ atomic orbital on carbon.

To a first order in perturbation theory, Q^H_{CH} is given by the expression

$$Q^H_{CH} = {}^{16\pi}/_{3} g\beta g_H \beta_H \; \delta(\vec{r}_i - \vec{r}_H)\phi_B\phi_A \, \Delta E^{-1} \iint \phi_B(1)\pi(2) \left| \frac{e^2}{r_{12}} \right| \pi(1)\phi_A(2) \, d\tau_1 d\tau_2 \qquad (18)$$

where $\delta(\vec{r}_i - \vec{r}_H)\phi_B\phi_A$ is the density $\phi_B\phi_A^*$ at the proton and ΔE is the difference in energy between ϕ_B and ϕ_A. The molecular orbitals ϕ_B, ϕ_A were approximated as follows

$$\phi_B = \left[\lambda^2 + 1 + 2\lambda\langle h_1 | s\rangle\right]^{-} (\lambda h_1 + s)$$
$$\phi_A = \left[\lambda_1^2 + 1 + 2\lambda_1\langle h_1 | s\rangle\right]^{-} (\lambda_1 h_1 + s) \qquad (19)$$
$$\lambda_1 = -(1 + \lambda\langle h_1 | s\rangle)/(\lambda + \langle h_1 | s\rangle)$$

where h_1, s are the carbon sp^2 hybrid orbital directed towards the proton and the hydrogen 1s orbital respectively and λ is the 'polarity' parameter of the C-H bond. The optimum value of λ, i.e. one which leads to a ϕ_B which most closely approximates the corresponding SCF orbital, was obtained by minimising the energy $E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$ with respect to λ. Slater type minimum basis set atomic orbitals were used to evaluate the exchange integral in equation (18). Q^H_{CH} was found to equal -27 gauss.

Previous calculations of Q^H_{CH}, except for Higuchi's,[24] took no account of C-H bond polarity. Some of those attempts, e.g. that of Jarrett[12] who used equation (11), also involved neglect of the 'overlap' term $\langle h_1(1)\pi(2)|\pi(1)s(2)\rangle$ arising from the expansion of the integral $\langle \phi_B(1)\pi(2)|\pi(1)\phi_A(2)\rangle$ in (18). Many calculations also neglected the overlap integral $\langle h_1(1)|s(1)\rangle = \int h_1(1)s(1)d\tau_1$ in equation (19) which Vincow estimated to be 0.71 atomic units and therefore of significant magnitude. For those reasons, Vincow's calculation represents a considerable improvement in rigour over previous attempts but is still of limited quantitative significance. This arises from the fact that SCF equations for a fragment, as distinct from a real molecule, cannot be solved and the approximations (19) involving λ must be used instead. Furthermore, a limited basis set of atomic orbitals has been used in constructing Ψ_0, Ψ_1, Ψ_2 and also incomplete configuration interaction has been used (see chapter III,B). The work is of considerable importance, however, as quantitative calculations of the sensitivity of Q^H_{CH} to variations in the parameters and approximations of the theory have been performed. Those are now discussed.

Q^H_{CH} was not found to be very dependent on the bond polarity parameter λ and variations of the latter from 0.8 to 1.2 caused Q_{CH}^{H} to decrease by only 10%. The optimum value of λ was found to be close to unity.

Q_{CH}^{H} was found to be extremely sensitive to the value of the hydrogen 1s orbital shielding exponent ζ_H and a 10% variation in the former corresponded to a change of only 0.03 in the latter. The sensitivity of Q_{CH}^{H} to variations in the $2p_z$, $2p_y$ orbital exponents was also of significant magnitude, though much less than for variations in ζ_H. This led Vincow to speculate that the difference in hyperfine splittings between the radical cations and anions of even-alternant hydrocarbons (p. 7) may result more from the influence of the excess π charge on the optimum value of the hydrogen 1s orbital exponent than on the orbital exponents of carbon. Pitzer[26] has performed molecular orbital calculations on methane and found the optimum value of $\zeta_H = 1.14$. Vincow shows that the use of this value of ζ_H in (18) results in an increase of Q_{CH}^{H} from about −25 gauss to about −45 gauss. He concludes that the excellent agreement of calculated and experimental values of Q_{CH}^{H} may be purely fortuitous.

The calculation was also extended to second and higher orders of perturbation theory but with the same two excited configurations $\Psi_1 \Psi_2$ admixed with Ψ_0, no change in the magnitude of Q_{CH}^{H} was found. Inclusion of a third configuration corresponding to a two-electron excitation from ϕ_B to ϕ_A, however, resulted in an increase of about 10% in Q_{CH}^{H}. Malrieu[28] had previously proposed a general second order perturbation treatment of proton hyperfine splittings and had estimated the second-order contribution to Q^{H}_{CH} to be about 25% of the first-order contribution. Although Vincow's result is smaller than Malrieu's, it nevertheless confirms the importance of pursuing the calculation to higher orders.

Hyperfine interactions of magnetic nuclei other than protons have been treated by McLachlan et alia[23] who removed a few minor restrictions from McConnell's theory and generalised this theory to include all magnetic nuclei lying in the nodal plane of a π-radical. Hence C^{13} and N^{14} splittings could also be related to Ψ_{π}(10). Their theory yielded the result

$$a_n = \mathrm{tr}\ \bar{Q}^n \bar{\rho} \qquad (20)$$

where $\bar{\rho}$ is the normalised π-electron spin density matrix and $\bar{Q}^n$ is a hyperfine coupling matrix whose elements depend on σ-π exchange integrals and excited σ triplet states. An expanded theory which considered not only spin polarisation of the C-H σ electrons but also the 1s carbon electrons and all electrons in the other two bonds of the sp^2 hybridised carbon atom was developed by Karplus and Fraenkel.[29] Their treatment was later extended to N^{14}[30,31 and refs.] and F^{19}[32] splittings. A good account of C^{13} and N^{14} splittings is given by Bolton in 'Radical Ions';[4] the F^{19} case is discussed in B of this chapter.

2. Previous Work on Radical Ions

Although the radical anions of a large number of compounds containing nitrogen,[30,33] phosphorus,[34,35] sulphur[36] and other heterocyclic atoms have been studied, particularly in recent years, much more work has been done on aromatic and substituted aromatic hydrocarbons. Chapter 8 of Ayscough[3] contains a comprehensive account of anion studies in solution.

Preparative techniques used for anion generation have been numerous and only a few of the more important ones are mentioned here. Electrolytic reduction[37] in organic solvents, pioneered by Maki and Geske, (see p. 39), has been used extensively, particularly for nitro and carbonyl species, and has been reviewed by Adams.[38] It is a more gentle reduction procedure than the widely used alkali[39] or alkaline-earth metals in THF, DME or liquid ammonia. The classic work of Levy and Meyers[40] on electrolytic reduction in liquid ammonia has provided the theoretician with experimental data for a range of important aliphatic species. An increasing amount of work on fast flow techniques[41] is also being reported.

The more important studies of radical cations in solution have been on benzenoid or polynuclear hydrocarbons or their alkyl or alkoxy derivatives[42] and representative oxidising systems include concentrated H_2SO_4,[43] $SbCl_5$-CH_2Cl_2,[44] $AlCl_3$-CH_3NO_2,[45] BF_3-SO_2[46] and more recently CF_3CO_2H-CH_3NO_2.[47] Unreported radical cations for which the corresponding anions have been prepared in solution are those of the even-alternant hydrocarbons, benzene, naphthalene, biphenyl and cyclooctatetraene. Those unsubstituted cations and especially the benzene cation, where the spin density is determined by symmetry, are of particular importance as, on account of their small size, the values of ρ_i(13) can be calculated more accurately than for the radical cations of anthracene, tetracene, pyrene etc. Analysis of their solution spectra would thus provide better data to test the pairing theorem and the theories of Colpa and Bolton and Giacometti et alia (p. 7). The preparation of the radical cation of azulene is also of importance as this species provides one of the few examples where molecular orbital and valence bond theory predict different unpaired spin distributions.[48]

A large and increasing number of heterocyclic cations containing nitrogen, oxygen, sulphur and phosphorus have also been reported for many of which electrolytic oxidation[49] has been employed. Chapter 4 of "Radical Ions"[4] contains a good account of heterocyclic cations and of some interesting work on amino and substituted amino systems.

This wealth of experimental data for radical ions has resulted in equation (13) being used to obtain 'experimental' values of ρ_i from the corresponding hyperfine splittings, a_i. Values of Q^H_{CH} of about -25, -29 gauss(p. 7) have usually been used for anions, cations respectively. Those values of ρ_i have been compared with 'theoretical' values calculated from a number of different types of π-electron approximations including Hückel molecular orbital, valence bond, McLachlan approximate SCF, restricted and unrestricted SCF-MO, etc. (see chapter III,B). The excellent agreement often obtained has been interpreted by many authors as a verification of the accuracy of π-electron theory to describe the ground states of molecules. Where poorer agreement has been obtained, the validity of π-electron theory has been questioned but equation (13) has usually been applied without due regard for its approximate character. The work of Vincow et alia[25](p.8) has shown that the magnitudes of Q^{H}_{CH} for radical cations and anions may well be larger, so that the values of ρ_i may well be smaller, and in less good agreement with π-electron theories. Such theories may therefore give somewhat less accurate descriptions of the ground states of radicals than has been previously thought to be the case. This, of course, does not apply to those radical ions where ρ_i is determined by symmetry but such cases are relatively few.

In addition, Vincow[25] has carried out SCF calculations on the C–H molecule, as distinct from the C–H fragment, and has shown that a large basis set of atomic orbitals and very extensive configuration interaction are necessary in order to obtain convergence of the hyperfine splitting. The SCF equations for a fragment cannot be solved but, in order to obtain more accurate values of Q^{H}_{CH} for radical cations and anions, a larger basis set of atomic orbitals than that employed by Vincow et alia (16) and more extensive configuration interaction, including doubly excited configurations, must be used. Minimum basis set atomic orbital exponents, determined for carbon and hydrogen in a positively and negatively charged C–H fragment, must also be used to evaluate the exchange integral in (18). Furthermore, the calculation must be extended to second and higher orders of perturbation theory.

3. Aims of this Study

When the work described in this thesis was begun, few π-type fluorinated radicals had been studied in solution. All were anions and all contained a stabilising and strongly electron-withdrawing group e.g. $-NO_2$[50] or $-C=O$[51]. With one exception,[52] they contained only one or two fluorine atoms per molecule.

Work on fluorinated systems is of considerable importance as aromatic fluorine provides the only direct analogy to aromatic hydrogen, being univalent and having the same nuclear spin ($I_n = \frac{1}{2}$). In addition, the aromatic bond lengths and atomic radii[53] are very similar and fluorocarbon chemistry is very similar to hydrocarbon chemistry. Fluorine is a many-electron atom, however, and in fluorine substituted aromatic compounds, the $2p_z$ orbital also contributes to the π-system. For those reasons, it had been anticipated that the fluorine analogue of (13), viz.

$$a_i^F = Q_{CF}^F \rho_i \qquad (21)$$

would be inadequate to account for aromatic fluorine hyperfine interactions and that a more complex relationship involving unpaired π spin density on the fluorine atom would need to be considered. By analogy with the work of Karplus and Fraenkel on C^{13} splittings,[29] Eaton[55] had proposed the equation

$$a_F = Q_{CF}^F \rho_C + Q_{F(FC)}^F \rho_F \qquad (22)$$

where ρ_C and ρ_F are the unpaired π spin densities on carbon and fluorine and Q_{CF}^F represents polarisation of the σ electrons in the C–F bond by ρ_C. $Q^F_{F(FC)}$ is the sum of two terms: Q^F_{FC} representing polarisation of the σ electrons in the C–F bond, and S_F that of the fluorine 1s and 2s inner shells both by ρ_F. $Q^F_{F(FC)}$ was thought to be $\gg Q^F_{CF}$ but $\rho_C \gg \rho_F$. Equation (22) can also be re-written as

$$a_F = \left[Q^F_{CF} + KQ^F_{F(FC)}\right]\rho_C$$
$$= Q_{eff}\rho_C \quad [56,57] \qquad (23)$$

where Q_{eff} (p. 26) varies as $K = \frac{\rho_F}{\rho_C}$. Although a number of attempts had been made to determine Q^F_{CF} and $Q^F_{F(FC)}$ [32,55] (see B), no set of values which consistently reproduced the observed magnitudes of a_F had been found. This arose from the uncertainty involved in calculating the true values of the very small terms, ρ_F for those anions which had been investigated.[32]

It was decided to attempt to obtain experimental data more truly representative of aromatic fluorine by preparation and subsequent E.S.R. investigation of the radical cations and anions of unsubstituted aromatic fluorocarbons. This data could then be used in conjunction with spin density calculations of ρ_C and ρ_F to establish whether equation (22) or any similar relationship was valid for those unsubstituted species and also to determine the accurate values of the spin polarisation parameters Q^F_{CF}, $Q^F_{F(FC)}$ and Q_{eff}. It was also desired to explain any difference in those parameters that might exist between the radical cations and anions of the same species, if necessary by calculation of the parameters.

As a result of previous work,[50,57] the instability of perfluorinated anions and their tendancy to lose the very stable F^- ion was suspected but a thorough investigation was required. Cationic species were predicted to be much more stable due to enhanced stabilisation of the positive charge by the highly electron-withdrawing fluorine atoms, and this was later vindicated when the radical cation of octafluoronaphthalene (p.60) was successfully prepared. Lack of success in forming the radical cations of hexafluorobenzene, octafluorotoluene and decafluorobiphenyl led to the preparation and successful investigation of a series of highly-fluorinated naphthalenes derived from octafluoronaphthalene (see chapter III,A). This work forms the subject matter of much of this thesis and complements the recent studies of Fischer and Zimmermann[58] on the radical cations of some mono- and difluorinated naphthalenes(p.23).

B. Previous Studies of Fluorinated Radicals in Solution

1. Experimental

Until recently,[59,60] only a few studies of fluorine containing π-radicals had been made in solution. Solid state studies had been previously made, however, and had been summarised by Rogers and Whiffen.[61] In addition, Fessenden[14] had extended his classic work on alkyl radicals in solution to the fluorinated methyl neutral radicals.[62] Such radicals are not the subject of this thesis and little reference to them will be made(see, however, ps.26, 29).

In 1960, Anderson, Frank and Gutowsky[52] obtained a quintuplet splitting of 4.14 gauss from the product obtained by oxidation of tetrafluoro-hydroquinone in basic ethanol, which they ascribed to the fluoranil semiquinone anion. This was later confirmed by Calvin et alia[63] by use of NaI in a THF-CH_3NO_2 solution as the oxidant. Other early work was by Ayscough et alia[50] who prepared the three isomeric monofluoronitrobenzene anions, both chemically and photochemically, in ethanolic solution. They found some ambiguity, since removed,[57,60] in assigning splittings to the meta isomer. The spectrum from the ortho anion was not completely interpreted as the species was unstable and rapidly lost fluoride ion, an effect since observed by later workers.[64] Carrington and co-workers[57] have prepared this species in a stable form by reduction with alkaline dithionite in aqueous ethanol as have Fischer and Zimmermann[60] by vacuum electrolysis in CH_3CN so that unambiguously assigned splittings are now available for all three isomers.

Ayscough also reported pronounced linewidth variations, previously unreported by Maki and Geske,[56] for the para isomer in CH_3CN. Those effects, which are discussed in chapter III, have since been observed in other fluorinated species.[65] A detailed study of them has been made by Carrington[57,66] who prepared the meta and para anions by U.V. irradiation of dilute solutions of the parent compounds in methanolic sodium methoxide. Under the same conditions, 1,2,4,5-tetrafluoronitrobenzene and pentafluoronitrobenzene interacted with the solvent but formed neutral radicals when their degassed solutions in THF were irradiated. The radicals were thought to be formed by proton abstraction from the solvent by one of the oxygen atoms in the $-NO_2$ group. Such species had previously been postulated by Ward[67] and other examples have recently been reported by Brown and Williams.[64] The much smaller ring proton and fluorine splitting constants observed by Carrington[56] for those species indicated much less density in the ring and more on the $-NO_2$ group. A recent study by Cowley and Sutcliffe,[68] however, maintains that those neutral radicals are different in structure.

Fischer and Zimmermann[60] have recently repeated Maki's[56] work on p-fluoronitrobenzene and Fraenkel's[32] on 3,5-difluoronitrobenzene and have also obtained spectra from the anions of the remaining two fluoronitrobenzene isomers formed in CH_3CN under vacuum electrolytic conditions. They have also studied several other difluorinated nitrobenzenes and a series of mono- and difluorinated nitrophenols. As previously noted by other workers,[57,64] replacement of hydrogen by fluorine in the aromatic nucleus seems to result in only a slight perturbation of the unpaired spin distribution so that proton splittings are usually about the same magnitude in both fluorine substituted and unsubstituted anions. This fact has been used by Fischer and by others to assign splitting constants with a high degree of success. Most of the splitting constants from Fischer's anions have been unambiguously assigned.

Previous work on fluorinated ketones was confined to studies of the anions of 4-fluoroacetophenone[69] and 2,7- difluorofluorenone.[51] Recently, Fischer and Zimmermann[59] have used vacuum electrolytic reduction to prepare the anions of four mono- and difluorinated benzophenones and have assigned most of the splittings. The fifth, decafluorobenzophenone, underwent reduction to give a species the spectrum of which could not be ascribed to the anion of the parent molecule but which was thought to result from the anion of its 4,4'-dicyano-derivative, formed by nucleophilic attack at the para position. As indicated by Tatlow,[70] this form of attack can readily occur at the ortho and para positions of highly-fluorinated systems. Another example of the effect has been postulated by Brown and Williams.[64]

Fischer[71] has also used the same techniqueto investigate the anions of 2,5-difluoro-1,4 benzo- and 2,3-difluoro-1,4-naphthaquinones. At higher reduction potentials, the former species lost fluoride ion to form another, possibly the anion of 2-fluoro-1,4 benzoquinone.

Other neutral radicals prepared in solution include di-(p-fluorophenyl) nitroxide[72] and meta and para tri-(fluorophenyl) methyl.[73] For the latter two species, the ratio of the fluorine splitting constant to the corresponding proton splitting constant in the unsubstituted radical was found to be ca. 2.5. This value compares favourably with the value of 2 which most workers have found for this ratio (p. 27), notable exceptions occurring in the 2,7-difluorofluorenone[51] and 2,5-difluoro-1,4-naphthaquinone[71] anions. Wang et alia[74] have found the ratio to be unity, however, for the ortho position of the perfluoro-triphenylmethyl radical. Kivelson[73] maintained that this was the result of a 10^{o} deviation from planarity in the perfluorinated radical.

Brown and Williams[64] have recently reported neutral radicals from the three monofluoronitrobenzenes and from pentafluoronitrosobenzen but, as noted above (p.20), their structure is probably different from that suggested by those authors. It must also be emphasised that they failed to prepare the radical anions of hexafluorobenzene and octafluoronaphthalene by reduction with potassium in THF, or those of tetra- and pentafluoronitrobenzene by electrolytic reduction in CH_3CN. This led them to infer that highly-fluorinated anions, even those containing a strongly electron-withdrawing group, are unstable and tend to lose fluoride ion, a fact confirmed by their detection of this ion in the residual THF. The author had previously attempted to prepare the radical anions of hexa-fluorobenzene, octafluorotoluene and octafluoronaphthalene by electrolytic reduction in CH_3CN (p. 39) and had formed the same conclusion regarding their instability.

All the fluorinated π-radicals which have been successfully prepared and discussed so far, have been anions of fluorinated nitrobenzenes, phenols, ketones or quinones, i.e. all contained a strongly electron-withdrawing substituent tending to decrease the spin density on the fluorine atoms. The first E.S.R. study of anions containing no substituent other than fluorine has recently been presented by Allred and Bush[75] who prepared the radical anions of 4,4'- and 3,3'-difluorobiphenyl by potassium reduction in THF at -80^{o}.

The first E.S.R. studies of a fluorinated cation, the octafluoronaphthalene cation, had previously been reported by Bazhin et alia[65] and independently, by Thomson and MacCulloch.[76] In addition, Fischer and Zimmermann[58] have recently reported the E.S.R. spectra of the monomer radical cations of 4-fluorobiphenyl, 4,4'-difluorobiphenyl and 1,5-difluoronaphthalene prepared by use of the $SbCl_5$-CH_2Cl_2 technique of Lewis and Singer.[44] Under the same conditions, 1-fluoronaphthalene and 6-fluorochrysene gave spectra which were ascribed to the dimer radical cations whereas the spectra from the oxidation products of 2-fluoronaphthalene and 3,3'-difluorobiphenyl were uninterpreted. The highly-fluorinated hydrocarbons octa- and decafluorobiphenyl, and octafluoronaphthalene, formed no paramagnetic species in this system. Lewis and Singer[44] had previously found that unsubstituted naphthalene also formed a dimer radical cation in $Sb\ Cl_5$-CH_2Cl_2 but the stability of the species was very dependent on the concentrations of hydrocarbon and $SbCl_5$ and on the temperature. By contrast, both the monomeric and dimeric fluorinated naphthalenes prepared by Fischer are very stable at room temperature and show no such concentration dependance. This was also found to be the case for the highly-fluorinated naphthalene cations discussed in chapter III. It is important to note that the anions prepared by Allred and Bush[75] are unstable at room temperature.

The most striking feature of the spectra of the radical cations is the very large fluorine hyperfine splittings observed e.g. the α fluorine splittings in the octafluoronaphthalene and 1,5-difluoronaphthalene (p.23) cations are 19.01 and 16.98 gauss respectively, whereas the fluorine splittings in most of the anions discussed above are of the order of 2-5 gauss. The work of Allred and Bush and of Fischer and Zimmermann has made available fluorine hyperfine splitting data for the radical cation and anion of a single species viz. 4,4'-difluorobiphenyl (Fig. 10). This data is presented in table 1.

As expected from the 'charge effect' (see A,1) the hyperfine splittings from the 4 equivalent ortho protons in the cation are bigger than the corresponding splittings for the anion. The meta splittings are in both cases lost in the linewidths. The fluorine splitting of 19.28 gauss in the cation is, however, very much larger than the corresponding splitting of 3.13 gauss observed in the anion. Biphenyl is an even-alternant hydrocarbon and the pairing theorem therefore predicts that the values of ρ_C ρ_F (22) should not differ greatly at the 4 and 4' positions of the cation and anion of the 4,4'-difluoro derivative. The large difference in fluorine splittings must therefore arise from some pronounced 'charge effect' on the magnitudes of the spin polarisation parameters in (23).

2. C-F Spin Polarisation Parameters

In order to account for aromatic fluorine hyperfine splittings, early workers proposed the equation

$$a_F = Q_{eff}\rho_C \qquad (24)$$

TABLE 1: Hyperfine splitting constants of the anion and cation of 4,4'-difluorobiphenyl.

Atom	Hyperfine splitting constants (gauss)	
	CATION	ANION
1	–	–
2	2.73	2.28
3	–	–
4	–	–
F	19.28	3.13

where a_F is the isotropic hyperfine splitting of a fluorine atom and ρ_C is the unpaired π spin density on the adjacent carbon atom. Q_{eff} is the effective σ-π polarisation parameter for the C-F fragment. By analogy with (13), Q_{eff} was thought to be negative in sign and assigned values of -39.3 gauss[52] and -47.5 gauss.[56]

The work of Eaton et alia[55] on the NMR contact shifts of a series of monofluorophenyl substituted chelates, however, firmly established that a_F and ρ_C were of the same sign so that Q_{eff} must be positive. This fact has since been confirmed by linewidth studies of the 2,5-difluoronitrobenzene anion,[32] by studies of irradiated single crystals of fluoroacetamide,[77] by Fessenden's work on fluorinated methyl radicals[62] and by the observations of Kivelson[73] on fluorine-containing neutral species.

By analogy with the work of Karplus and Fraenkel[29] on C^{13} splittings, Eaton[55] proposed the equation

$$a_F = Q^F_{CF}\rho_C + Q^F_{F(FC)}\rho_F \qquad (25)$$

where the terms have been defined on p.17. This equation may be rewritten as

$$\begin{aligned} a_F &= \left[Q^F_{CF} + Q^F_{F(FC)}K\right]\rho_C \\ &= Q_{eff}\rho_C \end{aligned} \qquad (26)$$

and is now equivalent to (24). Q_{eff} varies as $K = \frac{\rho_F}{\rho_C}$ but Carrington found the ratio approximately constant when he performed McLachlan spin density calculations on the three isomeric monofluoronitrobenzenes.[57]

Small changes in K, however, could result in large changes in Q_{eff} and a_F if $Q^F_{F(FC)}$, containing the atomic term S_F, were very large. Brown and Williams[64] have used Fraenkel's[32] value of $Q^F_{CF} = -38$ gauss and Whiffen's single crystal data[77] (K = 0.15) in (26) and obtain a value of $Q^F_{F(FC)} = +720$ gauss. They point out, however, that the uncertainties in the values of ρ_C, ρ_F and therefore K makes the values of $Q^F_{CF}, Q^F_{F(CF)}$ equally uncertain.

These authors also maintain that K, and therefore Q_{eff}, varies in the manner meta $>$ para $>$ ortho when McLachlan spin density calculations are performed on the isomeric fluoronitrobenzene anions.[57] This is the order found for Q_{eff} by direct comparison of the fluorine and proton splittings at the same position, having made the assumption that ρ_C is unchanged on fluorine substitution. The magnitudes of Q_{eff} and its range of variation, however, are in poor agreement with (26) when those values of K are used in conjunction with the values of $Q^F_{CF}, Q^F_{F(FC)}$ quoted above. On the other hand, Hückel spin density calculations using Hückel parameters also obtained from single crystal data predict K to be constant for some highly-fluorinated neutral species studied by Brown and Williams. When this value of K is used in (26) with $Q^F_{CF} = -38$ gauss and $Q^F_{F(FC)} = +720$ gauss, a value of $Q_{eff} = +62$ gauss is obtained.

This is in good agreement with Kivelson's value of $Q_{eff} =$ +57 gauss[73] obtained from a least squares fit of experimental a_Fs to values of ρ_C calculated from the proton hyperfine splittings at the corresponding positions. Those values were obtained from (13) with Q^{H}_{CH} = −23 gauss and a representative range of neutral and anionic species was considered. In addition, McLachlan spin density calculations were performed also over a representative range of species and it was found that K is not constant although the variation from species to species is slight. The magnitude of K was also found to be highly sensitive to the value of the Hückel coulomb parameter for fluorine, h_F, used in the calculations. By analogy with Q^{H}_{CH}, the term Q^{F}_{CF}, representing polarisation of the σ electrons in the C–F bond by density on carbon only, might be expected to be negative. Now the theory of Pople and Santry[78] maintains that the sign of the quotient Q^{X}_{CX}/U_X, where U_X is the magnetic moment of nucleus X, depends on the energy difference between the 2s and the 2p orbitals of atom X. This difference is relatively large for X = O,F and the quotient is positive whereas it is negative for X = C,N where the difference is smaller. The quantity U_X is positive for fluorine and, on this basis, Kivelson concludes that Q^{F}_{CF} is also positive. A least squares fit of the values of a_F to the McLachlan data for ρ_C and ρ_F, with h_F = 1.7, resulted in a value of Q^{F}_{CF} = +54.0 gauss. As Kivelson points out, however, this result is subject to uncertainty arising from uncertainty in the very small terms, ρ_F. The relative magnitudes of Q_{eff} = +57 gauss and Q^{F}_{CF} = +54 gauss seem to indicate that $Q^{F}_{F(FC)}K \ll Q^{F}_{CF}$ and that the major contribution to a_F is from $Q^{F}_{CF}\rho_C$. The latter concludes that the magnitude of $Q^{F}_{F(FC)}$ may be similar to a value of +36 gauss obtained from data for the free fluorine atom.[79] Kivelson's value for Q^F_{CF} is in very poor agreement with the negative value of −38 gauss obtained from single crystal data[55] and with the values of −37.5 gauss, −147 gauss respectively quoted by Kaplan et alia[32] and by Whiffen et alia.[77] Doubts are also raised over the value of Q_{eff} = +62 obtained by Brown and Williams on the basis of Q^F_{CF} = −38 gauss.

Fèssenden's data for the monofluoromethyl radical[62] may be used to obtain an estimate of Q_{eff} for neutral species without using approximate π-electron theory to calculate ρ_C. Substitution of the value of a_H = 21.1 gauss, found for this radical, and the value of Q^H_{CH} = −23 gauss for the methyl radical (p. 6) in (13) results in a value of ρ_C = 0.92. Further substitution of this value and the value of a_F = 64.3 gauss in (26) makes Q_{eff} = 70.1 gauss which is rather different from the value of +55 gauss obtained from Kivelson's data for the para tri-(fluorophenyl) methyl neutral radical.[73] This may be due to the fact that the $\dot{C}H_2F$ radical is not quite planar and that some slightly modified form of (26) is required in order to accurately calculate Q_{eff} or it may result from the different value of K. This value of K = (1−0.92)/0.92 = 0.09, neglecting overlap spin density in the C−H and C−F bonds, and is approximately 3 times larger than the value Kivelson found from McLachlan data for para tri-(fluorophenyl) methyl. When those values of Q_{eff} and K for the $\dot{C}H_2F$ radical are substituted in (26) with Q^F_{CF} = +54 gauss, a value for $Q^F_{F(FC)}$ of ca. 150 gauss is obtained.

The general form of McConnell's relationship for the hyperfine splitting from any aromatic nucleus, n, is given by (20) and, considering only spin density in a C-F aromatic fragment, this becomes

$$a_F = Q^F_{CC}\rho_C + (Q^{F'}_{CF} + Q^{F'}_{FC})\rho_{CF} + Q^F_{FF}\rho_F \qquad (27)$$

Q^F_{CC} and Q^F_{FF} are respectively equivalent to Q^F_{CF} and $Q^F_{F(FC)}$ of (25), so that (27) differs from the latter only by inclusion of the overlap spin density, ρ_{CF}, and the associated spin polarisation parameters, $Q^{F'}_{CF}$ and $Q^{F'}_{FC}$. This equation has been used by Murrell and Hinchliffe[80] to evaluate a_F for fluorinated nitrobenzene anions as detailed below. The Q factors in (27) were calculated by considering configuration interaction between a ground state σ function and $\sigma \rightarrow \sigma^*$ excited doublet configurations where both σ electrons in the C-F bond have parallel spins. The total excited state contribution[23] is to a first order in perturbation theory given by the expression

$$Q^{F^1}_{AB} = {}^{16\pi}/_{3}g\beta g_F\beta_F \sum_k\sum_r \delta(\vec{r}_i - \vec{r}_F)\Psi_k(i)\Psi_r(i)E^{-1}_{kr}\iint \Psi_k(1)\pi_A(1)\left|\frac{e^2}{r_{12}}\right|\Psi_r(2)\pi_B(2)dT_1dT_2 \qquad (28)$$

where Ψ_k, Ψ_r are bonding and anti-bonding σ orbitals, $\delta(\vec{r}_i - \vec{r}_F)\Psi_k(i)\Psi_r(i)$ is the value of the density $\Psi_k\Psi_r^*$ at the fluorine nucleus and E_{kr} is the energy gap between ground and excited states. π_A and π_B are the $2p_\pi$ fluorine or carbon atomic orbitals and g_F, β_F the g value of the fluorine nucleus and nuclear magneton respectively. A similar expression to (28) has been used to evaluate

[1] Footnote: This also means terms $Q^{F'}_{AB}$(27).

Q_{CH}^{H}(p. 9).

The Ψ_k s and Ψ_r s were based on Pople-Santry[81] independent electron closed shell theory and were constructed from valence shell atomic orbitals. The 1s orbitals of carbon and fluorine were assumed to be non-bonding.

If we write

$$\Psi_k = \sum_n a_{kn} X_n$$
$$\Psi_r = \sum_{n'} a_{rn'} X_{n'} \qquad (29)$$

where the X_ns are those atomic orbitals, the exchange integral in (28) becomes

$$\sum_n \sum_{n'} (a_{kn} a_{rn'} \iint X_n(1) \pi_A(1) \left|\frac{e^2}{r_{12}}\right| X_{n'}(2) \pi_B(2) dT_1 dT_2) \qquad (30)$$

Murrell evaluated the term $\delta(\vec{r}_i - \vec{r}_F)\Psi_k(i)\Psi_r(i)$ by taking the product of the fluorine 2s atomic orbital coefficients in Ψ_k, Ψ_r and the value for the fluorine 2s SCF electron density at the nucleus, obtained by Whiffen et alia[82]. The terms E_{kr} were evaluated by taking the difference of the appropriate one electron molecular orbital energies. The integrals (30) were computed using atomic orbital exponents for carbon and fluorine obtained from Slater's rules.[83]

In calculating Q_{CC}^{F}, $Q_{FC}^{F'}$ and $Q_{CF}^{F'}$ only excited configurations corresponding to

(1) Transitions between valence shell molecular orbitals.

(2) Transitions between the bonding σ orbitals and higher s orbitals on the fluorine atom were assumed to be sufficiently important to be considered. The latter contribution was neglected,

however, owing to the difficulty in accurately estimating it because of the infinity of the fluorine s orbitals. In calculating Q^F_{FF}, on the other hand, this type of transition must be considered as must those from fluorine 1s both to ns and to the anti-bonding valence molecular orbitals. Murrell found the total fluorine 2s density in the bonding molecular orbitals to be very close to 2 and therefore assumed that the total contribution to Q^F_{FF} from all types of excitation was equivalent to that of a free fluorine atom with zero orbital angular momentum. Using Goodings' data[84] for the free atom 1s, 2s spin densities at the nucleus, Q^F_{FF} was found to be +200 gauss.

Four slightly different atomic orbital models were used to construct the Ψ_ks (29) for the C-F fragment e.g. model (c) employs carbon and fluorine 2s, $2p_x$, $2p_y$ atomic orbitals with allowance for the adjacent bonds made by inclusion of nearest neighbour hydrogen 1s orbitals. The values of Q^F_{AB} given in table 2 were used in conjunction with spin density calculations of ρ_C, ρ_F, ρ_{CF} to evaluate the a_Fs from (27).

This table shows the atomic term to be largest and that the next largest term, $Q^{F'}_{FC}$, is negative. Q^F_{CC} which multiplies ρ_C in (27), is negligible by comparison and also negative and compares very unfavourably with the value of −38 gauss from single crystal studies and with Kivelson's value (p. 28).

Spin density calculations were performed on the anions of the isomeric fluoronitrobenzenes, 2,3,5,6-tetrafluoronitrobenzene and pentafluoronitrobenzene using restricted Hartree-Fock

TABLE 2: Spin polarisation parameters Q^{F}_{AB} for model (c)[80]

Q^{F}_{AB}	Value (gauss)
Q^{F}_{CC}	-11
$Q^{F'}_{CF}$	+5
$Q^{F'}_{FC}$	-62
Q^{F}_{FF}	+200

molecular orbital theory (p.104) and configuration interaction with all singly-excited states. The fluorine spin density, ρ_F, was found to be highly sensitive to the empirical parameter[85] $\delta W_F = U_{FF} - U_{CC}$ where U_{FF}, U_{CC} are one-centre coulomb integrals on carbon and fluorine. This parameter was adjusted to give the best agreement with the experimental values of a_F. Hence it is not surprising that his values of ρ_F are considerably larger and some of his values of ρ_C quite different from those obtained by others for the same species using Hückel or McLachlan calculations [57,86] or that his agreement with experiment is of the correct order.

Now SCF equations for a C-F fragment, as for a C-H fragment (p.10), cannot be solved and the σ orbitals must therefore be approximated e.g. in the manner of Murrell. Not only will this cause the atomic orbital coefficients a_{kn} (29) to be inaccurate but also the terms E_{kr} (28). In addition, equation (28) was derived from first order perturbation theory. The work of Vincow et alia[25] (p. 8) has shown that it is necessary to extend the calculation of Q^H_{CH} to second order in perturbation theory and may also be necessary for the more complex terms Q^F_{AB}. Furthermore, Murrell's σ orbitals were obtained for a neutral fragment and take no account of any 'charge effect' on the magnitudes of the coefficients a_{kn} that might occur in the anions studied. This would have been particularly important for the fluorine 2s atomic orbital coefficients being used to evaluate the density

$\Psi_k\Psi_r^*$ at the nucleus. Energy minimised carbon and fluorine atomic orbital exponents obtained for a $(C-F)^-$ fragment, instead of the Slater neutral atom values, should have been employed to evaluate the integrals in (30) as the latter do not allow for variation of the Q_{AB}^Fs with excess charge. By analogy with Q_{CH}^H (p. 11), this would have been particularly important for the fluorine 1s, 2s atomic orbital exponents. Too much significance should therefore not be attached to Murrell's values for the terms Q_{AB}^F. The atomic term, Q_{FF}^F, was calculated from Goodings' data[84] for the free fluorine atom total spin densities at the nucleus. More accurate calculations of this quantity have recently been made by Kaldor[87] and by Harris et alia[88] and result in values of Q_{FF}^F of +42 gauss, +70 gauss respectively. Those values are in reasonable agreement with an experimental value of +107 gauss from molecular beam data[89] and in fair agreement with the value of +36 gauss quoted by Kivelson.[73] All those values are of course based on the assumption that the fluorine atom in a C-F fragment behaves as if it had zero orbital angular momentum. Since the values of K (26) quoted by most authors[57,73,86] are of the order 0.03 to 0.05, it is difficult to reconcile negative values of Q_{CC}^F with the values of Q_{FF}^F quoted above and still obtain a positive value for Q_{eff}. The very large values of +848 gauss,[55] +1393 gauss,[77] +720 gauss[64] quoted for Q_{FF}^F were based on negative values of Q_{CC}^F and are probably erroneous. The small negative value, obtained by Murrell for Q_{CC}^F, implies that the terms $Q_{CF}^{F'}$, $Q_{FC}^{F'}$ may also be in error. It seems that experimental data for fluorinated anions is best accommodated by a positive value[73] of Q^F_{CC}.

This was further confirmed by Fischer and Colpa[86] who performed least squares fits of the experimental a_Fs for most of the anions and neutral species discussed in (1) of this section to the one, two and three parameter equations (24), (25), (27) using McLachlan spin density calculations of ρ_C, ρ_F and ρ_{CF}. This latter term was obtained from the equation[65]

$$\rho_{CF} = \sqrt{\rho_C \rho_F} \qquad (31)$$

which is valid where the ground state wave function can be represented by a single Slater determinant as in McLachlan's method (approximate Unrestricted Hartree-Fock). For the one parameter fit, a value of Q_{eff} = +54.4 gauss was obtained in excellent agreement with the values of +57 gauss and +50 gauss (approximate) respectively quoted by Kivelson[73] and Carrington.[57] The two parameter fit resulted in values of $Q^F_{CC} = Q^F_{CF}(25)$ = +48.1 gauss (c.f. Kivelson's value of +55 gauss for neutral radicals) and $Q^F_{FF} = Q^F_{F(FC)}$ = +146 gauss, the latter in excellent agreement with that previously quoted for the $\dot{C}H_2F$ radical (p.29). In addition, $Q^F_{FF}\rho_F$ was found to vary between 5 and 20% of $Q^F_{CC}\rho_C$ accounting for the similarity of the constants in the one and two parameter fits. Q^F_{FF} was found to be inversely proportional to ρ_F but Q^F_{CC} remained approximately constant when ρ_F was varied.

It is highly significant that the three parameter fit results in quite different values for Q^F_{CC} and Q^F_{FF} viz. +86.6 gauss, +931 gauss respectively. The large increase in those terms arises from the introduction of the term $(Q^{F'}_{CF} + Q^{F'}_{FC})\rho_{CF} = +345\rho_{CF}$ gauss where ρ_{CF} is negative if ρ_{C}, ρ_{F} are positive and vice versa. When used in (26) in conjunction with the values of Q_{eff} quoted above, the value of Q^{F}_{CC} implies that either Q^{F}_{FF} or K are negative. But Q^{F}_{FF} is unquestionably positive[89] and $K = \rho_{F}/\rho_{C}$, cannot be negative in sign or equation (31) would result in unreal overlap spin densities. For $\dot{C}H_2F$ (p.29) with $\rho_C = 0.92$ and $\rho_F = 0.08$, $\rho_{CF} = -0.27$ and, neglecting overlap spin density in the C-H bonds, the total spin density in the radical = 0.73 which is rather less than unity. It seems strange that ρ_{CF} should be so large and of opposite sign to ρ_C, ρ_F, since for C-H bonds ρ_{CH} has the same sign as ρ_C[90] and is of negligible significance ($<1\%$ of ρ_C for all but the smallest radical ions). It seems that correlation with the three parameter equation (27) gives values of Q^{F}_{AB} which are not easily explained and that the experimental data is best accommodated by the two parameter fit (25).

In addition, Fischer and Colpa have calculated the terms Q^{F}_{AB} in a manner similar to Murrell and Hinchliffe,[80] including fluorine 1s as well as 2s atomic orbitals in the Ψ_ks. Unlike Murrell, this enables them to calculate directly the contribution to Q^{F}_{FF} from the excitation $\sigma_{1s} \rightarrow \sigma$(anti-bonding) using an estimation of the excitation energy obtained from X-ray data[91] but they maintain that the other contributions to Q^{F}_{FF} detailed on p.32are probably small and accordingly neglect those. The values obtained for the Q^F_{AB}s vary with the amount of s character introduced into the fluorine $2p\sigma$ bonding atomic orbital. For 10% s character, Q^F_{FF} = +158.97 gauss in good agreement with that obtained from the two parameter least squares fit. The values found for the other terms Q^F_{AB} are approximately of the same order of magnitude as those of Murrell and Hinchliffe.

All this work on fluorine spin polarisation parameters has referred either to anions or neutral species. Although some experimental data for fluorinated cations has appeared in the literature,[58,65,76] with the exception of some comments made by Bazhin et alia,[65] no attempt to determine those parameters for fluorinated cations has been made. Vincow et alia[25] have shown (p.11) that the magnitude of Q^H_{CH} is highly dependent on the optimum value of the hydrogen 1s orbital exponent. By analogy with this, the magnitudes of Q^F_{CC}, Q^F_{FF}(25) should be highly dependent on the optimum values of the fluorine 1s, 2s orbital exponents. The magnitudes of the observed splittings for fluorinated cations (see table 1) are, as a rule, much larger than those for fluorinated anions and indicate that this dependence on charge is very pronounced.

Attempts to determine the magnitudes of fluorine spin polarisation parameters in cations and to explain their dependence on 'excess charge' is made in chapter III.

CHAPTER II: EXPERIMENTAL

In this chapter is given an account of the various experimental techniques used in attempts to prepare the radical anions and cations of perfluorinated aromatic hydrocarbons. The $SbCl_5$-SO_2 technique, used to prepare the radical cations of octafluoronaphthalene and other highly fluorinated naphthalenes (see chapter III) is then discussed in detail. This is followed by an account of the preparation and identification of the highly fluorinated naphthalenes.

1. Attempts to Prepare and Investigate Perfluorinated Anions

In situ electrolytic reductions of solutions of hexafluorobenzene, octafluorotoluene and octafluoronaphthalene in highly-purified, oxygen-free acetonitrile with 0.1M tetra-n-propyl ammonium perchlorate as supporting electrolyte were performed in the manner of Maki and Geske,[37] the appropriate reduction potentials having first been determined by plotting polarographic curves. Fig. 1 is a diagram of the apparatus used. Concentrations of fluorocarbon ranging from 10^{-2} to 10^{-4}M were employed but no E.S.R. signals were observed. The instability of these anions and their tendancy to lose fluoride ion on formation was suspected. This was later confirmed by Brown and Williams[64] who failed to observe signals from -80° upwards when solutions of hexafluorobenzene and octafluoronaphthalene were reduced by potassium in tetrahydrofuran and, furthermore, detected fluoride ion in the

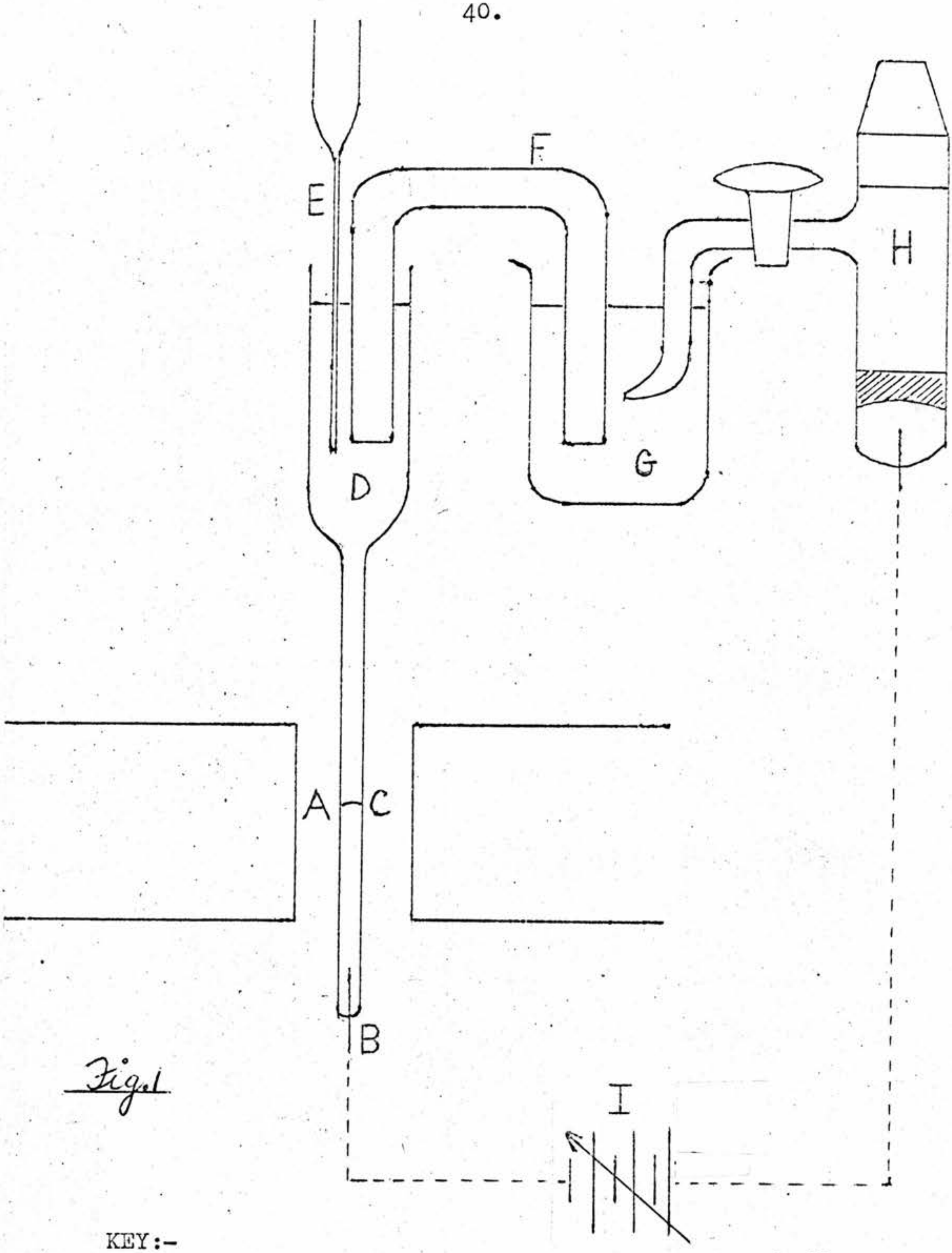


Fig.1

KEY:-
A, Spectrometer cavity B, Platinum electrode C, Mercury surface where anions are formed D, Solution E, Capillary for degassing F, Agar jel bridge G, KCl solution H, Calomel cell I, Polarograph.

residual solutions. No further attempts to prepare perfluorinated anions were made.

2. Attempts to Prepare and Investigate Perfluorinated Radical Cations

A series of Lewis acid-solvent type of oxidising system employing high vacuum conditions, and in addition, a number of strong acids, were used.

(i) The system $SbCl_5-CH_2Cl_2$

The apparatus (Fig. 2) and procedure were identical to those employed by Lewis and Singer:[44] a solution of perfluoronaphthalene ($C_{10}F_8$) in pure, dry CH_2Cl_2 was placed in capillary tube A, attached to the apparatus at B and thoroughly degassed at 10^{-5}mm. of mercury. A known amount of $SbCl_5$ vapour was trapped in the calibrated bulb C by controlling the temperature of reservoir D. Tap E was then closed and the $SbCl_5$ allowed to distill into the frozen solution. The sample tube was then sealed off at the constriction F and warmed to -80^o. No reaction was seen to occur at this temperature when solutions 10^{-3}, 10^{-4}M in $C_{10}F_8$ and 10^{-2}M in $SbCl_5$ were used. The samples were then placed in the low temperature cavity insert of the E.S.R. spectrometer (see6) and examined from -80^o to room temperature. No E.S.R. signals were observed.

(ii) The system $AlCl_3-CH_3NO_2$

A procedure similar to that employed by Forbes and Sullivan[45]

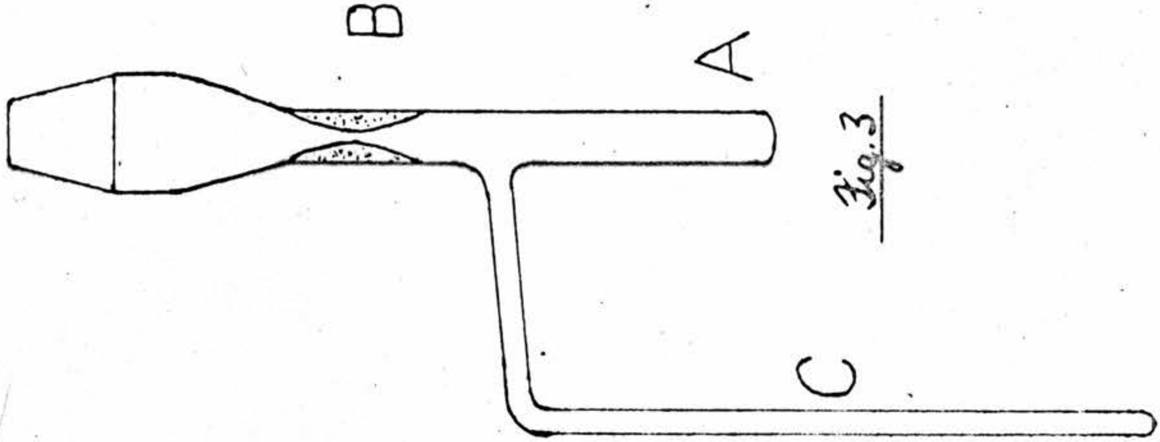


Fig. 3

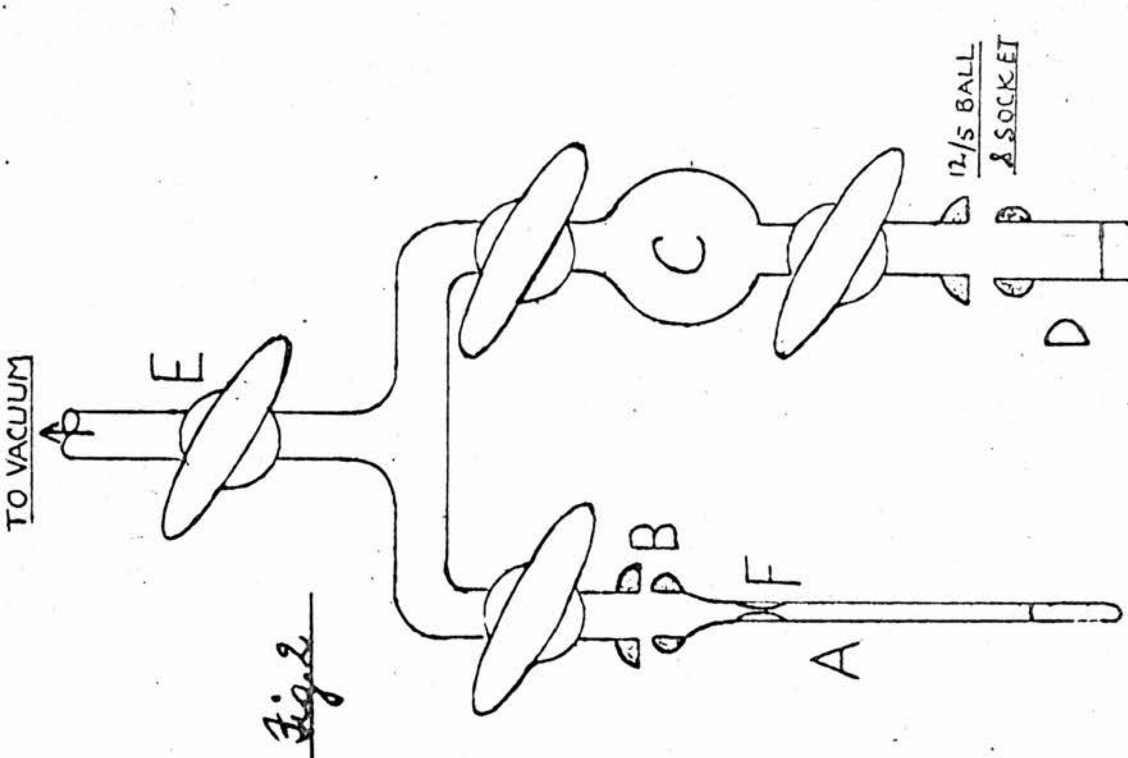


Fig. 2

was adopted. Perfluoronaphthalene (5 mgm.) and anhydrous $AlCl_3$ (20 mgm.) were placed in sample tube A (Fig.3) which was attached to a vacuum system and evacuated to 10^{-5} mm. of mercury. About 1 ml. of dry, oxygen-free CH_3NO_2, stored over Ca H_2 on the vacuum line, was then distilled in and the sample sealed off at constriction B. The sample was then warmed to room temperature but no reaction was seen to occur. The solution was then tipped into capillary tube C and examined in the E.S.R. spectrometer but no signals were observed.

(iii) <u>The system BF_3-SO_2</u>[46]

Sufficient perfluoronaphthalene to form a 10^{-3}M solution was placed in sample tube A (Fig.3) which was attached to a vacuum line and evacuated. About 1.5 ml of liq. SO_2 (BDH laboratory reagent, supplied in cannisters) was then distilled in under vacuum and the solution thoroughly degassed at 10^{-5}mm. of mercury. An excess of BF_3 (Cambrian Chemicals reagent grade, supplied in lecture bottles) with respect to the$C_{10}F_8$ was then distilled into the solution via a calibrated manometer on the vacuum line. The sample tube was then sealed off at B and allowed to warm to -80° but no reaction was seen to occur nor were any E.S.R. signals observed at any temperature.

(iv) <u>Strong acids</u>

(a) Solutions of hexafluorobenzene, octafluorotoluene, octafluoronaphthalene and decafluorobiphenyl in concentrated or 100% H_2SO_4, or in concentrated HNO_3, appeared to undergo no reaction and gave no signals. Neither were any signals observed from a degassed solution of $C_{10}F_8$ in a 50 : 50 CF_3CO_2H-CH_3NO_2[47] mixture.

(b) Octafluoronaphthalene slowly dissolved in fuming H_2SO_4 (oleum) to give a brilliant green colour and an essentially three line spectrum, with indications of further resolution in the wings, was obtained when the solution was examined in the Decca flat cell accessory (Fig.4). Under very high gain conditions, three additional lines, as later reported by Bazhin,[65] could be seen on either side of the centre triplet (Fig.5) but, although the solution was exhaustively examined at various dilutions and microwave power levels, those lines were not seen in such a high intensity ratio to the centre lines as reported by the latter. Bazhin's resolution of those lines compared very unfavourably with what he found for the same species, $C_{10}F_8^{+}$, in the SbF_5-$(CH_3O)_2SO_2$ system and he ascribed this to line-broadening effects, resulting from non-zero averaged dipole-dipole interactions, in the highly viscous oleum. His slightly superior resolution in oleum to that of the author may be due to a smaller excess of polar SO_3. As demonstrated by De Boer,[46] linewidths from spectra recorded in the non-polar SO_2 are relatively very narrow; hence the much better resolution obtained by Thomson and MacCulloch[76] for $C_{10}F_8^{+}$ in the $SbCl_5$-SO_2 system (see chapter III) than was obtained in either of Bazhin's media.

The visible spectrum of the oleum solution of $C_{10}F_8$ was recorded on a Unicam SP 800 Spectrophotometer and is shown in fig.6: similar spectra have been obtained by Hoijtink[92] for

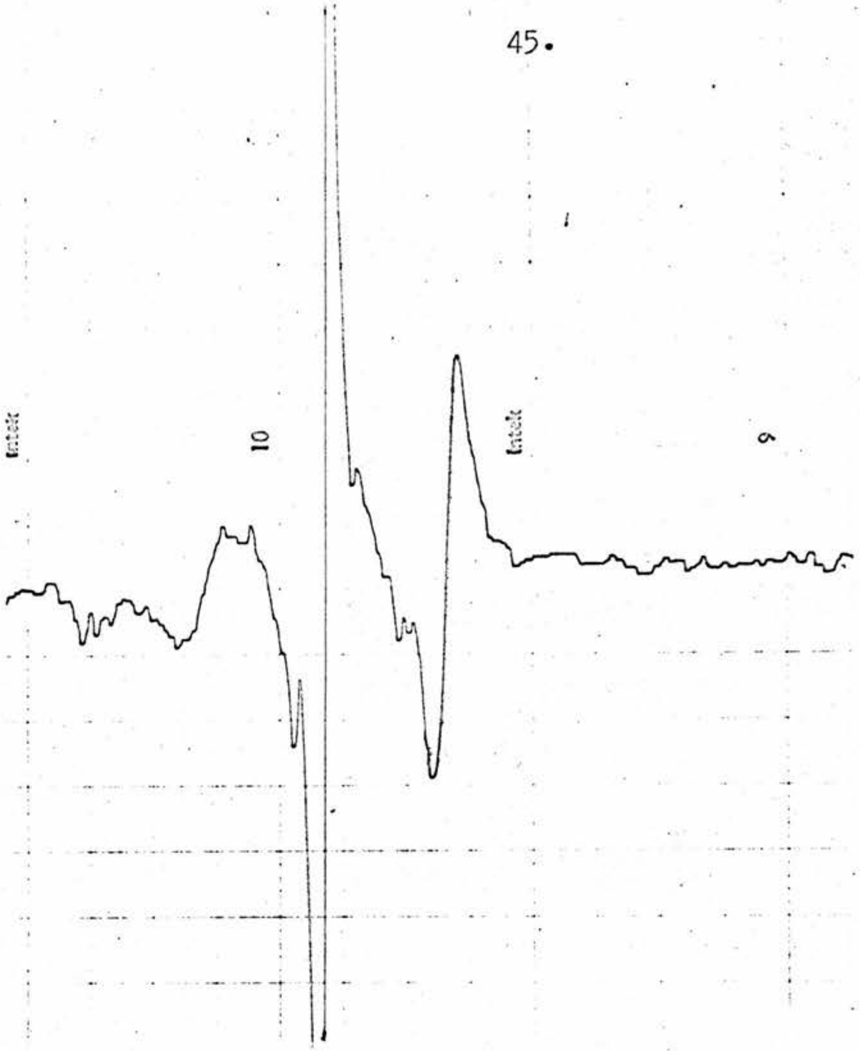


Fig. 4

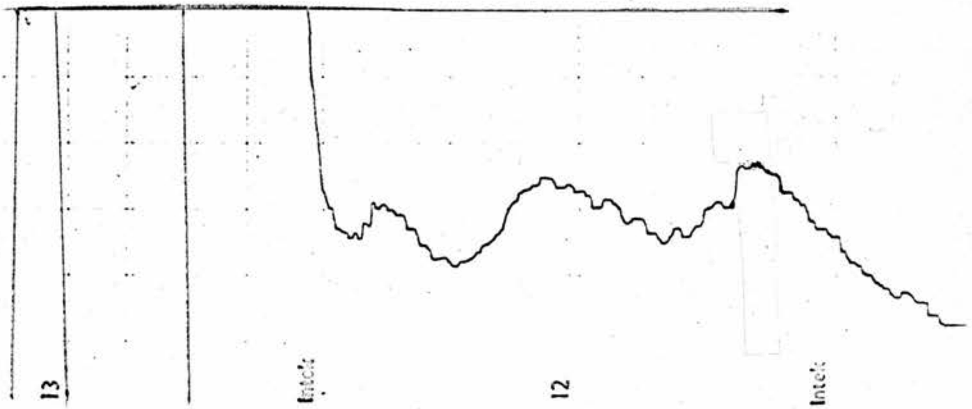
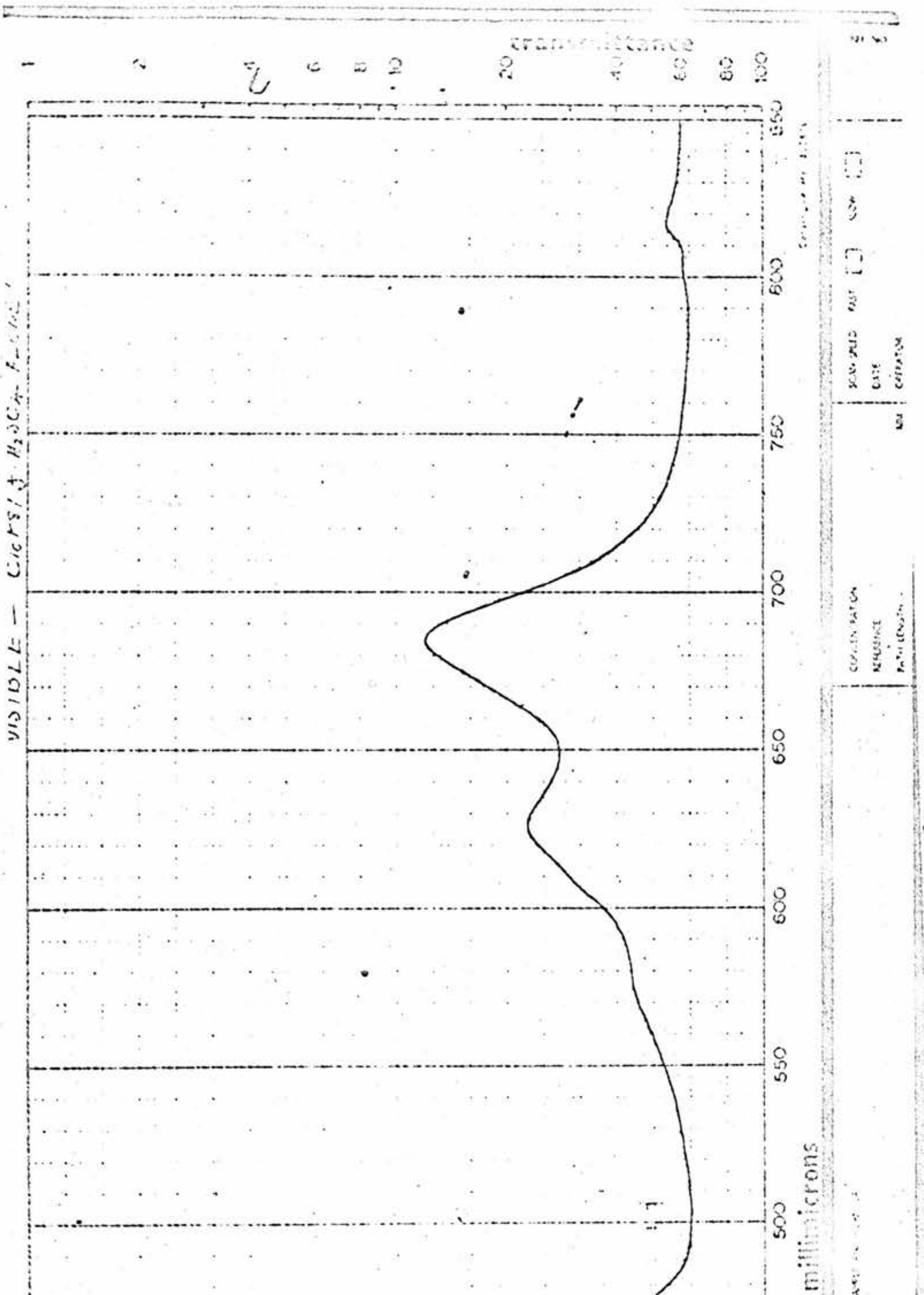


Fig. 5


VISIBLE —
transmittance
1
2
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550
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700
750
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850

Fig. 6

hydrocarbon cations in conc. H_2SO_4. It was then decided to compare this spectrum with the visible spectrum of $C_{10}F_8$ in $SbCl_5-SO_2$ (p. 60). Both spectra would be recorded by reference to the solvents and would be identical should they result entirely from $C_{10}F_8^{+\cdot}$ Further comparison, at low temperatures, with the visible spectra of solutions of C_6F_6 in $SbCl_5-SO_2$ might have yielded information about the composition of this diamagnetic green solution (p. 65) which gives no E.S.R. signals and rapidly becomes yellow at room temperature. To carry out such experiments, it was necessary to obtain vacuum U.V. cells which would be sealed on to sample tube C (Fig.7) while the oxidations were being performed on the vacuum line. Unfortunately, those cells did not arrive in the time available.

The series of hydrofluoronaphthalenes, prepared as in 4, all formed the same green solutions in oleum and for 2H-heptafluoronaphthalene the two λ_{max} values for the visible spectrum were displaced to the U.V. by only a few mμ relative to octafluoronaphthalene in the same solvent.

U.V. irradiation of those oleum solutions caused the E.S.R. signals to disappear immediately.

(v) The system $SbCl_5-SO_2$

A 10^{-3}M solution of octafluoronaphthalene in liq. SO_2, oxidised under high vacuum with $SbCl_5$, yielded a well-resolved signal which was later ascribed to the radical cation. A detailed account of this technique follows and the results obtained with it are given in chapter III.

3. The $SbCl_5$-SO_2 Oxidative Technique

Fig.7 shows the vacuum system.

SO_2 (BDH laboratory reagent, supplied in cannisters) was introduced under vacuum to reservoir A where it was thoroughly degassed at ca. 10^{-5}mm. mercury and stored under liq. nitrogen.

$SbCl_5$ (Fisons reagent grade) was dried over calcium hydride for several days, filtered, transferred to detatchable vessel B and vigorously degassed on the line where it was similarly stored. This liquid was found to be difficult to degass thoroughly because of small amounts of dissolved chlorine but, if degassing were not sufficiently complete, anomalous results were obtained.

Sufficient compound to form an approximately 10^{-3}M solution was weighed into sample tube C and about 1-1.5 ml. of liq. SO_2 distilled in, followed by an excess of $SbCl_5$ with respect to the compound. The mixture was then frozen and the sample sealed off at D under high vacuum and allowed to warm to -80^o in a cardice-acetone bath. The solution was tipped into capillary E and spectra were examined at appropriate temperatures from -80^o to room temperature.

No signals were observed from solutions where oxygen was deliberately introduced or where the $SbCl_5$ was not in excess but the actual excess did not seem important. Drying of the SO_2 appeared unnecessary but where no signals were initially observed, this extra precaution was effected by prior distillation under

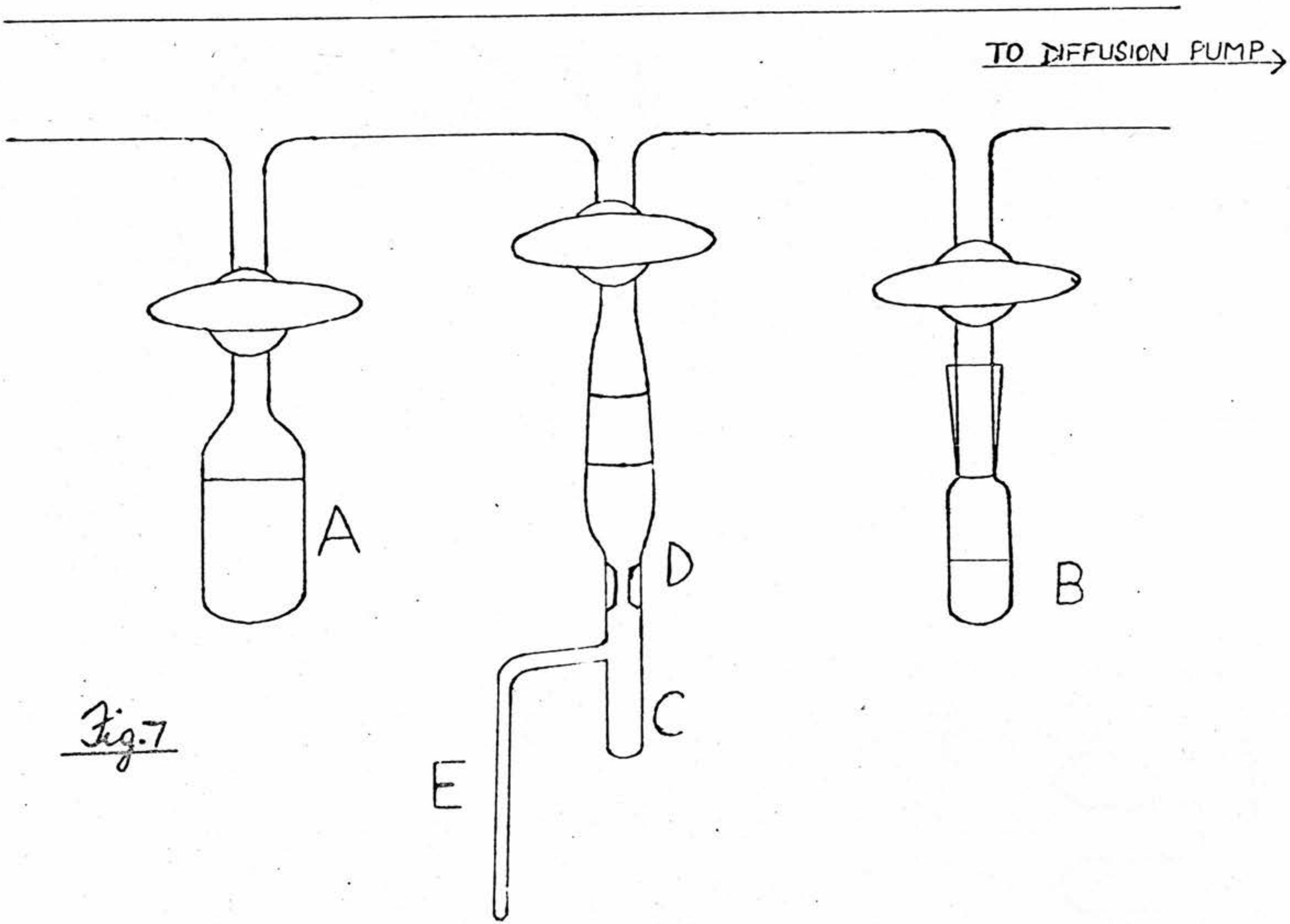


Fig.7

vacuum from a CCl_4/liq. nitrogen slush bath at -23° in order to freeze out any traces of moisture.

4. Preparation and Identification of Highly Fluorinated Naphthalenes

(i) Preparation

Tatlow has prepared 2H-heptafluoronaphthalene[93] by reaction of $C_{10}F_8$ with the theoretical quantity of $LiAlH_4$ for complete conversion to the former. After 40 hrs. refluxing in ether, the product formed was a mixture of the starting material and the 2H-compound, with substitution occurring only at the β-position Hence reaction with the quantity for complete conversion to tetra H-tetrafluoronaphthalene might have progressively yielded all the β H-substituted compounds as far as $C_{10}F_4H_4$.

Procedure: a solution of 1gm. $C_{10}F_8$ and 0.153 gm. $LiAlH_4$ was refluxed in sodium dried ether for 60 hrs., then cooled, dilute H_2SO_4 carefully added and the organic phase separated from the aqueous phase which was extracted with ether. The total ethereal solution was dried with $MgSO_4$, filtered and the ether evaporated. 770 mgm. of product were obtained.

This product was dissolved in 2.5 ml. of toluene and analysis performed at various temperatures on a Pye, Series 203, preparative gas chromatograph (column: 10% "carbowax" on "celite"). As there were a large number of peaks close together, adequate resolution could only be obtained at 80° at the concentration (ca. 0.35 gm. per ml.) and sample size (50 microlitres) used but the solution was not diluted as this would merely increase the length of time required to complete the separation. Under those conditions, a single "run" lasted 4.5 hr. and could not be carried out automatically so that separation was effected manually at 100 microlitres per day, at 80°, and took about 6 weeks to perform. The advantage of this laborious procedure was that the major constituents A,B,C,D(Fig.8, with the residual $C_{10}F_8$ not shown) were completely separated from the minor ones.

G.l.c. analysis of A,B,C and D at 150° (same column) showed each to contain about 10-20% of a mixture of the others as impurity. This was thought to be caused by condensation in the metal lead from the column to the flame ionisation detector and subsequent leakage through the outlet needle during the long retention times.

Having removed the minor constituents, however, complete separation of A,B,C and D from one another was effected at 150° at the optimum dilution using the same column (about 3 days) and g.l.c. analysis showed them to be highly pure. The separation is shown in Fig.9 where the peaks corresponding to the compounds (see below) are reassigned the letters A,B,C,D and E.

(ii) Identification (see table 3)

The structural formulae were partly determined from the fluorine NMR spectra recorded on a Varian HA -100 spectrometer. Solutions in CCl_4 with CCl_3F as an internal reference were used. Since only small amounts of compound were available, the spectra were recorded using the Varian C1024 time-averaging computer enabling relatively dilute solutions (M/10) to be used. The

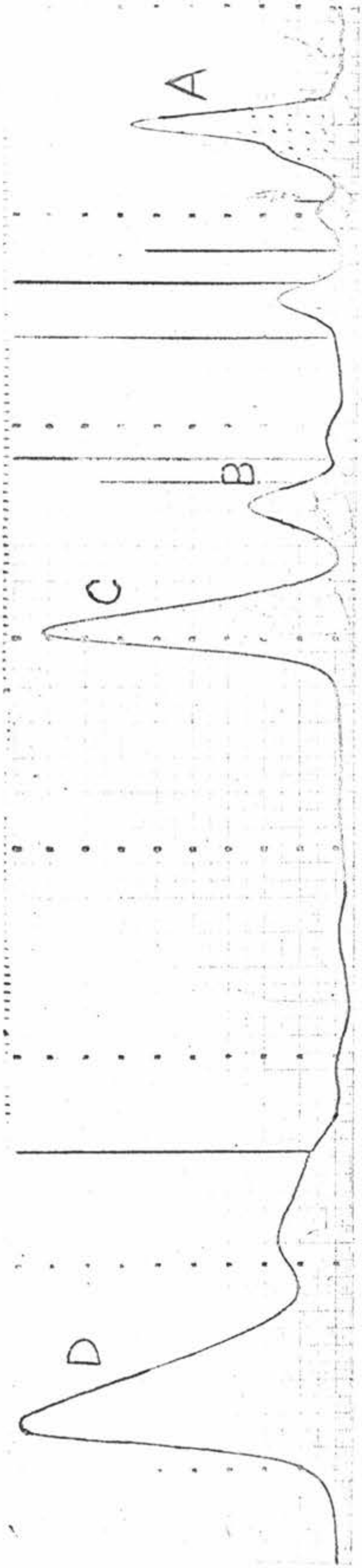


Fig. 8

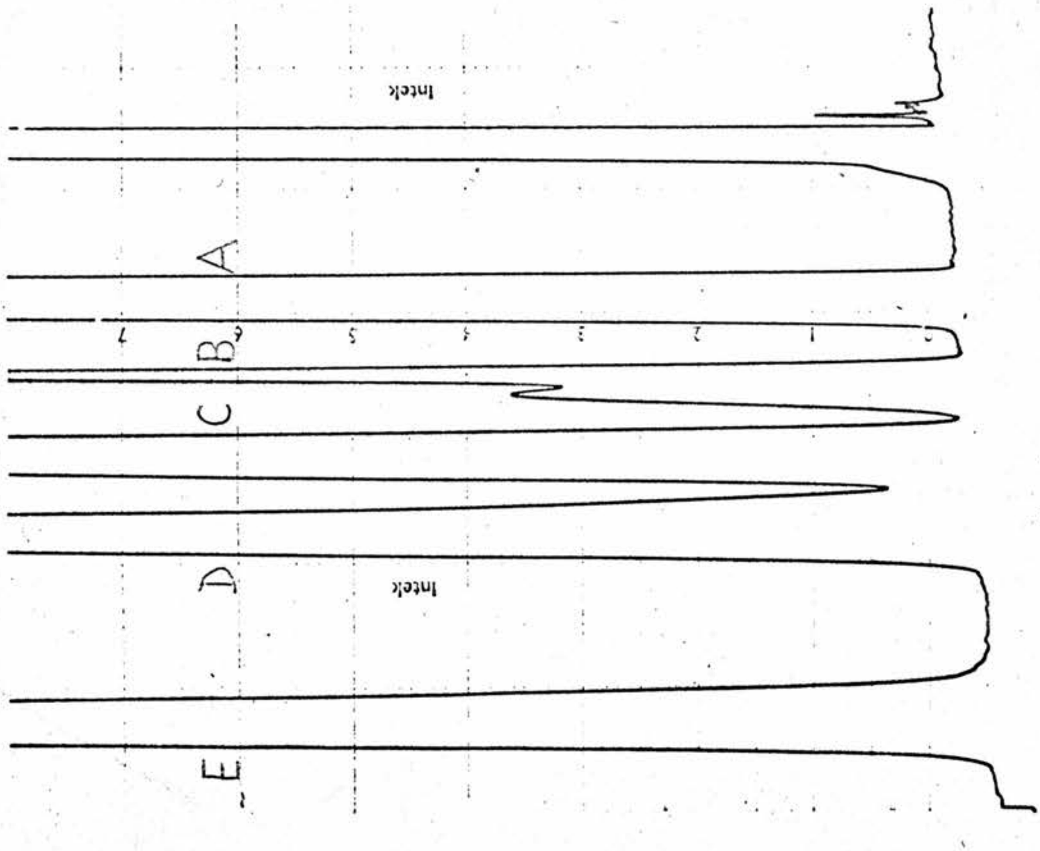


Fig. 9

TABLE 3 : Determination of molecular formulae of highly fluorinated naphthalenes.

Compound	Mass of Parent Peak	Microanalysis Found %C	Found %H	Theoretical %C	Theoretical %H	Hence Molecular Formula	M.Pt.
A	272	43.89	0	44.12	0	$C_{10}F_8$	80 °C
B	200	59.7	1.74	60	2	$C_{10}F_4H_4$	103 °C
C	254	47.5	0.22	47.3	0.40	$C_{10}F_7H$	63 [63-65]
D	218	54.82	1.26	55.05	1.38	$C_{10}F_5H_3$	102 °C
E	236	50.67	0.77	50.85	0.85	$C_{10}F_6H_2$	74 °C

spectra were complex and their complete analysis made even more difficult by the absence of any reports in the literature of NMR of highly fluorinated naphthalenes. When used in conjunction with E.S.R. data, however, sufficient evidence to establish the structural formulae was obtained. Insufficient $C_{10}F_7H$ was obtained to enable the spectrum to be recorded but the excellent agreement of the observed melting point with that reported by Tatlow[93] and the nature of D and E, suggests the structure given in fig. 10.

(a) $\underline{C_{10}F_6H_2}$

The spectrum has three absorptions at τ = 117.2, 136.3 and 148.4. Two of those show an ortho coupling of 7.2 c/s[93a] whereas τ = 136.3 is a singlet. Such a spectrum could only be obtained from either of the three isomeric, β-substituted isomers viz. 2,3H-; 2,6H- and 2,7H-hexafluoronaphthalene. McLachlan spin density calculations (p.117) were performed on the radical cations and the values found for position 2 were, in each case, compared with an 'experimental' spin density. This was calculated from the proton hyperfine splitting (p.74) in the E.S.R. spectrum of $C_{10}F_6H_2^{\ +}$ using (13), with Q^{H}_{CH} = -28 gauss. The agreement was very much better for the radical cation of the 2,6H- isomer (Fig.10) than for the other two isomers.

(b) $\underline{C_{10}F_5H_3}$

Singlet absorptions at τ = 109.6, 122.6 and 138.3 and doublets at τ = 111.0 and 148.3 (J = 5.8 c/s) were obtained. The close similarity and nature of the absorptions at τ = 111.0, 138.3 and 148.3 to those observed for $C_{10}F_6H_2$ suggest

1) That one ring of $C_{10}F_5H_3$ is identically substituted to either ring of $C_{10}F_6H_2$.

2) That the remaining two fluorines are at the α positions. The structure of $C_{10}F_5H_3$ is shown in fig.10.

(c) <u>$C_{10}F_4H_4$</u>

Singlet absorptions at τ = 117.0 and 111.3 were obtained. This suggests the presence of two fluorines meta to one another in both rings. Only two structures are therefore possible viz. 2,4,5,7H- and 1,3,5,7H-tetrafluoronaphthalene. The E.S.R. spectrum (p. 82) of the oxidation product of $C_{10}F_4H_4$, however, could not possibly be assigned to either of those structures both of which would give a spectrum consisting of 4 sets of interacting triplet splittings for the monomer radical cation and 4 sets of interacting quintuplet splittings for the dimeric species. Indeed, it was possible to assign the spectrum only to the dimer radical cation of 2,3,6,7H-tetrafluoronaphthalene (p. 85). Furthermore, the values of τ seem too near each other to be respectively associated with α and β fluorines as seen by comparison with the values for $C_{10}F_6H_2$ and $C_{10}F_5H_3$. For those reasons and because of the nature of C,D and E, the structure shown in fig. 10 was assigned to $C_{10}F_4H_4$. The fluorine NMR spectrum of this compound is thus 'anomalous'.

Neither $C_{10}F_6H_2$, $C_{10}F_5H_3$ nor $C_{10}F_4H_4$ have been previously reported. The large increase in melting point between $C_{10}F_6H_2$ and $C_{10}F_5H_3$ is a classic example of the effect of hydrogen bonding.

5. Chemicals

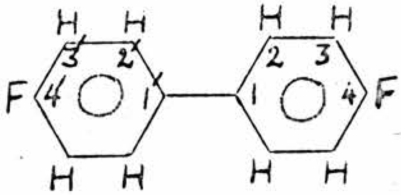
Hexafluorobenzene, octafluorotoluene, decafluorobiphenyl and octafluoronaphthalene were all Imperial Smelting Corporation reagent grade. The other fluorinated naphthalenes used were prepared as in 4 except for 1,2,3,4H-tetrafluoronaphthalene which was a gift from Dr. R. D. Chambers of Durham University. All other chemicals used were reagent grade.

6. E.S.R. Spectrometer

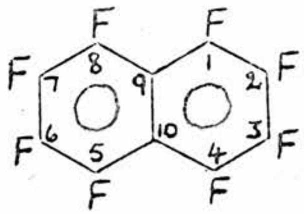
Spectra were recorded on a Decca X3 E.S.R. spectrometer employing 100 kc./sec. magnetic field modulation and phase sensitive detection. The microwave frequency klystron operated at 9270 Mc./sec. so that g = 2.0023 (see chapter III, 10) corresponded to a magnetic field value of ca. 3308 gauss. A wide range of values of microwave power and modulation amplitude could be used. The magnetic field was provided by a Newport Instruments 11"electromagnet of 50 milligauss homogeneity and could be swept through the resonance position at widely variable rates. This field could be measured accurately at 10 gauss intervals by means of a proton resonance meter situated behind the microwave cavity. The cavity operated in the TE 102 mode.

For low temperature studies the Decca variable temperature accessory MW235 was employed. The temperature was varied by passing nitrogen gas at different flow rates through the metal coil, immersed in liq. air, of a heat exchanger and then through an evacuated Dewar vessel inserted into the cavity. Sample tubes (see 2,3) were inserted into this Dewar stem. The temperature at the sample was measured by a platinum resistance thermometer and fine control of the temperature was obtained by electronic means. With this device temperatures accurate to $\pm 2^{o}$ were obtained.

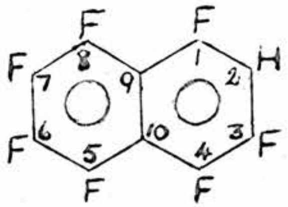
For sulphuric and nitric acid studies (see 2) the standard quartz flat cell was used and for other solvents of high dielectric loss e.g. CH_3NO_2, CH_2Cl_2 (see 1,2) sample tubes having internal diameters less than 2mm. were usually employed.



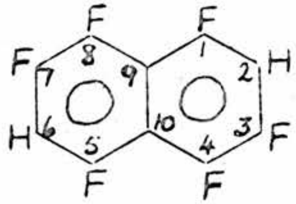
$C_{12}F_2H_8$



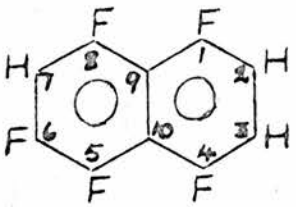
$C_{10}F_8$



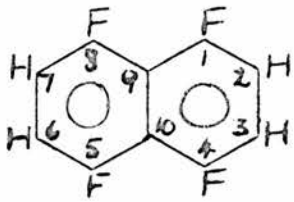
$C_{10}F_7H$



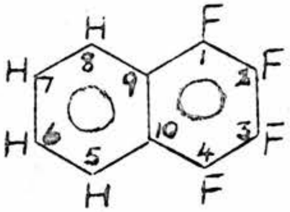
$C_{10}F_6H_2$



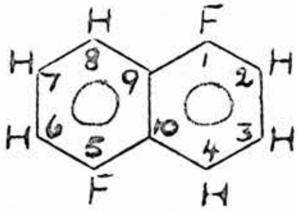
$C_{10}F_5H_3$



$C_{10}F_4H_4$



iso$C_{10}F_4H_4$



$C_{10}F_2H_6$

Fig. 10

CHAPTER III : RESULTS AND DISCUSSION

A. Experimental Results

The results obtained with the $SbCl_5$-SO_2 technique, discussed in chapter II, are now presented. All hyperfine splittings and g values were measured by reference to a solution of Fremy's salt as detailed in 10.

1. Octafluoronaphthalene, $C_{10}F_8$ (Fig. 10)

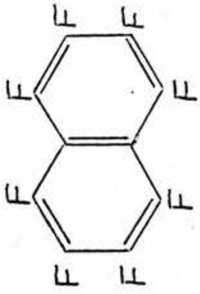
A 10^{-3}M solution of octafluoronaphthalene in SO_2 reacted with the $SbCl_5$ at -80° to form a red-brown solid at the bottom of sample tube C (Fig.7). On shaking, this dissolved forming a faint brown solution which gave an 11 line E.S.R. signal (Fig.11) when examined at room temperature. This signal slowly increased in strength, reaching its maximum intensity 12 hrs. after reaction when the colour was light brown. Ten more lines were observed when the wings of the spectrum were examined under high gain conditions (Fig.12).

A line diagram (Fig.13) representing two sets of interacting quintuplet splittings with

$a_1 = 19.01 \pm 0.05$ gauss

and $a_2 = 4.78 \pm 0.01$ gauss,

so that $a_1/a_2 \simeq 4$, exactly reproduces the positions of the observed 21 lines. This spectrum was assigned to the monomer radical cation of octafluoronaphthalene with a_1, a_2 the α, β fluorine



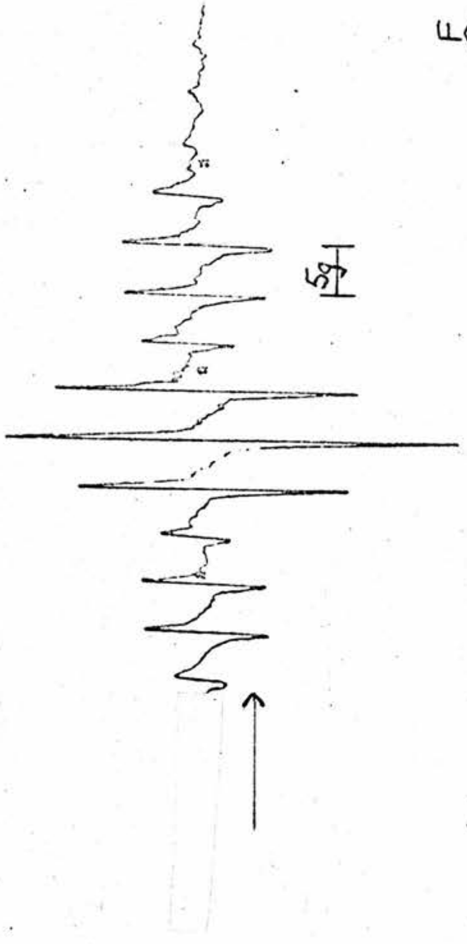


Fig. 11

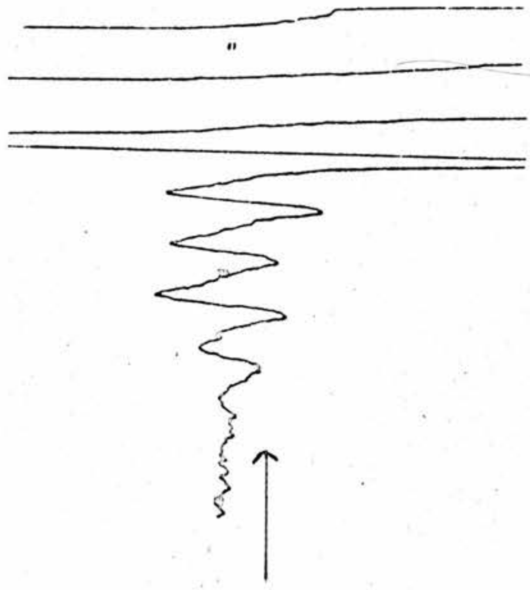


Fig. 12

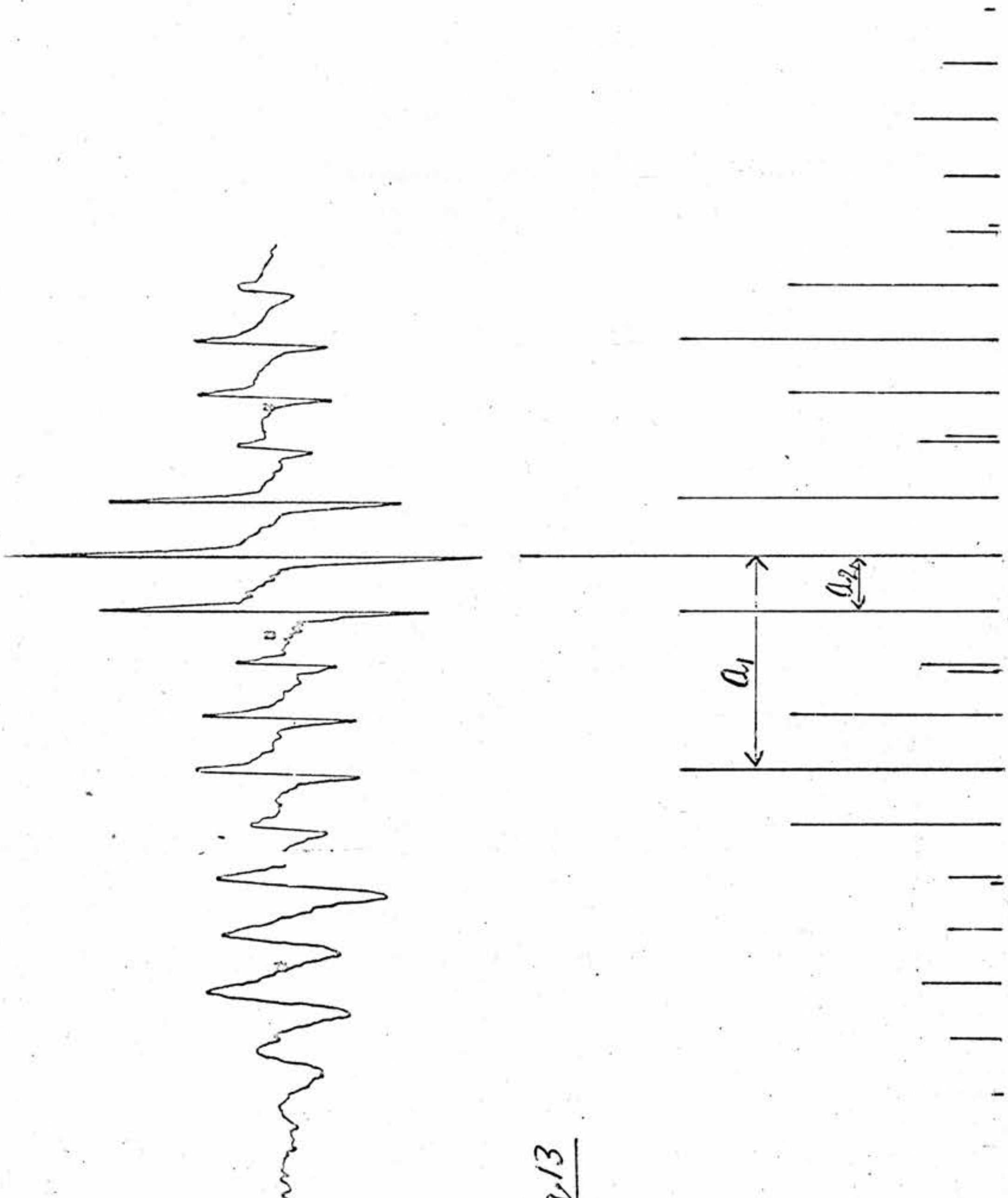


Fig. 13

splittings respectively. As the quantity a_1-4a_2 is less than their width, four of the observed lines are formed from superpositions of two Lorentzians and hence 21 lines, instead of 25, are obtained. Owing to pronounced linewidth variations, the relative intensities are in poor agreement with those in the line diagram. Similar variations have been reported in other fluorinated species.[50,66] The solution was diluted until the lines did not narrow and the widths and relative intensities recorded at slow magnetic field scans at a level of microwave power to ensure no signal saturation. This data is presented in table 7, p.103.

When examined at -30°, the same solution gave another signal superimposed on the first. This relatively weak signal is narrow in extent and contains a large number of lines. It is shown in Fig.14 under high gain conditions, but no assignment was attempted.

On further standing at room temperature, the solution slowly became dark red and a broad, superimposed signal (ca. 0.5 gauss in width) increased in intensity as the $C_{10}F_8^+$ signal decreased. Eventually a green diamagnetic solution was formed.

The inert nature of fluorocarbons[54] to electrophilic attack is well-understood and may account for the slow increase in radical concentration in contrast to the hydrogen substituted species discussed below where a more intense signal is initially obtained and increases only slightly with time.

The remarkable stability of this species and of other highly

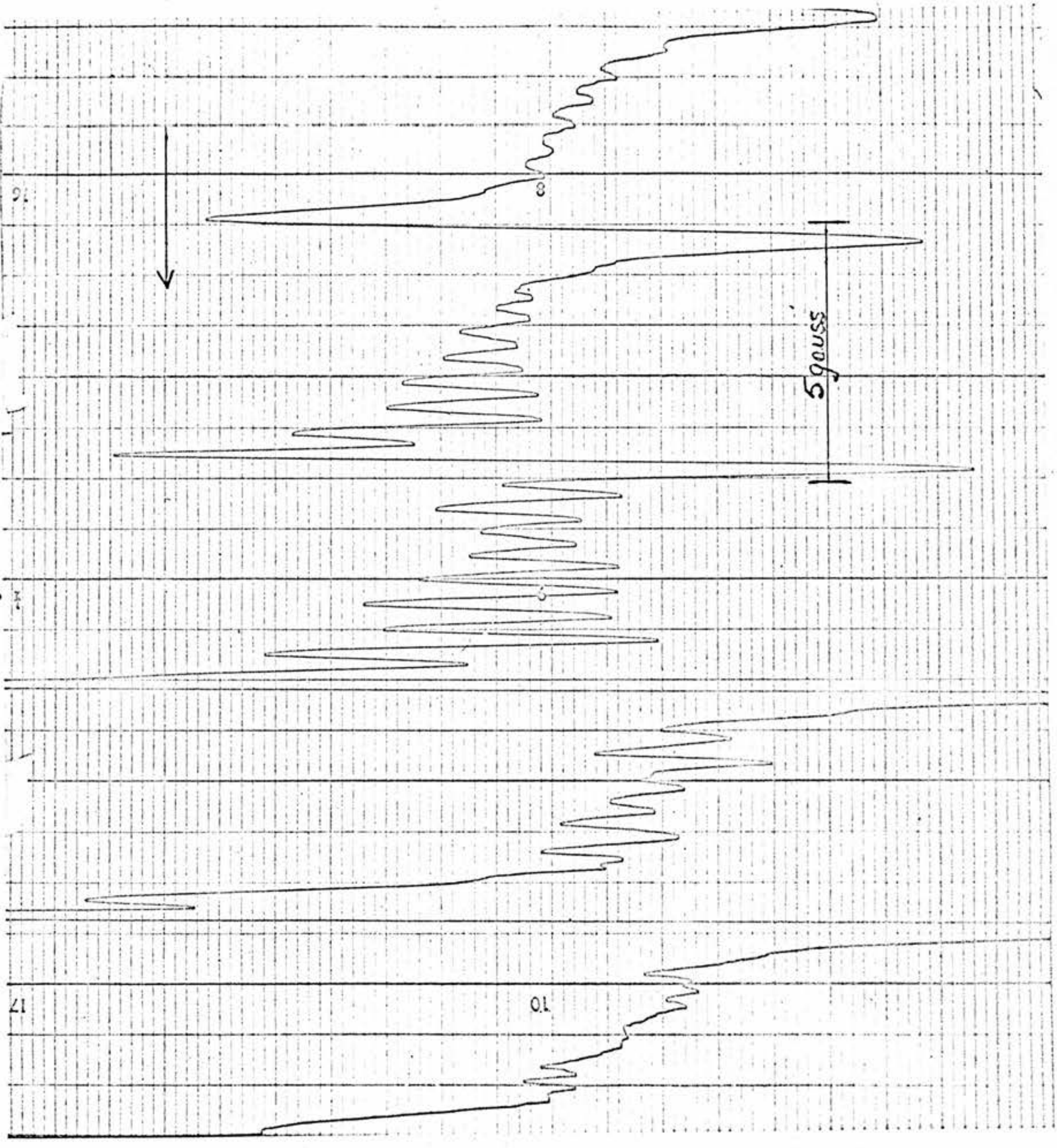


Fig. 14

fluorinated cations discussed in this section probably results from enhanced stability of the positive charge by the strongly electron-withdrawing fluorines. Much less-highly fluorinated naphthalene cations have comparable stability (p. 23). The unsubstituted species, by contrast, forms only the dimer cation, stable at -70°. That $C_{10}F_8^{+}$ forms in SO_2 and not in CH_2Cl_2 (chapter II, 2) with the same Lewis acid is further evidence for the importance of the ion-solvating medium in cation formation.

Bazhin et alia[65] later reported a study of $C_{10}F_8^{+}$ in the new system SbF_5 - $(CH_3O)_2SO_2$ (p. 44) but their resolution was poorer than the author's and their analysis incorrect as they observed only 17 of the 21 lines.

2. Hexafluorobenzene, C_6F_6

On reaction with the $SbCl_5$ at -80°, a 10^{-3}M solution of C_6F_6 in SO_2 formed a light green solution which was examined at 5° temperature intervals over a wide range of dilutions. No signals were detected. The extra muros solution in C (Fig.7) rapidly changed to pale-yellow after warming-up for about five minutes.

3. Octafluorotoluene, C_7F_8 and decafluorobiphenyl, $C_{12}F_{10}$

Solutions of C_7F_8 and $C_{12}F_{10}$, prepared as in 2 underwent no colour change and gave no E.S.R. signals. Fischer[58] also found $C_{12}F_{10}$ unreactive but mono and difluorobiphenyls formed radical cations in $SbCl_5$-CH_2Cl_2 (p. 23).

Note:

The monomer radical cations of anthracene, tetracene and other fused-ring hydrocarbons are prepared relatively easily whereas those of naphthalene, benzene or biphenyl do not form in solution under the same conditions. Our success with perfluoronaphthalene thus renders it highly likely that perfluoroanthracene, perfluorotetracene etc. will also form radical cations in $SbCl_5$-SO_2. In fact, this system may well be the fluorocarbon analogue of Lewis and Singer's $SbCl_5$-CH_2Cl_2 technique.[44] Tatlow has prepared perfluoroanthracene[94] but we were unable to obtain it from him or from any other source. In view of this, and because of their smaller size and greater amenability to theoretical studies, the preparation of the fluorinated naphthalenes described in chapter II was undertaken.

4. 2H-heptafluoronaphthalene, $C_{10}F_7H$ (Fig.10)

A 10^{-3}M solution of $C_{10}F_7H$ in SO_2 reacted with the $SbCl_5$ forming a red solid similar to that seen for $C_{10}F_8$ and a brilliant green solution. No signals were observed at temperatures other than room temperature. At this temperature a moderately strong signal containing many lines (Fig.15) was obtained. In contrast to $C_{10}F_8^+$, the signal strength did not increase with time and began to decrease $1\frac{1}{2}$ hrs. after reaction, disappearing entirely after 2 hrs.

The sample was diluted until the lines narrowed no further

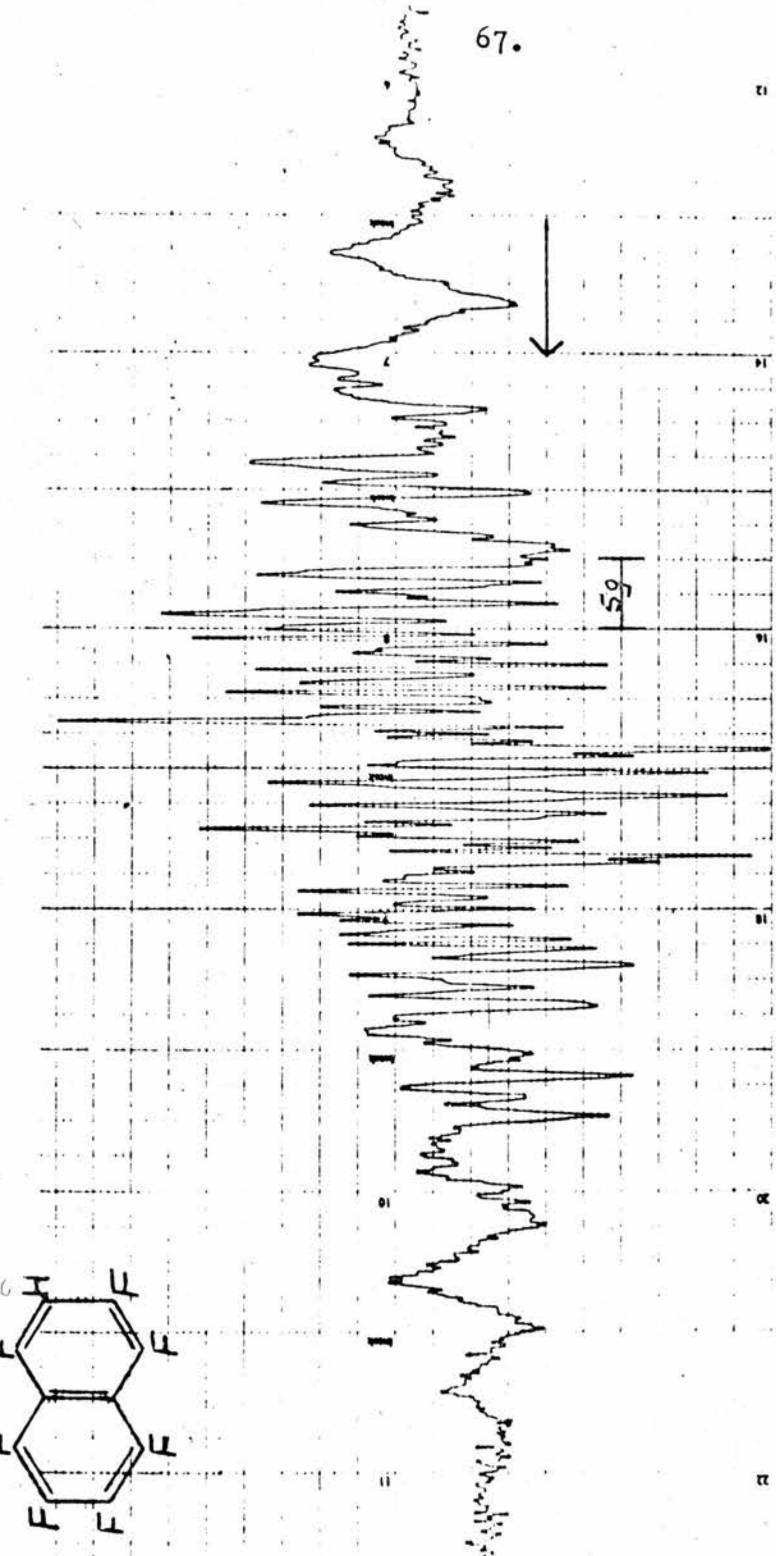


Fig. 15

but full resolution of the wings was not obtained, probably as a result of the linewidth effects observed in $C_{10}F_8^+$ and the close proximity of the lines. Fig. 16 shows half the spectrum of such a dilute sample at a slower field scan. The signal was also studied under grossly overmodulated conditions (Fig.17) to eliminate the smaller splittings and so facilitate obtaining the larger ones. No unequivocal analysis was, however, possible.

The substitution of one β-fluorine in $C_{10}F_8^+$ by hydrogen to give $C_{10}F_7H^+$ was expected to result in only slight spin perturbation at the α-positions and also to give a quintuplet splitting for the latter. Only a small perturbation at the α positions was found for the cation of the dihydro compound, $C_{10}F_6H_2$(p.74).

<u>5. 2,6H - hexafluoronaphthalene, $C_{10}F_6H_2$</u>

A 10^{-3}M solution of $C_{10}F_6H_2$ (Fig.10) reacted with the $SbCl_5$ to form a red solid and green solution which gave a 13 line spectrum at room temperature (Fig.18). Two additional outside lines were seen under higher gain conditions (Fig.19) and a slower field scan clearly showed the structure seen on the centre line to be a very small partially-resolved triplet splitting (Fig.20).

A line diagram representing interaction of a quintuplet with a triplet splitting is shown (Fig.21) and exactly reproduces the positions of the observed 15 lines with

$a_1 = 17.89 \pm 0.10$ gauss

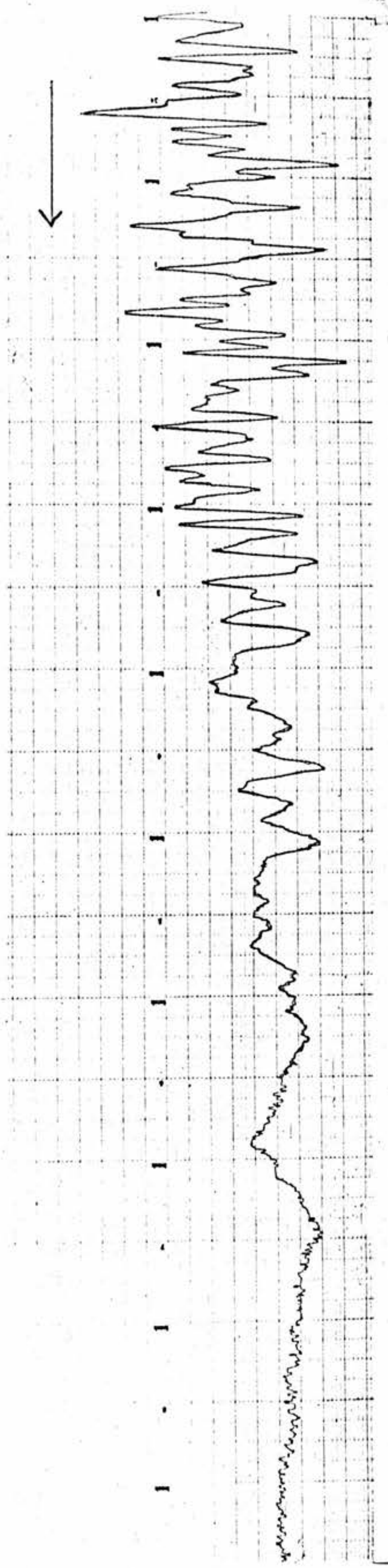


Fig. 16

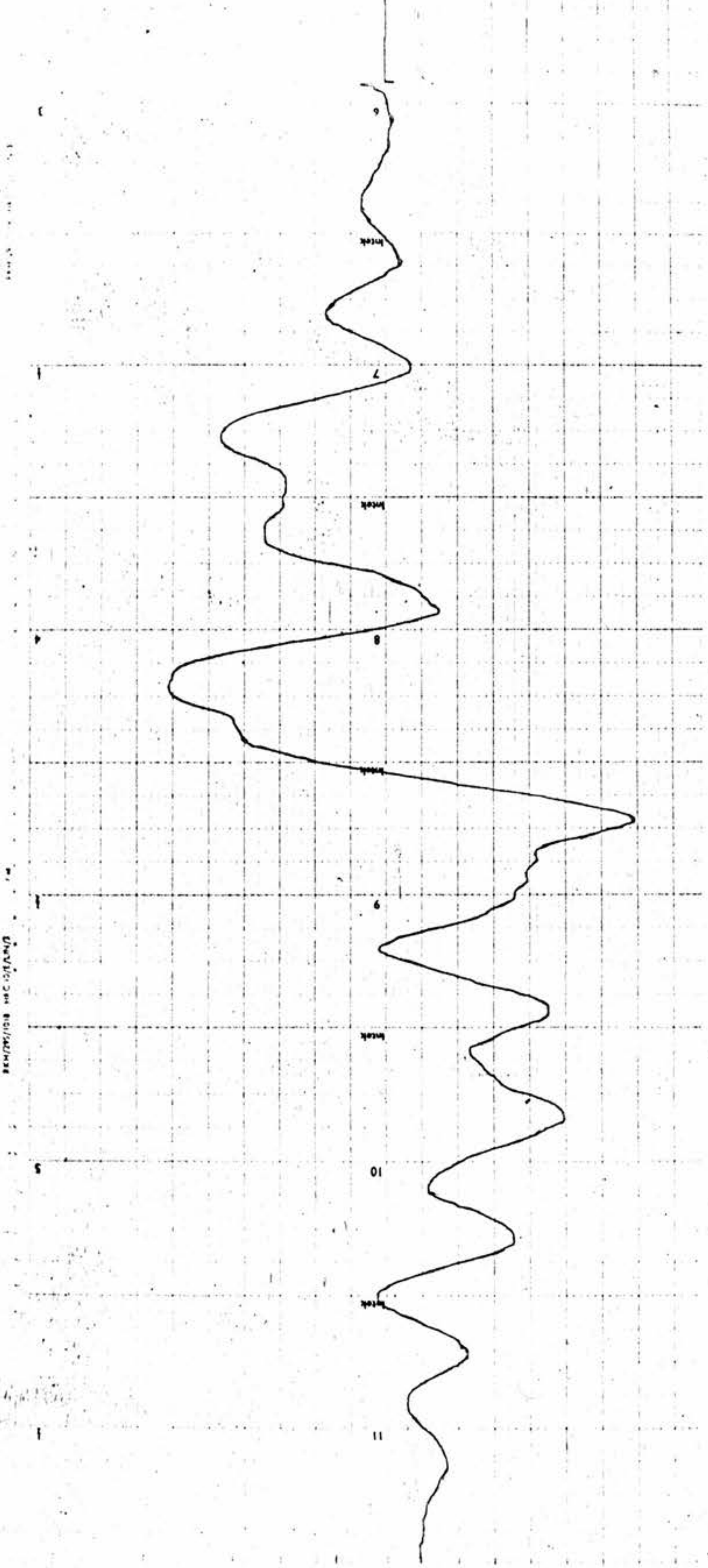


Fig. 17

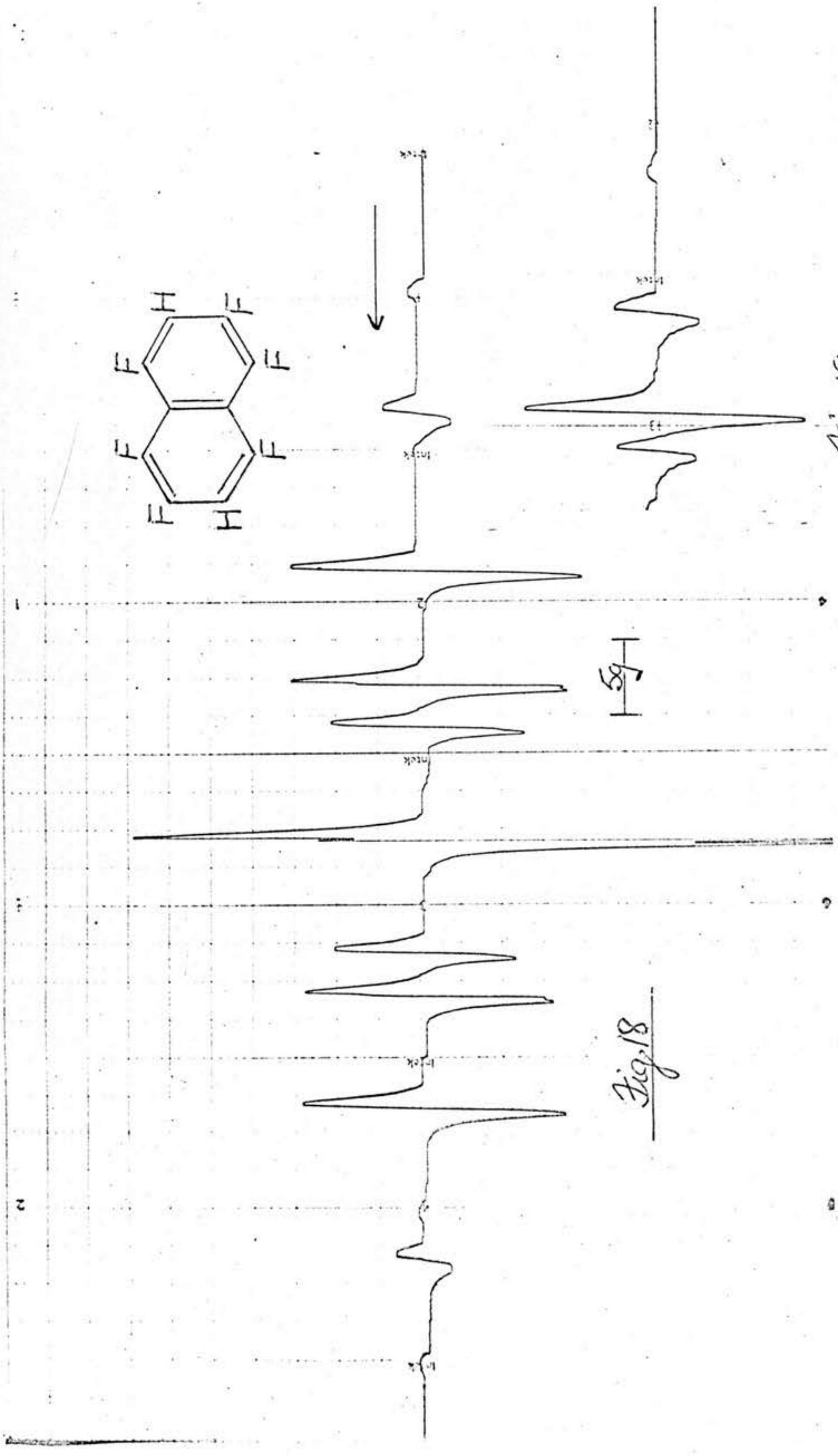


Fig.18

Fig.19

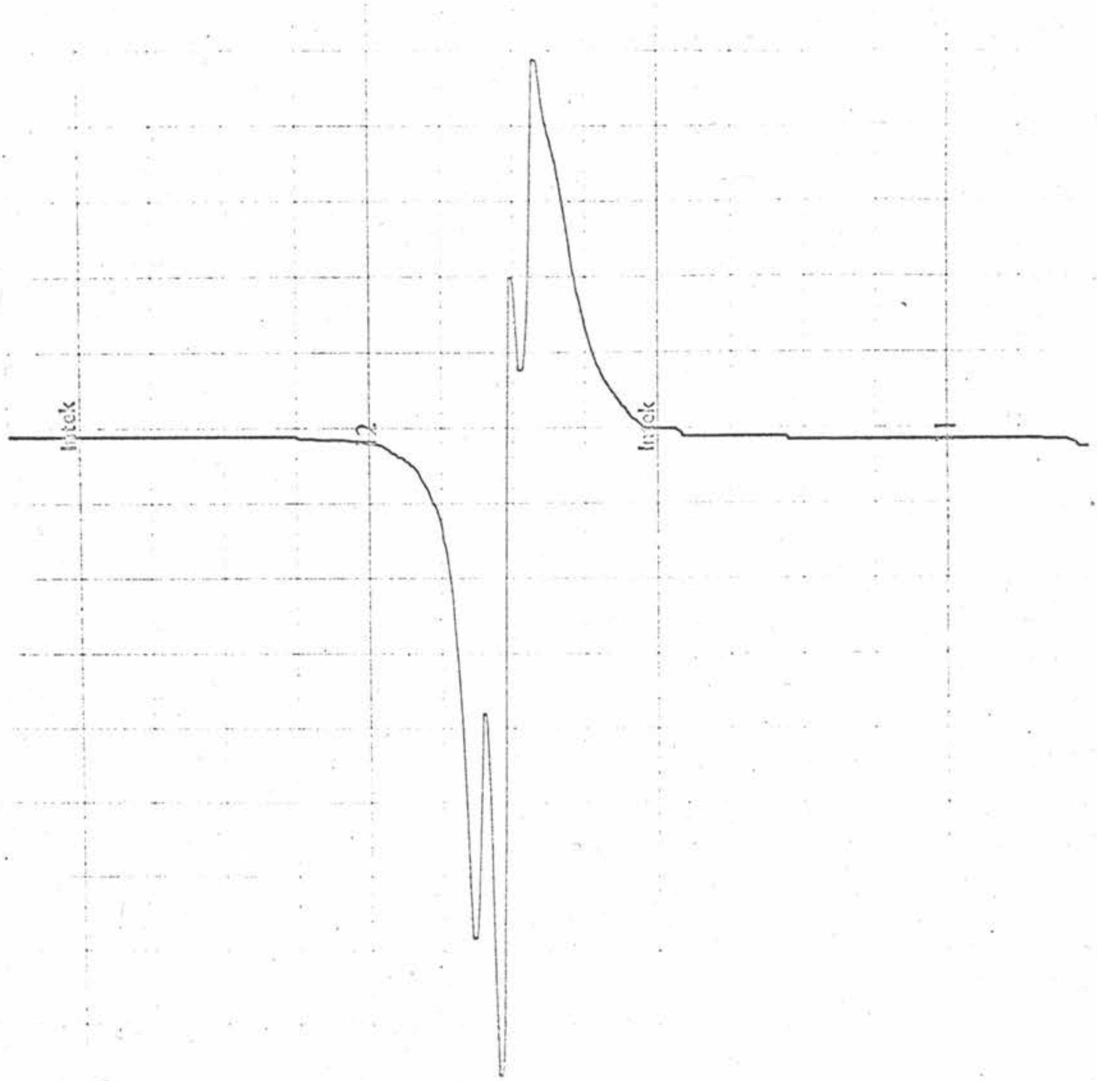
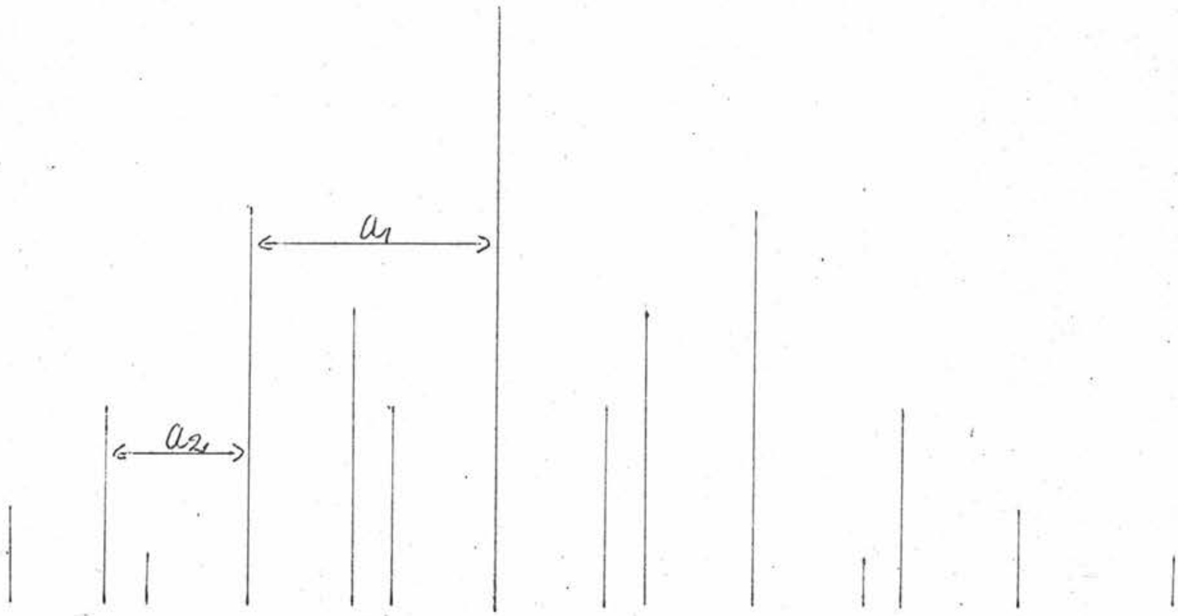


Fig 20

Fig. 21



and $a_2 = 10.29 \pm 0.10$ gauss

Those splittings were respectively assigned to the four α fluorines and to the equivalent 3,7 fluorines of the radical cation of $C_{10}F_6H_2$. The presence of a quintuplet splitting instead of the two sets of interacting triplets expected by symmetry, and the magnitude of a_1, indicates only slight α spin perturbation from the perfluorinated cation. This is by no means true for the β positions where the fluorine splitting has more than doubled leaving a much smaller spin density at the 2 and 6 positions. The resulting proton triplet splitting, a_H, is less than the linewidths (250-700 milligauss) except for the relatively narrow centre line, and has been measured as accurately as possible using a slow field scan under conditions of optimum dilution.

$a_H = 0.29 \pm 0.02$ gauss

This splitting is much smaller than the β-proton splitting in the naphthalene anion[95] where $a_H = 1.83$ gauss. The large spin change at the 2,6 positions in progressing from $C_{10}F_6H_2^+$ to $C_{10}F_8^+$ contrasts with the observations of others on fluorinated anions[57,73] where little change was found at a position when hydrogen was substituted by fluorine. Such small changes have been observed by Fischer for the cations of 1,5-difluoronaphthalene, 4- fluorobiphenyl and 4,4'-difluorobiphenyl.

The signal intensity increased only slightly over two hours and then slowly decreased but was still strong after five hours when a black precipitate slowly began to form on the bottom of the sample tube. When shaken up, this formed a suspension and a large broad signal (ca. 3 gauss in width) was superimposed on the original. Howarth and Fraenkel[96] have found that aromatic hydrocarbons also form black paramagnetic complexes with $SbCl_5$ in CH_2Cl_2.

Pronounced linewidth variations and a correspondingly poor agreement between the relative intensities and those in the line diagram were again observed. In particular, the intensities of the lines forming any of the four fluorine triplets, other than the centre, were found to be in the ratio 1 : 1.5 : 0.2 instead of the theoretical 1 : 2 : 1.

Neither increased radical stability nor resolution was obtained from studies of this species, or of any of the others discussed below, at lower temperatures. Similar behaviour for the less highly-fluorinated cations was reported[58] by Fischer and Zimmermann. The signal from $C_{10}F_6H_2^+$ was found to be proportionately the most intense of all those discussed in this chapter.

6. 2,3,7H - pentafluoronaphthalene, $C_{10}F_5H_3$ (Fig.10)

A 10^{-3}M solution of $C_{10}F_5H_3$ also formed a green solution on reaction. The signal observed at room temperature slowly increased over 20 minutes and then remained constant for 2 hrs. but was appreciably weaker than that of $C_{10}F_6H_2^+$. After this time, specks of black paramagnetic material began to appear and the signal slowly began to decay but was still quite strong 7 hrs.

after reaction.

The spectrum (Fig.22)shows 35 lines of about the same width with further resolution at the centre. No more lines were seen when the wings were examined under high gain conditions. A line diagram representing interaction between a quintuplet a_1 and three doublet splittings a_2, a_3, a_4 is shown (Fig.23) and adequately accounts for the line positions with

$a_1 = 16.1 \pm 0.2$ gauss

$a_2 = 7.11 \pm 0.1$ gauss

$a_3 = 4.19 \pm 0.15$ gauss

and $a_4 = 2.18 \pm 0.15$ gauss.

The distance between the fourth and fifth of each set of 8 lines formed by splitting of each line of the quintuplet is less than their widths so that 35 lines and not 40 are observed. This can be clearly seen in fig. 24 which shows one half of the spectrum at a much slower field scan with the overlapped member of the outside set indicated by a broken line. The splittings a_1, a_2 were respectively assigned to the four α fluorines and to the single β fluorine of the radical cation of $C_{10}F_5H_3$. The splittings a_3, a_4 were assigned to protons 2,3 respectively on the basis of McLachlan spin density calculations (p.122) which predicted the spin densities at those positions to be approximately in the ratio a_3/a_4. The spin density predicted at position 7 was such that when a value of $Q^H_{CH} = -28$ gauss (p.14) is used, the resulting hyperfine splitting is less than the linewidth (ca. 950 milligauss).

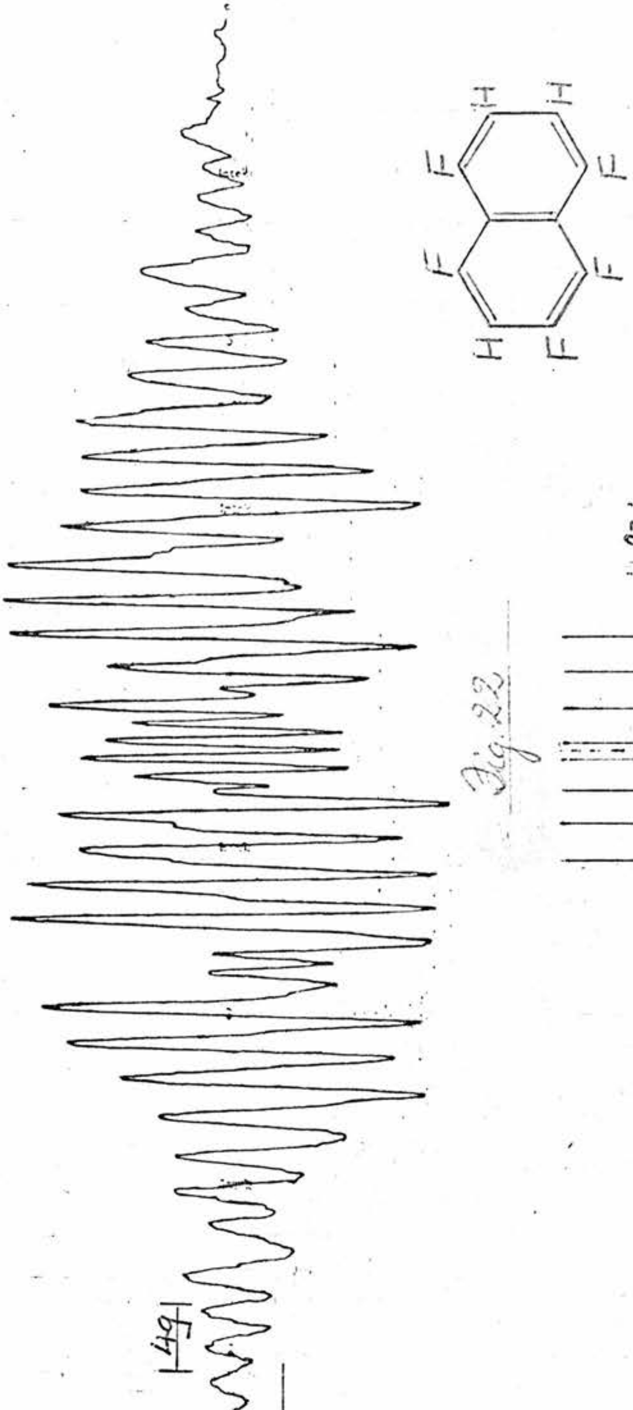


Fig. 22

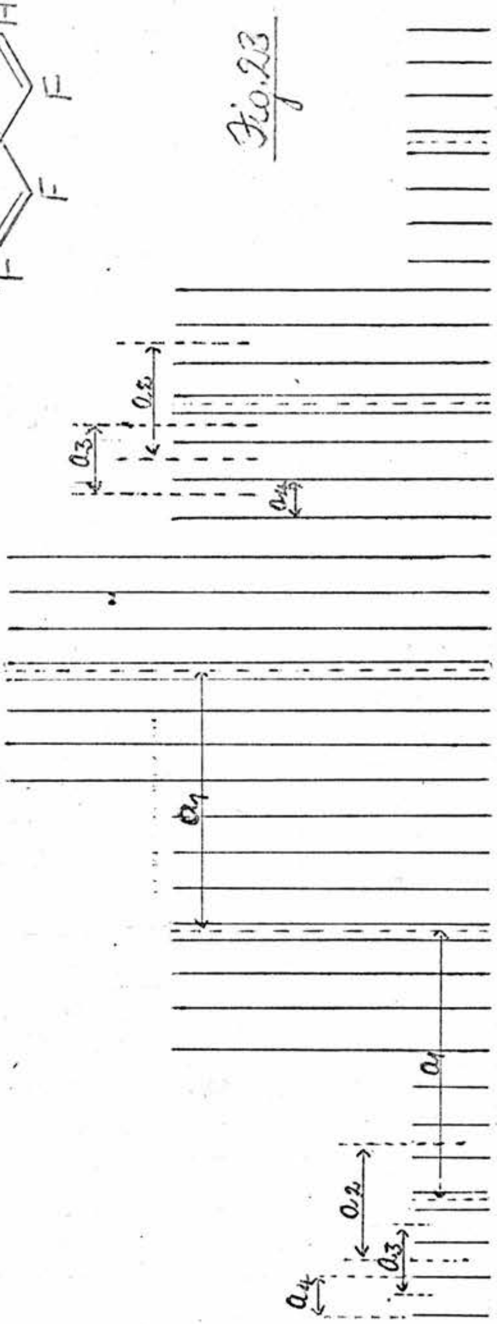


Fig. 23

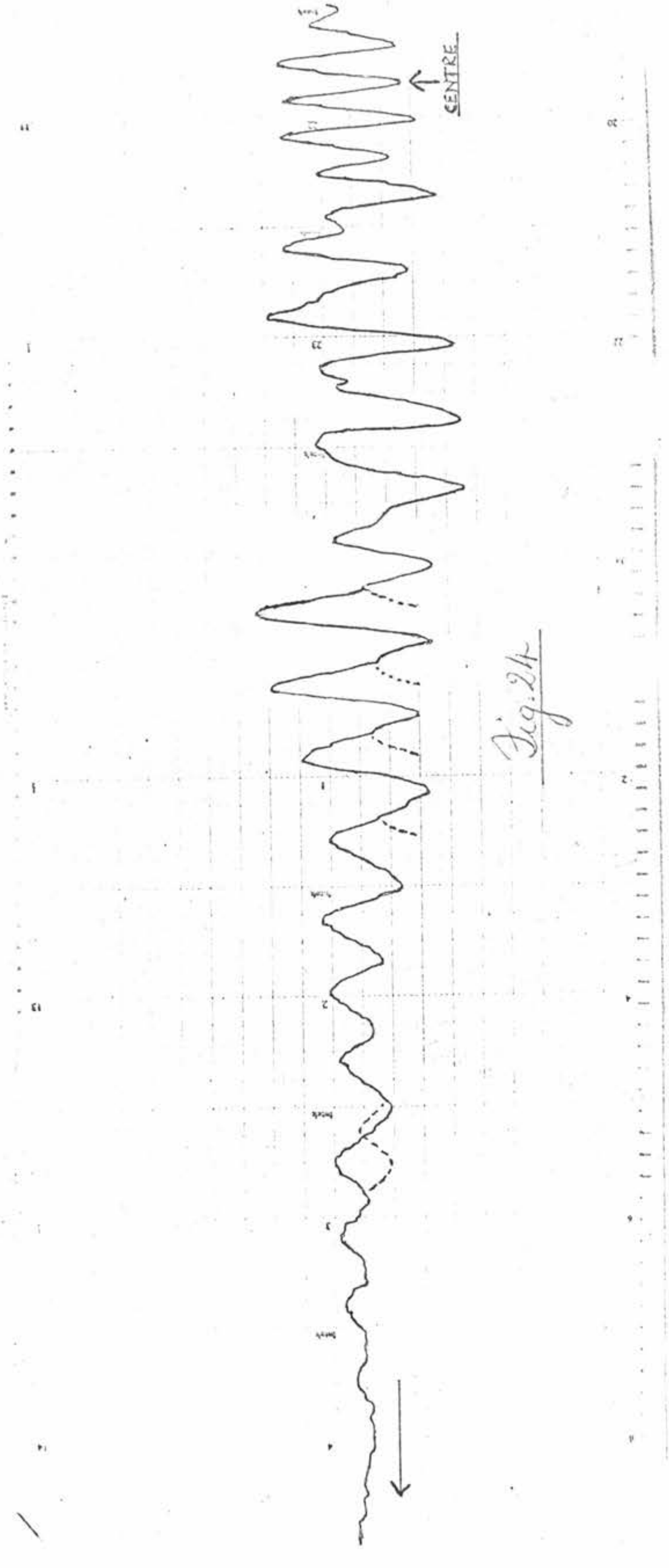


Fig. 21

This splitting was therefore unobserved.

The relative intensities of the observed lines are in poor agreement with those in the line diagram. This arises from the fact that the quintuplet splitting is composed of a doublet splitting, a_1^1, and a quadruplet splitting, a_1^2, as shown in fig. 25. The difference between those splittings is just less than the linewidth for all but the centre three lines which are slightly narrower and are partially resolved into doublets (Fig.22). The second lines of the quintuplet are formed by superpositions of two lines of relative intensities 1 :3 and this can also be seen in fig. 24 where the components of relative intensity unity are shown as broken lines. The outside lines of the quintuplet, and therefore the eight outside lines on each side of the spectrum, are by contrast non-superposed lines. This experimental evidence for a slight perturbation from spin equivalence at the α positions is also supported by McLachlan spin density calculations (p.122) which predict slightly different densities at positions 1,4,8 and a larger spin density at position 5. The doublet splitting $a_1^1 = 16.8 \pm 0.2$ gauss is therefore assigned to position 5 and the quadruplet splitting $a_1^2 = a_1 = 16.1 \pm 0.2$ gauss to positions 1, 4,8 equivalent to within the width of all the lines in the spectrum.

The magnitudes of a_1^1, a_1^2 and the α fluorine splitting in $C_{10}F_6H_2^+$ (p. 73) indicate a gradual decrease in the α fluorine splittings as $C_{10}F_8$ becomes progressively substituted at the β positions. Although the β fluorine splitting in $C_{10}F_5H_3^+$ is

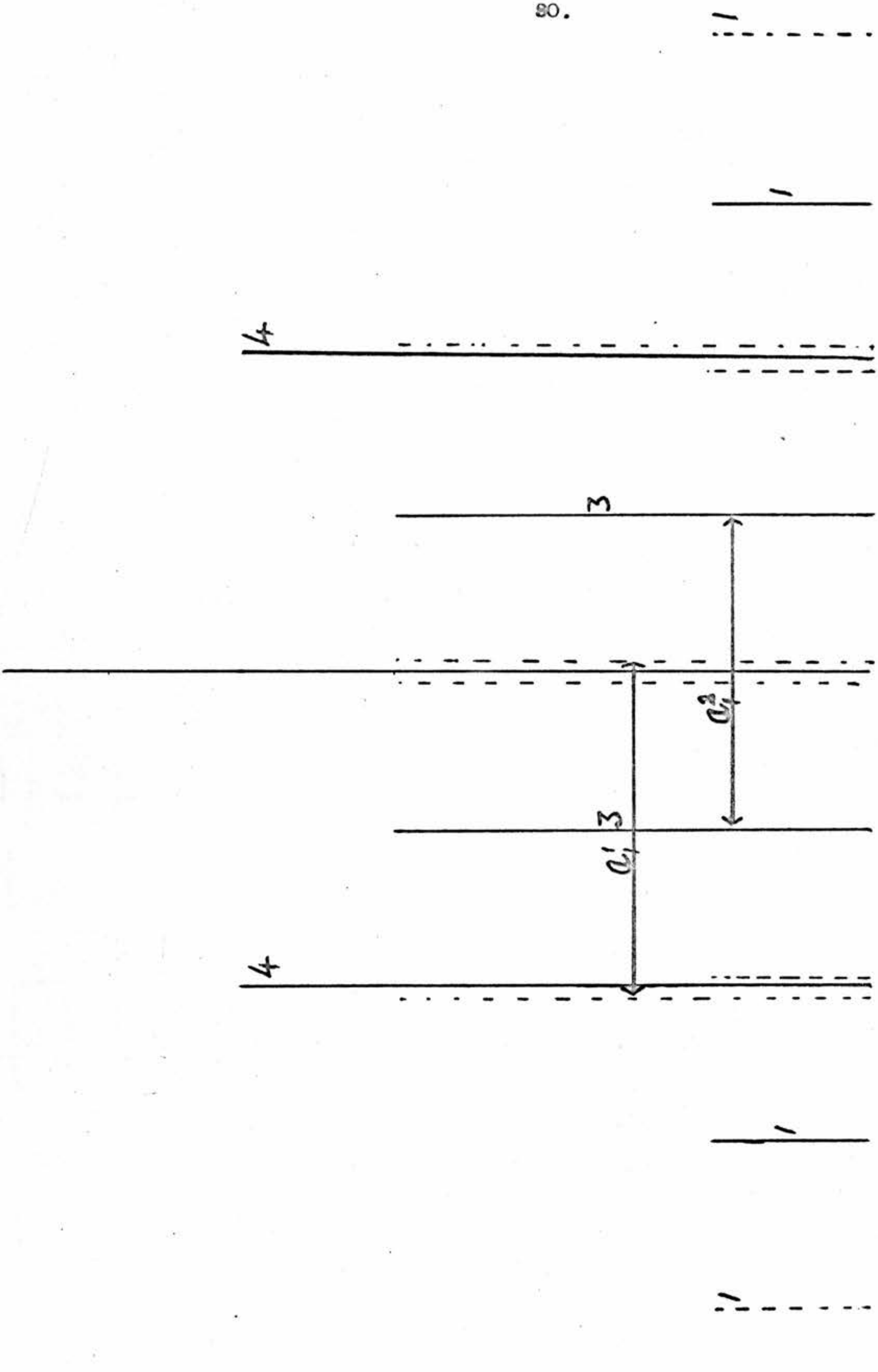


Fig. 25

smaller than the 10.3 gauss observed for $C_{10}F_6H_2^+$, it is still larger than the corresponding value of 4.7 observed for $C_{10}F_8^+$ and the electron-withdrawing effect of this fluorine atom is sufficiently large to cause the splitting from position 8 to be less than the linewidth. The splittings from protons 2,3 are much larger than the β proton splitting of 0.29 observed for $C_{10}F_6H_2^+$ and that of proton 3 is comparable to the β proton splitting of 1.83 gauss in the naphthalene negative ion.[95]

7. 2,3,6,7H - tetrafluoronaphthalene, $C_{10}F_4H_4$ (Fig.10)

A 10^{-3}M solution of $C_{10}F_4H_4$ in SO_2 formed the characteristic red solid and green solution on reaction and gave a 29 line spectrum when examined at room temperature (Fig.26). Four additional lines were seen under high gain conditions (Fig.27). The spectrum is fully symmetrical and Fig. 28 shows half of it at a slower field scan where the lines are seen to have approximately the same width (950-1050 milligauss) and to be equally spaced. In the absence of any prominent linewidth variations, therefore, the correct line analysis must reproduce the observed intensities as well as the line positions. The experimental intensities of all lines relative to the centre line were calculated.

This 33 line spectrum could not be ascribed to the monomer radical cation of $C_{10}F_4H_4$ where the maximum possible number of lines is 25. Fig. 29 is a line diagram for the two sets of inter-

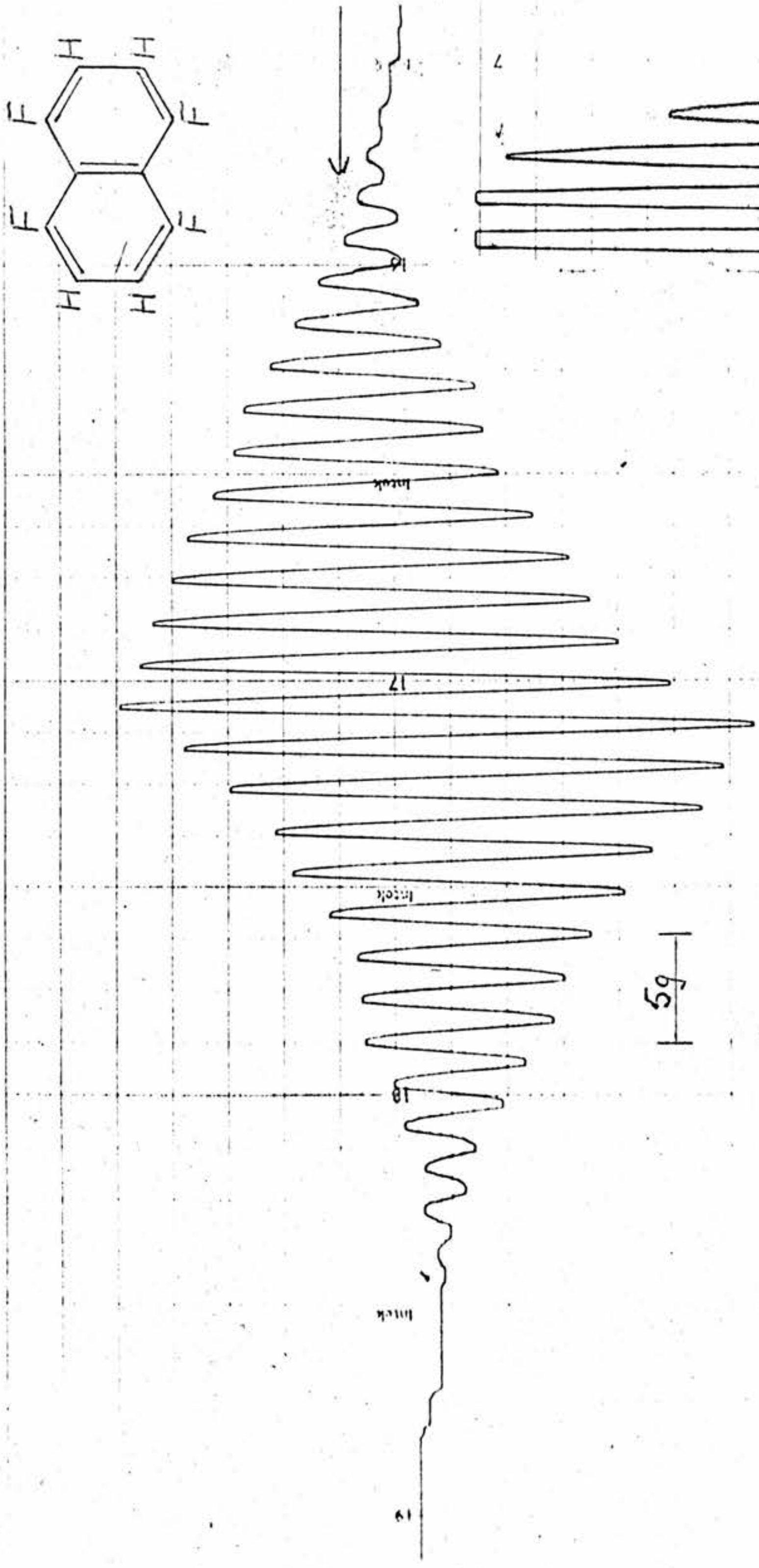


Fig. 26

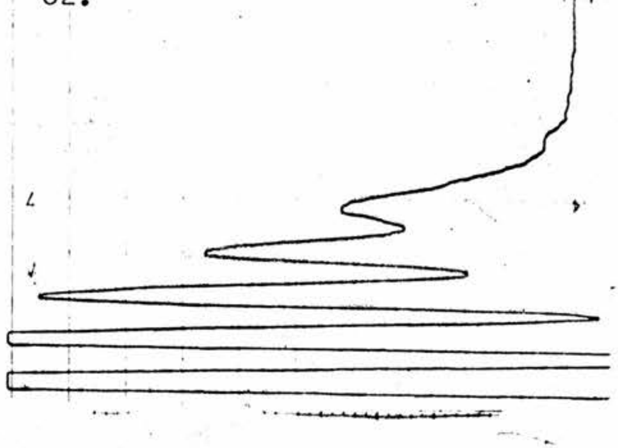


Fig. 27

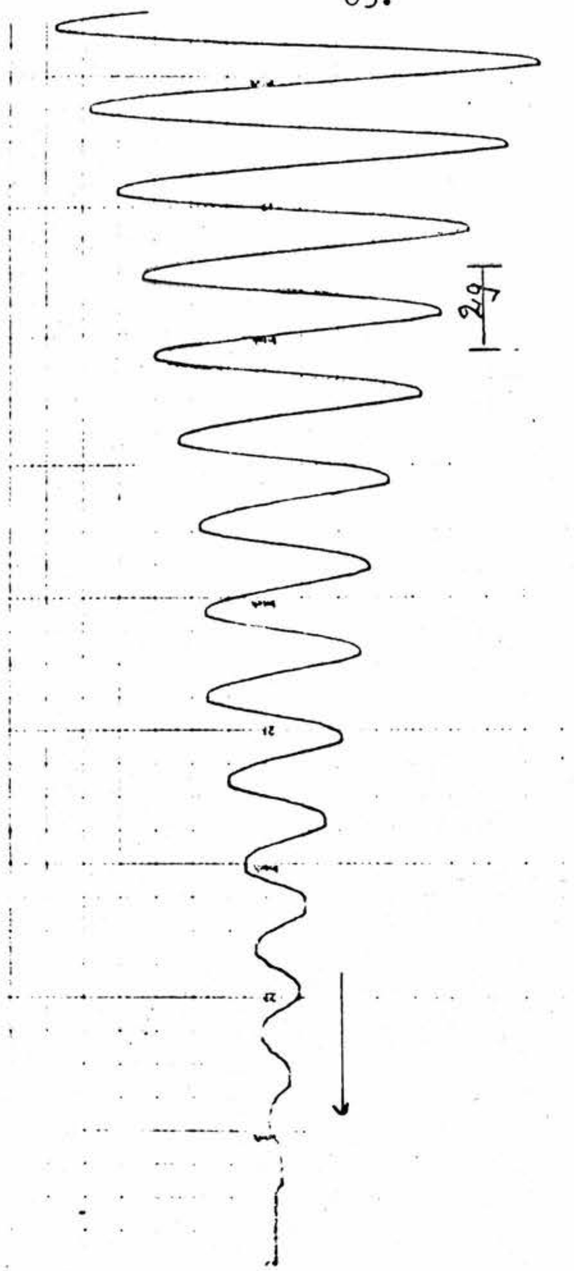


Fig. 28

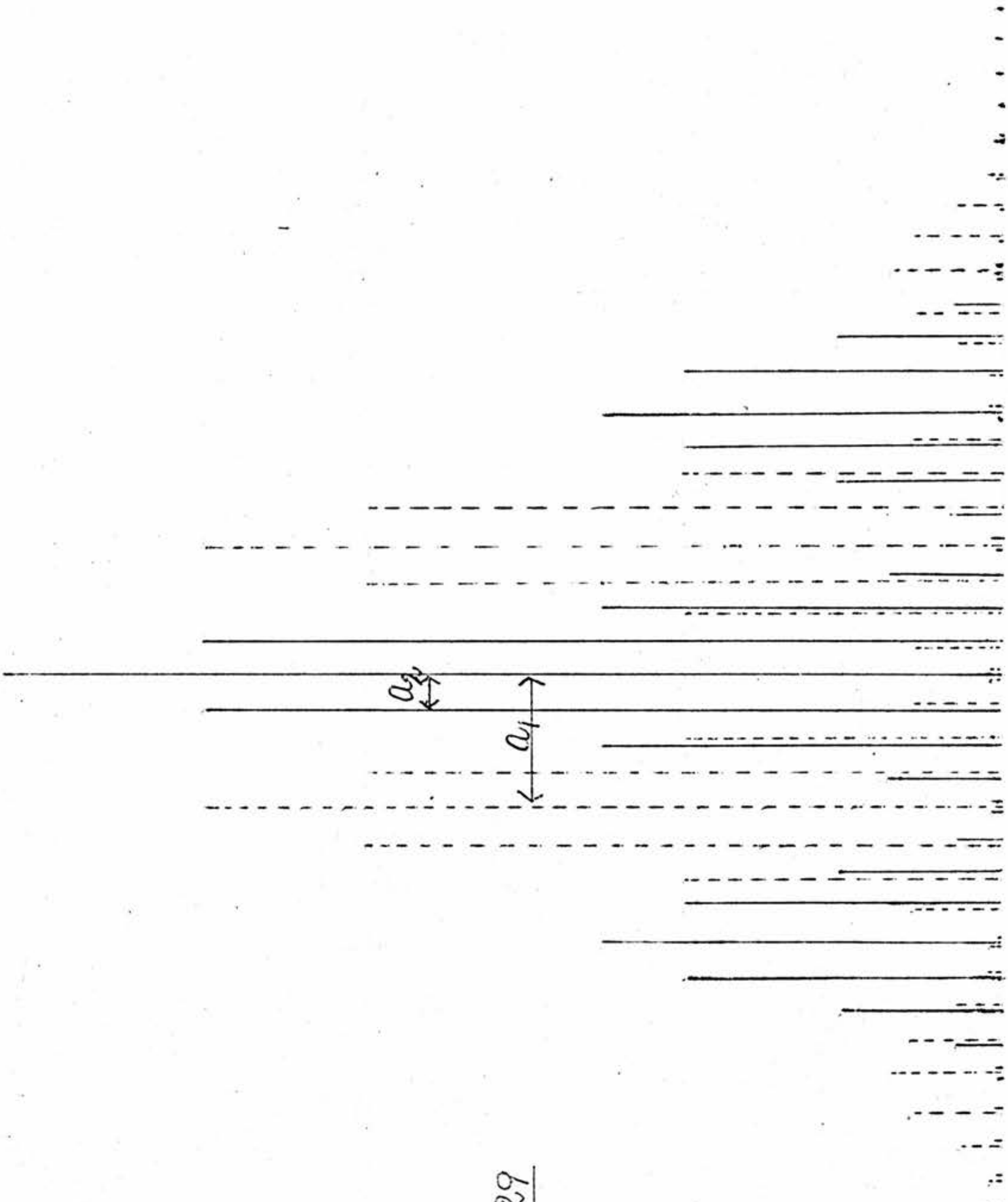


Fig. 29

acting nine line splittings expected from a dimeric species. With $a_1 = 4a_2$, each line in the diagram is doubly superimposed except for the centre line of each nontuplet which is a triple superimposition and the four outside lines on either side which are non-superimposed. A total of 41 lines is obtained. The intensities of those lines relative to the centre line have also been calculated and are compared with experiment in table 4. The agreement is very good. Both line diagram and table show that the 4 outside lines on either side are too small to observe being 1/100 of less the intensity of the centre line and hence 33, instead of 41 lines, are obtained. Under high gain conditions, modulation broadening or signal saturation limit the relative line intensities that may be observed. No other ratio of a_1/a_2 will give the correct number of equally spaced lines in the observed intensity ratio e.g. the relative intensities for $a_1 = 5a_2$ and $a_1 = 3a_2$ are also given in table 4 and are seen to be in poorer agreement with experiment.

The spectrum was therefore ascribed to the dimer cation of $C_{10}F_4H_4$ with

$$a_1 = a_F = 8.08 \pm 0.1 \text{ gauss},$$

$$a_2 = a_H = 2.02 \pm 0.05 \text{ gauss}$$

$$\text{and } a_1/a_2 = 4.$$

Other workers have found the splittings in monomer radical cations to be exactly twice those of the corresponding dimers.[44,97] The splittings in the hypothetical monomer cation are therefore

$a_F = 16.16$ gauss

and $a_H = 4.04$ gauss

and, as in $C_{10}F_8^+$ (p.60), only 21 lines would be observed. The small amount of spin perturbation with respect to the naphthalene anion that Fischer[58] found for the 1,5-difluoronaphthalene cation (p.74) contrasts with the magnitude of a_H which shows an increase of two in β spin density for this hypothetical species.

The signal intensity slowly increased over 3 hrs. and then began to decrease but quite strong signals were still obtained 6 hrs. after reaction. Black specks of paramagnetic material slowly began to form and a superimposed signal appeared 2 hrs. after reaction.

8. 5,6,7,8H - tetrafluoronaphthalene, iso. $C_{10}F_4H_4$ (Fig. 10)

A 10^{-3}M solution of iso. $C_{10}F_4H_4$ in SO_2 also formed a red solid and green solution when reacted with the $SbCl_5$. The signal obtained increased slowly over 2-3 hrs. and then slowly decreased but quite strong signals were obtained 7 hrs. after reaction. A 23 line spectrum was observed (Fig.30) with 4 additional lines seen under high gain conditions (Fig.31). Unresolved structure on the centre lines was clearly seen to be a small, partially-resolved triplet splitting when a solution diluted by a factor of 5 was examined at a slower field scan (Fig.32).

Fig. 33 shows half of the spectrum at a slow scan and a line diagram representing 3 sets of interacting triplet splittings

TABLE 4 : Comparison of experimental and 'theoretical' intensities for the dimer cation of $C_{10}F_4H_4$

Line (from centre)	Experiment	Theory		
		$a_F = 4a_H$	$a_F = 5a_H$	$a_F = 3a_H$
1	1	1	1	1
2	0.84	0.87	0.81	0.96
3	0.73	0.71	0.49	0.88
4	0.66	0.74	0.43	0.81
5	0.62	0.80	0.65	0.69
6	0.51	0.67	0.80	0.54
7	0.41	0.47	0.66	0.43
8	0.37	0.40	0.37	0.32
9	0.32	0.40	0.25	0.21
10	0.23	0.33	0.33	0.14
11	0.16	0.20	0.40	0.09
12	0.11	0.13	0.32	0.05
13	0.08	0.12	0.17	0.02
14	0.03	0.09	0.09	0.01
15	0.014	0.05	0.10	0.005
16	0.003	0.02	0.11	0.001
17	0.001	0.02	0.09	0.000
18		0.01	0.05	
19		0.01	0.019	
20		0.002	0.013	
21		0.000	0.014	
22			0.011	
23			0.006	
24			0.002	
25			0.000	

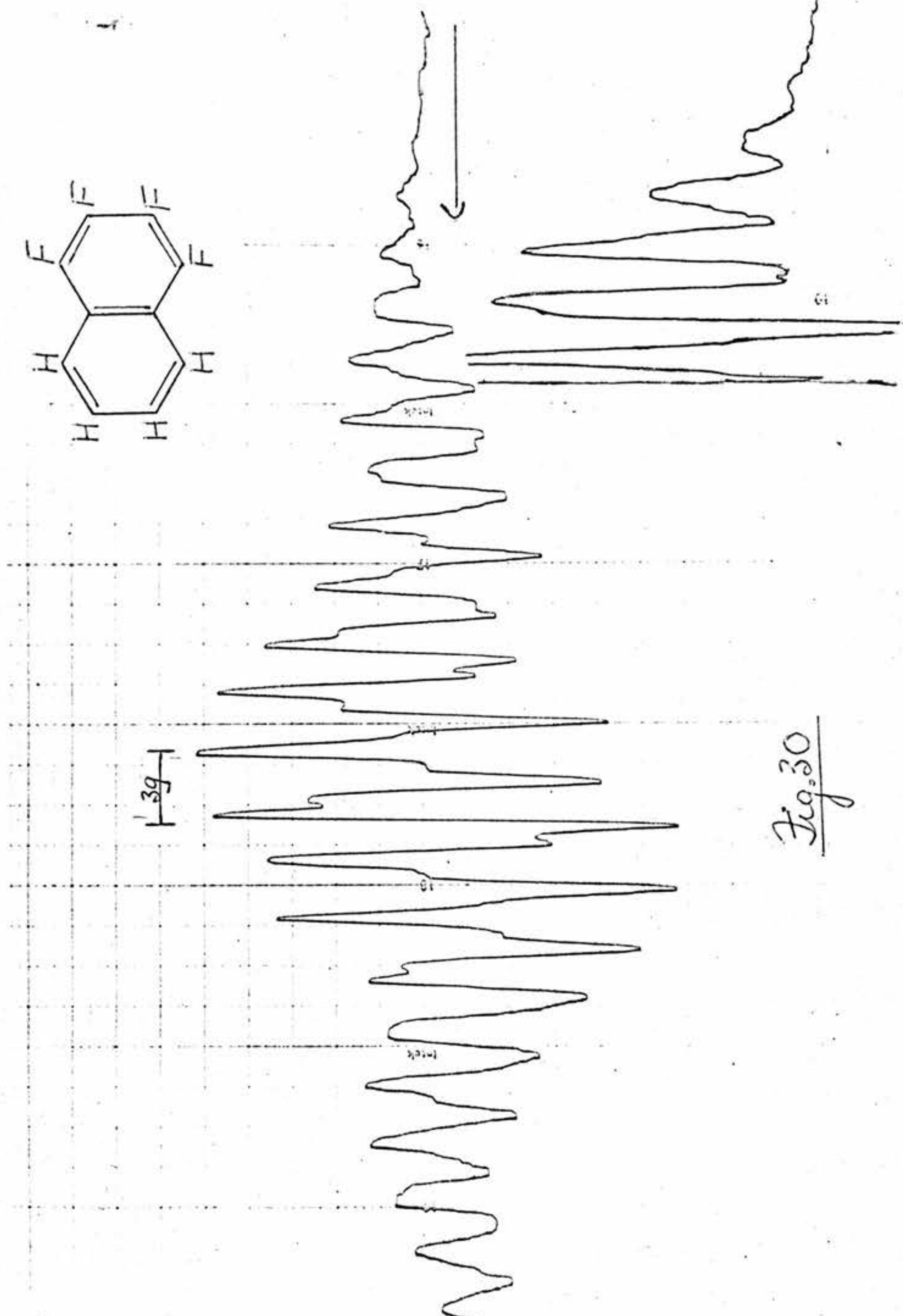


Fig. 30

Fig. 31.

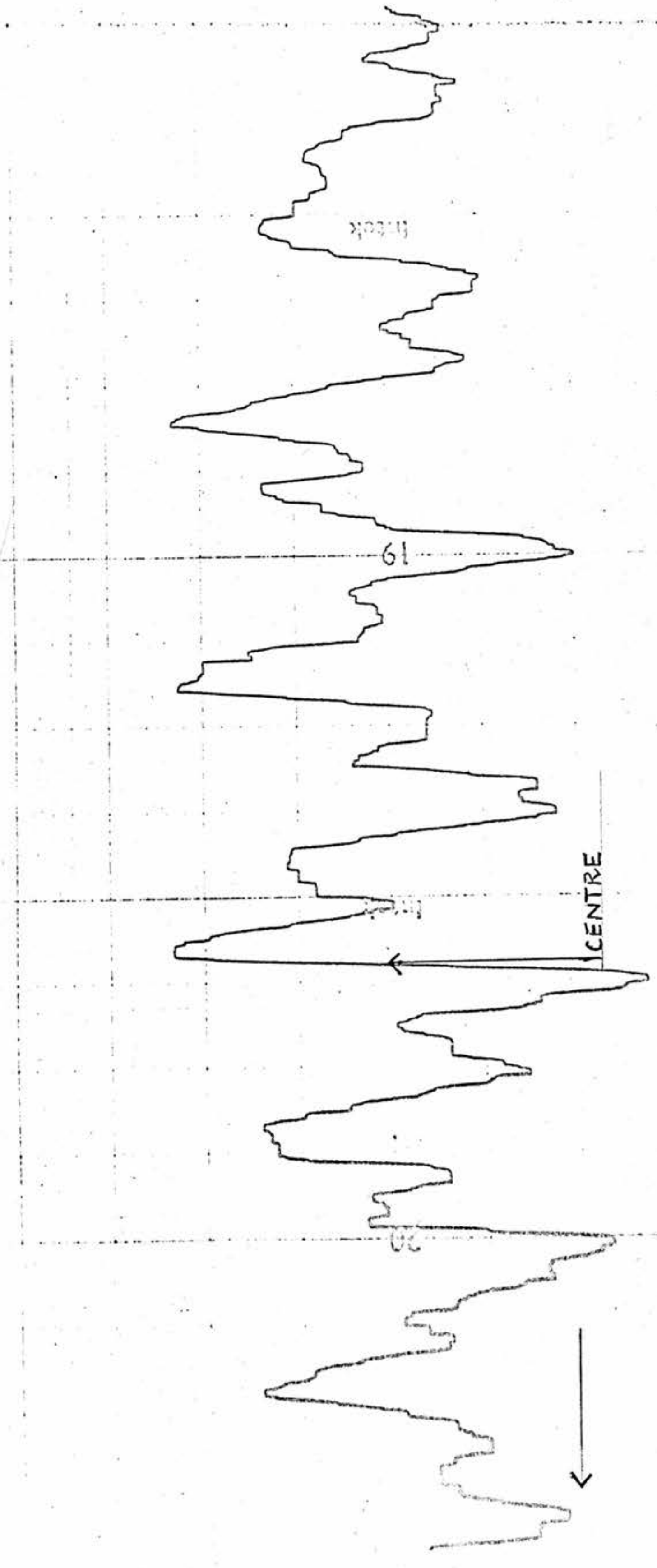


Fig. 32

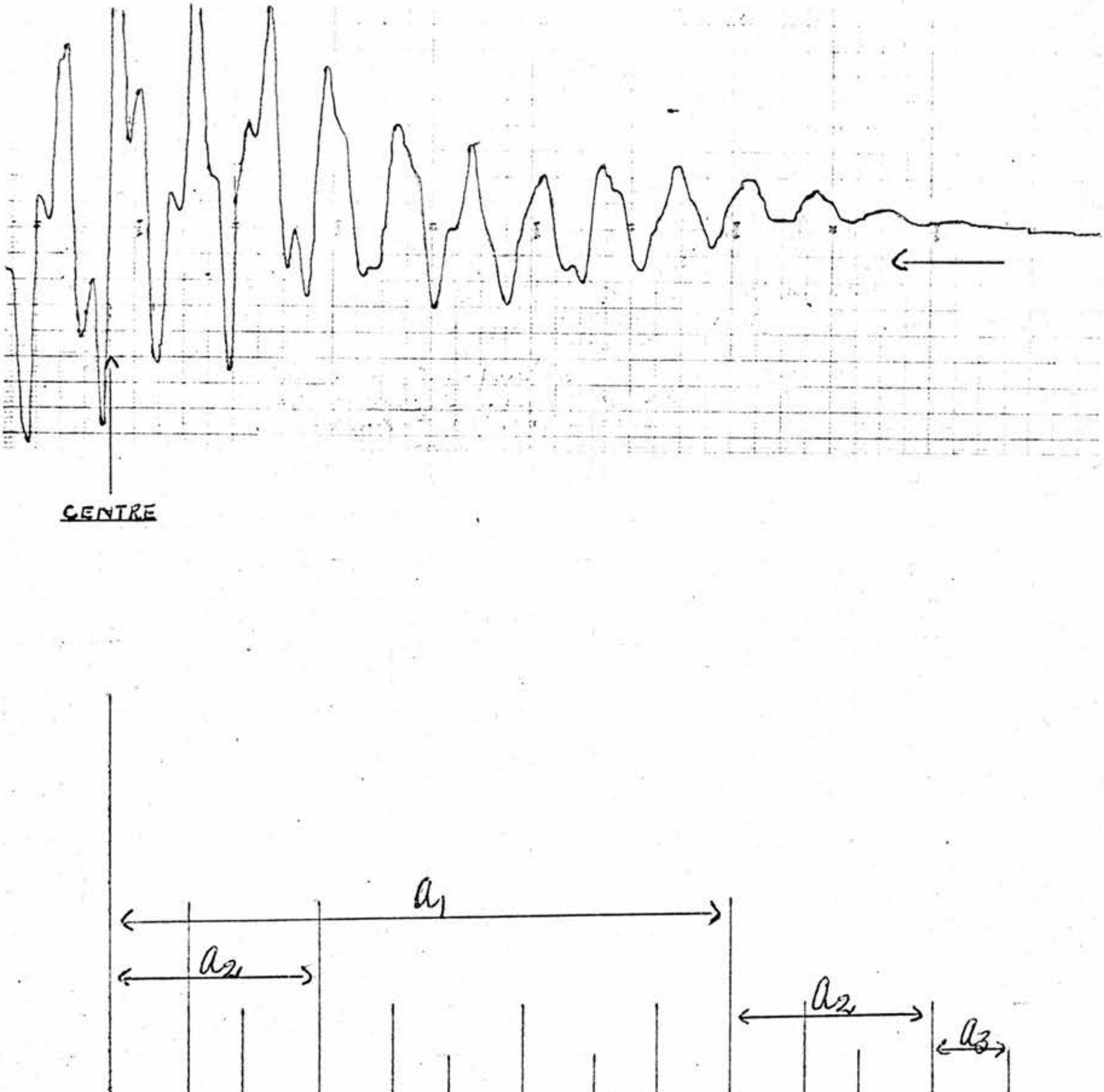


Fig. 33

9. TABLE 5 : Experimental splitting constants for radical cations

Cation[1]	Equivalent positions and multiplicity	Splitting (gauss)
$C_{10}F_8$	1,4,5,8 - quintuplet	$a_F = 19.01 \pm 0.05$
	2,3,6,7 - quintuplet	$a_F = 4.78 \pm 0.01$
$C_{10}F_6H_2$	1,4,5,8 - quintuplet	$a_F = 17.89 \pm 0.10$
	3,7 - triplet	$a_F = 10.29 \pm 0.10$
	2,6 - triplet	$a_H = 0.29 \pm 0.02$
$C_{10}F_5H_3$	1,4,5,8 - quintuplet[2]	$a_F = 16.1 \pm 0.2$
	6 - doublet	$a_F = 7.11 \pm 0.1$
	2 - doublet	$a_H = 4.19 \pm 0.15$
	3 - doublet	$a_H = 2.18 \pm 0.15$
$C_{10}F_4H_4$(dimer)	1,4,5,8 1',4',5',8' - nontuplet	$a_F = 8.08 \pm 0.1$
	2,3,6,7 2',3',6',7' - nontuplet	$a_H = 2.02 \pm 0.05$
iso.$C_{10}F_4H_4$	1,4 - triplet	$a_F = 19.53 \pm 0.2$
	2,3 - triplet	$a_F = 6.51 \pm 0.15$
	5,8 - triplet	$a_H = 2.37 \pm 0.1$
	6,7 - triplet	$a_H = 0.59 \pm 0.15$

[1] See fig.10.
[2] See, however, p.79

accounting for the positions of the 27 lines with

$a_1 = 19.53 \pm 0.2$ gauss,

$a_2 = 6.51 \pm 0.15$ gauss,

$a_3 = 2.37 \pm 0.1$ gauss.

The splittings a_1, a_2 were respectively assigned to the equivalent 1,4 and 2,3 fluorines of the radical cation of $C_{10}F_4H_4$ and a_3 to the equivalent 5,8 protons. The splitting $a_1 = 3a_2$ but $a_2 < 3a_3$. The partially-resolved splitting, a_4, was measured as accurately as possible at a very slow scan and assigned to the 6,7 protons.

$a_4 = 0.59 \pm 0.15$ gauss

The ratio a_1/a_2 is less than the value of 4 for the octafluoronaphthalene cation and nearer $a_{H\alpha}/a_{H\beta} = 2.67$ in the naphthalene anion[95] but the magnitudes of a_3, a_4 and their ratio of 4 are in poor agreement with the same data. The α spin density is again little perturbed from that in the octafluoronaphthalene cation.

Comparison of the spectrum with the line diagram again indicates large intensity anomalies resulting from linewidth variations.

10. g values

Equation (2) can be used to calculate the isotropic g values of free radicals in solution (see p.1). At constant ν, the value of H at the centre of the spectrum of a standard radical of fixed g can be calculated from this equation. The field value at the centre of the spectrum of the radical whose g value is required can then be found by measuring the distance between the centres of the superimposed signals and using the appropriate calibration of field versus distance on the recorder. The value of g can then be found by substitution of this value of H in (2). A solution of Fremy's salt (potassium nitrosodisulphonate) in saturated aqueous potassium carbonate was used as a standard[98] to determine g values for the fluorinated naphthalene cations. This radical has a well-resolved nitrogen triplet splitting of 13.09 gauss and $g = 2.0055 \pm 0.00005$[99]. The difference in field between the two extreme lines = 26.18 gauss and was used to re-calibrate the field for every g value measurement in order to compensate for variations and non-linearity in field scan. Those calibrations were also used for accurate measurement of the hyperfine splittings. The solution was contained in a melting-point tube attached to the outside of the capillary of sample tube C (Fig.7). Fig. 34 shows the signal from Fremy's salt superimposed on the spectrum of the 5,6,7,8H-tetrafluoronaphthalene cation.

The g values of most organic free radicals are within 1% of the free electron value ($g_o = 2.0023$) whereas those of hydrocarbon radical ions are within 0.1% of g_o.[100] The deviations are due to a combination of spin-orbit coupling and orbital Zeeman interactions and , although small, can be measured to a high degree of accuracy. The spin-orbit coupling constant, λ , increases with

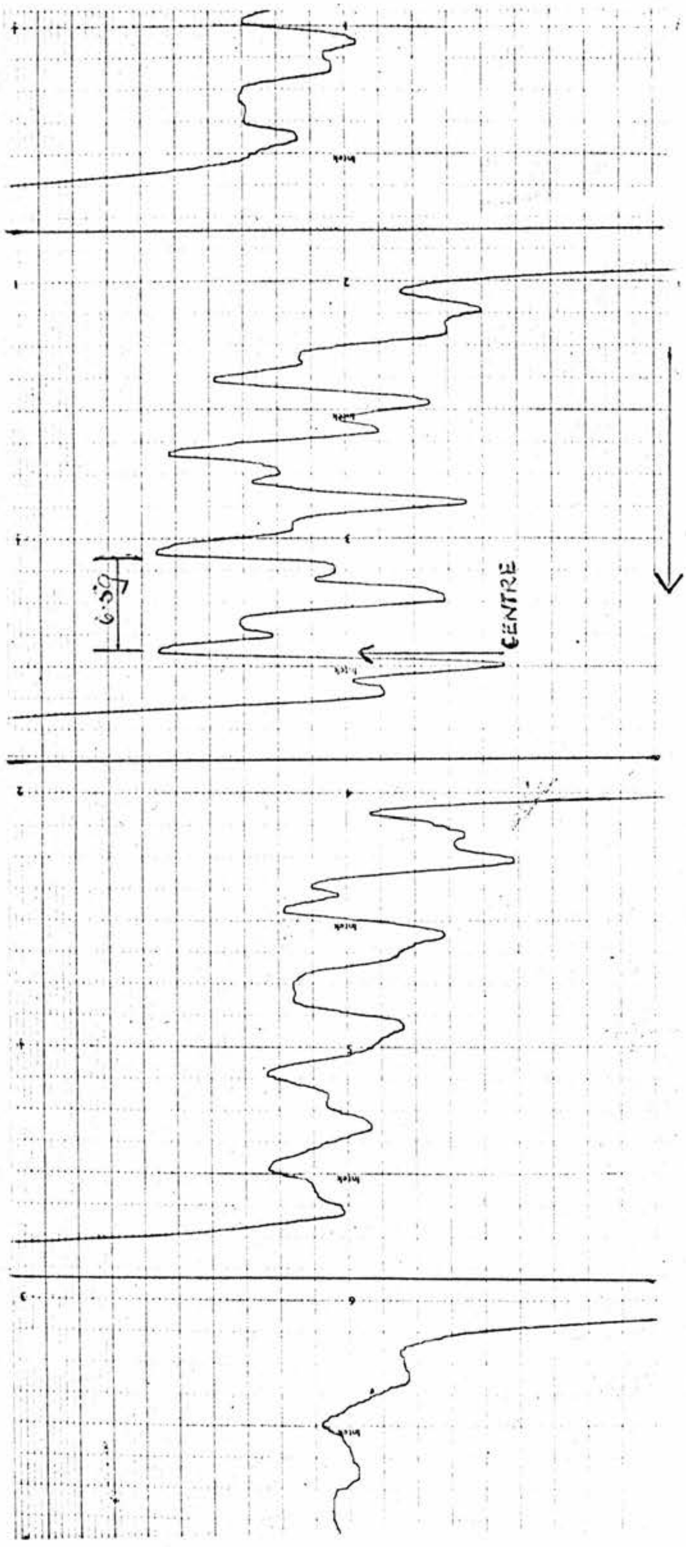


Fig. 34

increasing atomic number and Blois et alia[101] found that for a series of monohalogen-substituted hydrocarbon ions and semiquinones, g increased in the order I $>$ Br $>$ Cl $>$ F $>$ H and further increased on polyhalogenation. In addition, a very nearly linear relationship between δg and λ was found for the tetrahalogenated p-benzosemiquinone ions. Similar data has been reported by Kivelson[73] for halogen-substituted triphenylmethyl radicals.

Those g value variations can be used to distinguish between radicals containing relatively heavy atoms e.g. nitroxides or -OH or -CHO substituted species, and those containing only atoms of smaller atomic number e.g. hydrocarbon ions. Only minimal information on molecular electronic structure may be obtained, however, from a study of the deviations. The g values for the fluorinated naphthalene cations are given in table 6.

The value of ca. 2.004 for $C_{10}F_8^+$, $C_{10}F_6H_2^+$ and probably $C_{10}F_7H^+$, is higher than the value of 2.002 around which most hydrocarbon ion radicals cluster. The increase in g from $C_{10}F_6H_2^+$ to $C_{10}F_8^+$ is 0.0002, i.e. 0.0001 per additional fluorine atom, and compares favourably with a change of 0.00015 observed by Kivelson[73] in fluorinated triphenylmethyl radicals. Further decreases for $C_{10}F_5H_3^+$ and iso. $C_{10}F_4H_4^+$ are expected but instead relatively large increases are obtained. Singer[44] found the g value of the dimer cation of naphthalene little changed from the naphthalene anion: accordingly the value for the dimer cation of $C_{10}F_4H_4$ is expected to be less than that of the hypothetical $C_{10}F_8$ dimer

TABLE 6 : g values of fluorinated naphthalene cations

CATION	g value
$C_{10}F_8$	2.0042
$C_{10}F_7H$[1]	—
$C_{10}F_6H_2$	2.0040
$C_{10}F_5H_3$	2.0055
$C_{10}F_4H_4$(dimer)	2.0064
Iso. $C_{10}F_4H_4$	2.0070

[1] The g value of $C_{10}F_7H$ could not be measured as the centre of the spectrum was not accurately determined but would probably be ca. 2.0041 for the monomer cation.

cation which, by analogy, should also be 2.0042, the value for the monomer. But again a large increase is obtained instead. We cannot explain those anomalous results.

g values of radical ions of aromatic hydrocarbons substituted only by fluorine have not been previously reported.

11. Linewidths

Although the g tensor (p. 1) for radicals in solution is almost completely isotropic, information can still be obtained on its anisotropic component by studies of the widths of E.S.R. absorption lines and Carrington[66] has deduced the principal components of the fluorine anisotropic g tensor from studies of the linewidth variations in the isomeric fluoronitrobenzene anions. In addition, Fraenkel et alia[32] have obtained approximate values of the π-spin densities on fluorine by linewidth studies of the 2,5-difluoronitrobenzene anion. The use of linewidth variations in the study of such topics as cis-trans isomerism, ring- inversion, restricted rotation and proton exchange has been reviewed by Hudson and Luckhurst.[102]

The width is determined by Heisenberg's Uncertainty Principle

$$\Delta E \tau = h/2\pi \qquad (32)$$

where τ is the relaxation time and ΔE the uncertainty in the energy. Since $\Delta E = h\Delta\nu$, the uncertainty in frequency or linewidth is given by

$$\Delta\nu = \Delta E/h = 1/(2\pi\tau) \qquad (33)$$

i.e. it is governed by the time the radical can stay in the higher spin state without reverting to the lower one.

$$1/\tau = 1/T_1 + 1/T_2 \qquad (34)$$

where T_1 and T_2 are the spin-lattice and spin-spin relaxation times respectively. T_1 is controlled by spin-orbit coupling which is very small in organic free radicals so that T_1 is relatively large (of the order of seconds) and makes negligible contribution to the width. Because T_1 is so large, the mechanism whereby the spin system can lose energy and so preserve the Boltzmann distribution between the two levels is weak. If the number of spins per unit time being excited from lower to upper level, exceeds the number returning, the resonance line broadens and eventually disappears when the populations become equal. This is known as saturation and may result in broadening the whole spectrum or merely part of it. Under non-saturation conditions, the major contribution to the linewidth comes from T_2 which is a reduction of the time spent in either of the two states because of dipolar interactions with the surrounding electrons and nuclei. As the electron has a very much larger magnetic moment than any nucleus, the greater contribution is from electron-electron interaction and therefore highly dependent on concentration. This effect is reduced as much as possible by dilution until no further narrowing is observed. The same mechanism can also broaden the lines through dipolar interaction with a polar solvent or conjugate ion. A classic example of the effect is observed in the spectrum of $C_{10}F_8^+$ in f.H_2SO_4 (p.44).

Line-broadening is also caused by electron-nuclear dipolar interactions and depends on the separation of the dipoles and the angle between the direction of the applied field and the vector joining them. The expression for this contribution contains a term of the form $\langle(3\cos^2\theta - 1)/r^3\rangle$ Av.. If the sample is random and the radicals in a polycrystalline mass, the vectors from the nuclei to the electrons make a great many angles θ with the applied field and the line is broadened. On the other hand, if the nuclei are allowed to rotate freely with respect to the position of the electron, the angular term averages out and there is no contribution to the width. This is never the case in solution but the contribution from this term increases with increasing viscosity.

A general theory of linewidths was developed by Kubo and Tomita[103] following the work of Bloembergen et alia[104] on nuclear relaxation and was extended by Kivelson[105] to E.S.R. linewidths in solution. This theory was in good agreement with experiment where the lines all had approximately the same width but could not explain the linewidth variations later observed by a number of authors. This effect was shown by Fraenkel and Freed[106] to arise from the degeneracy of the nuclear spin states in the presence of several equivalent nuclei for which the Kivelson theory makes no allowance. In their treatment of the degeneracy problem, those authors use the alternative to the Kubo-Tomita theory of nuclear relaxation viz. the theories of Bloch and Redfield[107]. Those use an approximate form of the equation of motion for the density matrix of the spin system in terms of what may be called a relaxation matrix. They showed that a degenerate E.S.R. line arising from sets of equivalent nuclei may consist of a superposition of several Lorentzian lines of different widths thus accounting for the alternating linewidth effect. A single Lorentzian line was still observed, however, when variations in the widths of the composite lines were small compared to the average width.

Carrington[66] has used the Fraenkel-Freed theory to relate some of the linewidths in the spectra of the fluoronitrobenzene anions to sums and products of the fluorine and nitrogen quantum numbers associated with each line, but no line examined arose from degenerate transitions and his relaxation matrix was of the order unity. For radicals containing sets of equivalent nuclei, lines arising from n degenerate transitions have matrices of order n^2. For the $C_{10}F_8$ cation, the matrix for the centre line would be of order $6^2 \times 6^2$ i.e. 1296, and the matrices for many of the other lines would also be very large. Complete analysis of the effects involve finding both diagonal and off diagonal matrix elements and present a large computational problem. The linewidths and intensities relative to the centre line have been measured for the eleven centre lines of the $C_{10}F_8$ cation using sufficiently-dilute solutions under non-saturation conditions but no such analysis has been attempted. This data is given in table 7.

If the widths of the individual components of a degenerate hyperfine line are significantly different from the average width, the line is not truly Lorentzian in shape. Studies of relative line shapes can also be used to demonstrate linewidth effects and have been employed by Fraenkel et alia[108] to show how their theory improves on Kivelson's where there are large intramolecular anisotropic dipolar contributions to the linewidths as in the fluorinated naphthalene cations. Such studies are not usually made, however, as the information they yield can just as easily be obtained from the linewidths themselves. The relative line shapes are defined by the expression

$$S_{r_i} = (A_{r_i} D_o/D_i)^{\frac{1}{2}} \delta_{r_i} \qquad (35)$$

where $S_{r_i} = {}^{S_i}/_{S_o}$, $A_{r_i} = {}^{A_i}/_{A_o}$, $\delta_{r_i} = {}^{\delta_i}/_{\delta_o}$ are respectively the shape factor, amplitude and width of line i measured relative to the centre line of the spectrum and D_i, D_o are the degeneracies of line i and of the centre line. If the lines all have the same shape, the values of S_{r_i} are unity. Table 7 also gives those values for the eleven centre lines of the radical cation of octafluoronaphthalene. The changes from line to line are much larger than those observed by Fraenkel[108] for the tetracyanoethylene anion. The shape factors for corresponding lines on either side of the centre line are approximately equal except for the third lines from the centre, indicated by brackets, which are doubly overlapped (Fig.13).

B. Spin Density Calculations

The experimental hyperfine splittings a_F, a_H (table 5) have been correlated with McLachlan spin density calculations of ρ_C, ρ_F(25) and ρ_i(13). Before presenting this data, a discussion of methods used to calculate spin densities and their limitations is given, in order to show why the McLachlan method was selected.

1. Review of Methods

The simplest method of calculating π spin densities is the Hückel method and is critically examined in chapter two of Streitweiser.[109] Several simplifying approximations are usually made in setting up the secular determinant, depending on the type of Hückel theory used, the most drastic of which is the complete neglect of the overlap matrix elements, S_{ij}, between atomic orbitals i,j. One major defect is that the theory makes no allowance for σ-π interaction and treats the σ electrons as an unpolarisable core. Neither does it allow for electron correlation (p.104) in any form. Such interactions can significantly affect the magnitudes of the spin densities. Despite those approximations, the spin densities obtained are often in excellent agreement with experimental values calculated from (13) and the method is still widely used. It cannot account, however, for negative spin densities such as are obtained at the 9,10 positions of the

TABLE 7 : Relative intensities, linewidths and shape factors for the octafluoronaphthalene cation

Line[1]	Relative Intensities		Relative Linewidths	Relative Shape Factors[2]
	Experimental	Theoretical		
1	0.12	0.44	3.00	1.49
2	0.27	0.67	2.20	1.33
3	0.24	0.44	1.90	1.43
4	(0.21)	0.31	(1.60)	(1.31)
5	0.67	0.67	1.10	1.04
centre	1	1	1	1
7	0.53	0.67	1.05	0.96
8	(0.13)	0.31	(2.50)	(1.77)
9	0.21	0.44	1.85	1.41
10	0.18	0.67	2.45	1.34
11	0.09	0.44	3.30	1.49

[1] In order of increasing field

[2] Calculated using the formula $S_{r_i} = (A_{r_i} D_o/D_i)^{\frac{1}{2}} \delta_{r_i}$ (p.101)

naphthalene anion and more sophisticated theories are necessary. Some discussion of Hückel spin densities for the fluorinated naphthalene cations is given in 2.

The spin-independent Hamiltonian, H, for a radical can be written as the sum of one and two electron operators.

$$H = \sum_i h_i + \tfrac{1}{2}\sum_{ij}{}' 1/r_{ij} \qquad (36)$$

and could be solved to give an exact wave function were it not for the presence of the electron correlation terms, $1/r_{ij}$. The various SCF types of π-electron approximation allow for some correlation by using the one-electron orbitals, ϕ_i, obtained by the variation method, in the form of a Slater determinant. For $n\pi$-electrons the wave function,

$$\Psi = | \phi_1(\vec{x}_1) . . . . \phi_n(\vec{x}_n)| \qquad (37)$$

where the $\vec{x}_n$s denote both space and spin co-ordinates. This is equivalent to replacing the two-electron operator in (36) by a one-electron operator which appears as an average of the two-electron terms. Physically, each electron moves in the field of the nuclei and the self-consistent field formed by the 'averaged' fields of the electrons. SCF methods have been reviewed by Amos and Hall[110] and are discussed in Salem.[111]

In the restricted Hartree-Fock SCF approximation, the wave function is given by

$$\Psi = | \phi_1(1)\alpha(1) . . . \phi_p(p)\alpha(p)\ \phi_1(p+1)\beta(p+1) . . . \phi_q(n)\beta(n)| \qquad (38)$$

Each spatial orbital, ϕ_i, is doubly occupied by electrons of spin α, β except for the highest, containing only the unpaired electron and Ψ is an eigenfunction of $\hat{S}^2$, where $\hat{S}$ is the total spin angular momentum operator for the radical. The equations satisfied by those molecular orbitals are found by use of the variation principle and techniques for their solution when expressed as a linear combination of atomic orbitals have been developed by Roothaan.[112] As in Hückel theory, the π spin densities are given by the squares of the atomic orbital coefficients in the unpaired orbital and can never be negative. The method, however, takes no account of correlation between electrons of opposite spin.

To allow for such correlation different spatial orbitals for electrons of different spin must be used and this is the basis of the unrestricted Hartree-Fock approach. As it forms the basis of the McLachlan approximation, the method is discussed in more detail. The wave function

$$\Psi = |\phi_1(1)\alpha(1)\ldots\phi_p(p)\alpha(p),\theta_1(p+1)\beta(p+1)\ldots\theta_q(n)\beta(n)| \quad (39)$$

where the functions $\{\theta_r\}$ and $\{\phi_r\}$ form two different orthonormal sets. Pople and Nesbet[113] have deduced the equations satisfied by the ϕ_i, θ_i and when written in terms of the basis set $\{w_r\}$ of $M\pi$ atomic orbitals,

$$\phi_i = \sum_s^M w_s a_{si}, \quad \theta_i = \sum_s^M w_s b_{si} \quad (40)$$

The co-efficients a_{si}, b_{si} are eigenvaluss of the matrices $\bar{F}^{\alpha}$ and $\bar{F}^{\beta}$ where

$$\bar{F}^{\alpha} = \bar{H} + \bar{G}^{\alpha}, \quad \bar{F}^{\beta} = \bar{H} + \bar{G}^{\beta} \quad (41)$$

are the SCF matrices for electrons with α,β spins respectively.

The matrix elements are given by

$$H_{su} = \int w_s(1) h_1 w_u(1) d\tau_1 \qquad (42)$$

where h_1 is a one-electron Hamiltonian.

$$G^{\alpha}_{su} = \sum_{vt} \left[(P_{vt} + Q_{vt})(st|uv) - P_{vt}(st|vu) \right],$$
$$G^{\beta}_{su} = \sum_{vt} \left[(P_{vt} + Q_{vt})(st|uv) - Q_{vt}(st|vu) \right] \qquad (43)$$

$$\text{and } (st|uv) = \int w_s(1) w_t(2) \, {}^1\!/\!r_{12} \, w_u(1) w_v(2) d\vec{r}_1 d\vec{r}_2. \qquad (44)$$

The unrestricted bond-order matrices $\bar{P}$ and $\bar{Q}$ are defined as

$$P_{uv} = \sum_{r=1}^{p} a_{ur} a^{*}_{vr} \,, \quad Q_{uv} = \sum_{r=1}^{p} b_{ur} b^{*}_{vr} \qquad (45)$$

and are analogous to the charge and bond-order matrices of ordinary SCF theory. The spin density matrix

$$\bar{\rho} = \bar{P} - \bar{Q} \qquad (46)$$

and the densities are given by the diagonal elements so that

$$\rho = \phi_p^{\ 2} + \sum_{i=1}^{q} (|\phi_i|^2 - |\theta_i|^2) \qquad (47)$$

where ϕ_p contains the unpaired electron with spin α. Unlike the restricted Hartree-Fock, the method predicts negative spin densities where $|\theta_i|^2$ exceeds $|\phi_i|^2$ at a node of ϕ_p but those densities are usually in unsatisfactory agreement with experiment. This arises because Ψ is no longer an eigenfunction of $\hat{S}^2$ and is contamined by states of multiplicity higher than doublet. Löwdin[114] has shown how those states may be removed by applying a projection operator to the wave function but it is extremely difficult to find expressions for the spin densities after such a procedure. Amos and Hall[115] have shown, however, that only the most important of the contaminating spin multiplets need be removed as the others have relatively little effect and Snyder[116] has used such a function to obtain formulae for the spin densities in terms of $\bar{P}$ and $\bar{Q}$. The agreement with experiment was found to be much better.

Unrestricted Hartree-Fock spin densities may also be found using the perturbation theory of McLachlan.[117] The SCF orbitals of the neutral molecule are regarded as zero-order unrestricted molecular orbitals. If

$$\bar{P} = \bar{P}' + \bar{P}^{o} \tag{48}$$

where $\bar{P}'$ is constructed from the lowest q orbitals containing electrons of α spin and $\bar{P}^{o}$ from the remaining orbital, then

$$\bar{P}'(0) = \bar{Q}(0) \tag{49}$$

The notation is similar to that previously used (p.106) and the zero-order unrestricted bond-order matrices $\bar{P}'(0)$ and $\bar{Q}(0)$ for α, β spins respectively are half the bond-order matrix for the neutral molecule. The zero-order unrestricted SCF matrices $\bar{F}^{\alpha}(0)$, $\bar{F}^{\beta}(0)$ are both equal to the SCF matrix for the neutral molecule. It can be seen from (41) that the effect of the unpaired electron comprising $\bar{P}^{o}$ is to perturb $\bar{F}^{\alpha}$ and $\bar{F}^{\beta}$. The corrections are to a first order given by

$$\begin{aligned} F^{\alpha}_{rs}(1)-F^{\alpha}_{rs}(0) &= -P^{o}(0)_{rs}\gamma_{rs} + \delta_{rs}\sum_{t} P^{o}(0)_{tt}\gamma_{rt} \\ F^{\beta}_{rs}(1)-F^{\beta}_{rs}(0) &= \qquad\qquad\qquad\;\; \delta_{rs}\sum_{t} P^{o}(0)_{tt}\gamma_{rt} \end{aligned} \tag{50}$$

where the Pariser-Parr[118] approximation for the integrals has been used.

To a first order, both sets of orbitals alter equally under the perturbation of the Coulomb field of the odd electron as represented by the sum in (50). The change in spin density thus results from the exchange term $\bar{F}^{\alpha}(1)-\bar{F}^{\alpha}(0)$. McLachlan uses the perturbation theory of Coulson[119] to express the first order spin density in terms of polarisability co-efficients, π_{rs}. After neglecting various small terms and assuming that the one centre coulomb integral, γ_{rr} has the same value for all atoms r, the spin density on the r th atom is given by

$$\begin{aligned} \rho_r &= P^o_{rr} - \tfrac{1}{2}\gamma_{rr}\sum_s \pi_{rs}P^o_{ss} \\ &= c^2_{or} - \tfrac{1}{2}\gamma_{rr}\sum_s \pi_{rs}c^2_{os} \end{aligned} \qquad (51)$$

where c_{or}, c_{os} are the co-efficients of atoms r,s in the orbital containing the unpaired electron. McLachlan also shows that the use of Hückel instead of SCF orbitals makes little difference to the values of ρ_r provided that their energies are suitably modified by appropriate choice of a Hückel resonance integral. This is effected by replacing $\frac{1}{2}\gamma_{rr}$(51) by $-\lambda = \frac{1}{2}\gamma_{rr}/\beta_{eff}$ where

$$\beta_{eff} = \beta_{rs} - \tfrac{1}{2}P_{rs}\gamma_{rs} \qquad (52)$$

is the effective Hückel resonance integral obtained as an average over all bonds in the radical and β_{rs}, γ_{rs} are respectively the Hückel resonance integral for the bond between atoms r,s and the corresponding two-centre coulomb integral. Using Pariser and Parr's[118] values of γ_{rr}, γ_{rs} and β_{rs}, λ is found to be approximately equal to 1.2. Most authors use values of λ between 1.1 and 1.2.

In practice, the Hückel orbitals for the radical are first determined but (51) is not used to calculate the values of ρ_r as this would involve prior calculation of the terms π_{rs}. Instead equation (47) is used with ϕ_p, $\phi_1 \ldots \phi_q$ the Hückel orbitals and $\theta_1 \ldots \theta_q$ modified Hückel orbitals, calculated with β_{rs} unchanged but with the coulomb integral for atom r, $\alpha_r = +2\lambda c_{or}^2 \beta_{eff}$.

Atoms other than carbon within the π-framework are treated in this approximation by using the appropriate Hückel parameters h_x and k_{cx} where

$$\alpha_x = \alpha_o + h_x\beta_{cc}$$
$$\text{and } \beta_{cx} = k_{cx}\beta_{cc} \qquad (53)$$

The terms α_x, β_{cx} are respectively the coulomb integral of atom X and the resonance integral of the bond C-X. The corresponding quantities for carbon atoms and C-C bonds, α_o and β_{cc}, are standard.

Although the McLachlan method predicts negative spin densities where those are required by experiment, the overall agreement with exact unrestricted Hartree-Fock (UHF) is very poor. This arises from the fact that first order UHF (McLachlan) and exact UHF are, in essence, quite different. If a UHF function is used from which the unwanted spin components have been annihilated, however, the resulting spin densities are very similar to those obtained by the McLachlan method. Those densities are usually in very good agreement with experiment.

The configuration interaction[120] approach of Hoijtink may also be used to calculate spin densities in π-radicals. For a doublet state with (2n+1) electrons the one-electron orbitals $\phi_1 \ldots \phi_{2n+1}$ are considered and the lowest (n+1) of those used to form a restricted Hartree-Fock wave function, Ψ_o. Those orbitals could be either SCF or more usually Hückel.

$$\Psi_o = |\phi_1\bar{\phi}_1 \cdot \cdot \cdot \phi_n\bar{\phi}_n\phi_o| \tag{54}$$

where α-spin orbitals are denoted by ϕ_i and β by $\bar{\phi}_i$. Allowance is made for correlation between electrons of opposite spin by admixing with Ψ_o the singly-excited doublet configurations

$$^2\Psi^{jk} = 1/6^{\frac{1}{2}}\left[2|\phi_j\bar{\phi}_o\phi_k| - |\phi_k\bar{\phi}_j\phi_o| - |\phi_o\bar{\phi}_k\phi_j|\right) \tag{55}$$

where $j \leqslant n$ and $k \geqslant n+2$, and the function then becomes

$$\Psi = \Psi_o + \sum_{jk}\lambda_{jk}\,^2\Psi^{jk} \tag{56}$$

The resulting spin density matrix, Ψ^2, is given by

$$\bar{\rho} = \bar{\rho}_o + 2\sum_{jk}\lambda_{jk}\langle\Psi_o|\hat{S}_z\hat{D}\,^2\Psi^{jk}\rangle + \text{terms in } \lambda_{jk}^2 \tag{57}$$

where $\bar{\rho}_o$ is the matrix from (54) and the operator $\hat{D}_{uv}$ selects the co-efficient of the atomic orbital product $w_u w_v$ from the integral. Densities on individual atoms are given by diagonal elements of the matrix.

The method also predicts negative spin densities and the spin densities obtained are similar in magnitude to those obtained using the McLachlan method but only if many, or all, of the configurations $^2\Psi^{jk}$ are included in the wave function. This is impracticable for many-electron radicals e.g. the fluorinated naphthalene cations. In addition, Lefebvre[121] has shown that it is incorrect to use perturbation theory to find the λ_{jk}s.

Although those SCF methods improve on Hückel theory by making allowance for electron correlation, they too assume σ-π separability and treat the σ electrons as an unpolarisable core. Pople et alia[122] have developed an approximate SCF theory whereby all chemically effective electrons, both σ and π, are considered by using a basis set constructed from all valence shell atomic orbitals e.g. carbon 2s and $2p_{x,y,z}$ for planar aromatic radicals and radical ions. The principal approximation involved is the neglect of some of the less important electron repulsion integrals when computing the matrix elements of the Hartree-Fock Hamiltonian operator. The approximation is effected by neglect of differential overlap (NDO) i.e. terms $\phi_u(1)\phi_v(1)$ in the electron repulsion integrals are equated to zero. This serves to eliminate all three and four centre repulsion integrals thus substantially reducing the computation time and allowing calculations to be performed on large polyatomic molecules. Two centre integrals may also be eliminated depending on the degree to which the approximation is applied.

The CNDO (Complete Neglect of Differential Overlap) method[123] results in the elimination of all one, two, three and four centre repulsion integrals from the matrix elements of the Hartree-Fock Hamiltonian operator with the exception of one and two centre coulomb integrals. The matrix elements can then be expressed in terms of experimentally observable quantities such as ionisation potentials and electron affinities which serve to calibrate the method and compensate for its approximations. Such an approach has been used for the π-electron approximations previously discussed and CNDO is essentially an extension to the σ electrons as well. Both restricted and unrestricted Hartree-Fock wave functions may be used and the method predicts bond lengths, bond angles and bending force constants in good agreement with experiment. When used to calculate spin densities in π aromatic radicals, however, the method presents little improvement over the exact UHF because of neglect of σ-π exchange integrals which are responsible for in-plane σ densities e.g. at the nuclei of H and F. For this reason and because of inadequate computing facilities for performing CNDO calculations on many-electron systems, such calculations were not performed on the fluorinated cations. CNDO calculations were performed, however, on the hypothetical cation and anion of perfluorobutadiene. (see C)

The INDO method[124] is a slight modification of CNDO such that the overlap distribution $\phi_u(1)\phi_v(1)$ is retained if both atomic orbitals are centered on the same atom. One centre exchange integrals are now present in the simplified matrix elements of the Hartree-Fock Hamiltonian and, when chosen semi-empirically from atomic Slater-Condon parameters, serve as an additional calibration for the method.

As INDO specifically considers σ-π interaction within its framework, unpaired spin density at the nuclei of π-aromatic radicals, and hence the corresponding hyperfine splittings, can be directly evaluated. Equations of general form (20) relating hyperfine splittings to π spin densities via σ-π spin polarisation parameters are therefore no longer required. Those parameters are now only of academic interest as the accuracy of a restricted or unrestricted Hartree-Fock wave function to describe the ground states of radicals can be assessed by direct comparison of experimental hyperfine splittings with those calculated from the INDO method. The technique is of very recent origin, however, and the author has been unable to obtain a computer programme for performing calculations on the fluorinated naphthalene cations at the time of writing this thesis.

It is apparent from this review that the McLachlan method presents the best approach to performing spin density calculations on the fluorinated naphthalene cations in the absence of facilities for performing INDO type calculations. The method, however, is an approximate one and cannot be expected to give completely accurate results. The percentage errors in the spin densities are most likely to be large where those densities are small e.g. values of ρ_F (25).

2. McLachlan Spin Densities

In chapter I, B, it has been shown that use of the three parameter equation (27) to correlate fluorine hyperfine splittings with calculated values of ρ_C, ρ_F, ρ_{CF} results in values of

Q^F_{CC} and Q^F_{FF} which are in poor agreement with those obtained from the two parameter fit (25) and are probably erroneous. This arises because (31) is only an approximate relationship and because of uncertainties in ρ_{CF} (p.37) as well as in ρ_F. The values of ρ_F and K (26) are larger for cations than for anions (see p.35 and tables below), and the errors in using (31) would therefore be even greater. For those reasons, the two parameter equation(25) has been used to correlate the a_Fs obtained for the fluorinated cations (see A and p.91) with McLachlan spin density calculations of ρ_C and ρ_F. By using this equation in the one parameter form (26), values of Q_{eff} can be directly evaluated from the corresponding values of ρ_C and the data is therefore presented in this manner and then discussed. For those positions at which the values of ρ_C were considered to be sufficiently accurate, least squares fits of a_F to the one and two parameter equations were then performed. The values of Q_{eff}, Q^F_{CC} and Q^F_{FF} so obtained are given on p.132.

The coulomb and resonance parameters h,k (p.109) were respectively varied in units of 0.5 from h = 2 to 3 and from k = 0.6 to 0.7. As found by other workers,[73,86] the values of ρ_C,ρ_i(13) were fairly insensitive to the parameter variations whereas the reverse was true for the values of ρ_F which increased with increasing k and decreased with increasing h. Although there exist no definite Hückel parameters for fluorine,[125] the densities obtained from h = 2.0 and k = 0.70 were considered to be most accurate for several reasons: Kaplan et alia[32] have made independent estimates of ρ_F from linewidth studies in the 3,5-difluoronitrobenzene anion and have found that $h_F = 2.25$ and $k_{CF} = 0.72$ adequately reproduced those values. In addition, I'Haya[126] has performed molecular orbital calculations on fluorobenzene and suggests values of h_F from 1.5 to 2.1 and k_{CF} from 0.5 to 0.7. From carbon-fluorine overlap integral data and by analogy with k_{C-N} and k_{C-O},[125] values of k_{C-F} from 0.6 to 0.7 seem reasonable. Furthermore, the values of ρ_i(13) calculated using those values of h = 2 and k = 0.70 were generally found to be in best agreement with 'experimental' values obtained from the corresponding proton splittings using a value of $Q^H_{CH} = -28$ gauss (p.14). As discussed extensively in chapter I, A, however, this value of Q^H_{CH} may be inaccurate and hence lead to erroneous 'experimental' values of ρ_i. It should be mentioned, however, that some of those values of ρ_i could be exactly reproduced using a larger value of k viz. 0.85 - 0.9 (see below). Overlap integral data indicates,[125] however, that this value of k is too large. Accordingly, spin densities obtained using this value of k were not used in the least squares fits but some discussion of them is given below. Hückel spin densities were obtained from the McLachlan output data and are also discussed in some detail.

In the data presented below, ρ_{C_n}, ρ_{F_n} refer to the carbon and fluorine spin densities at position n and a_{F_n} (see table 5) refers to the corresponding hyperfine splitting. All spin

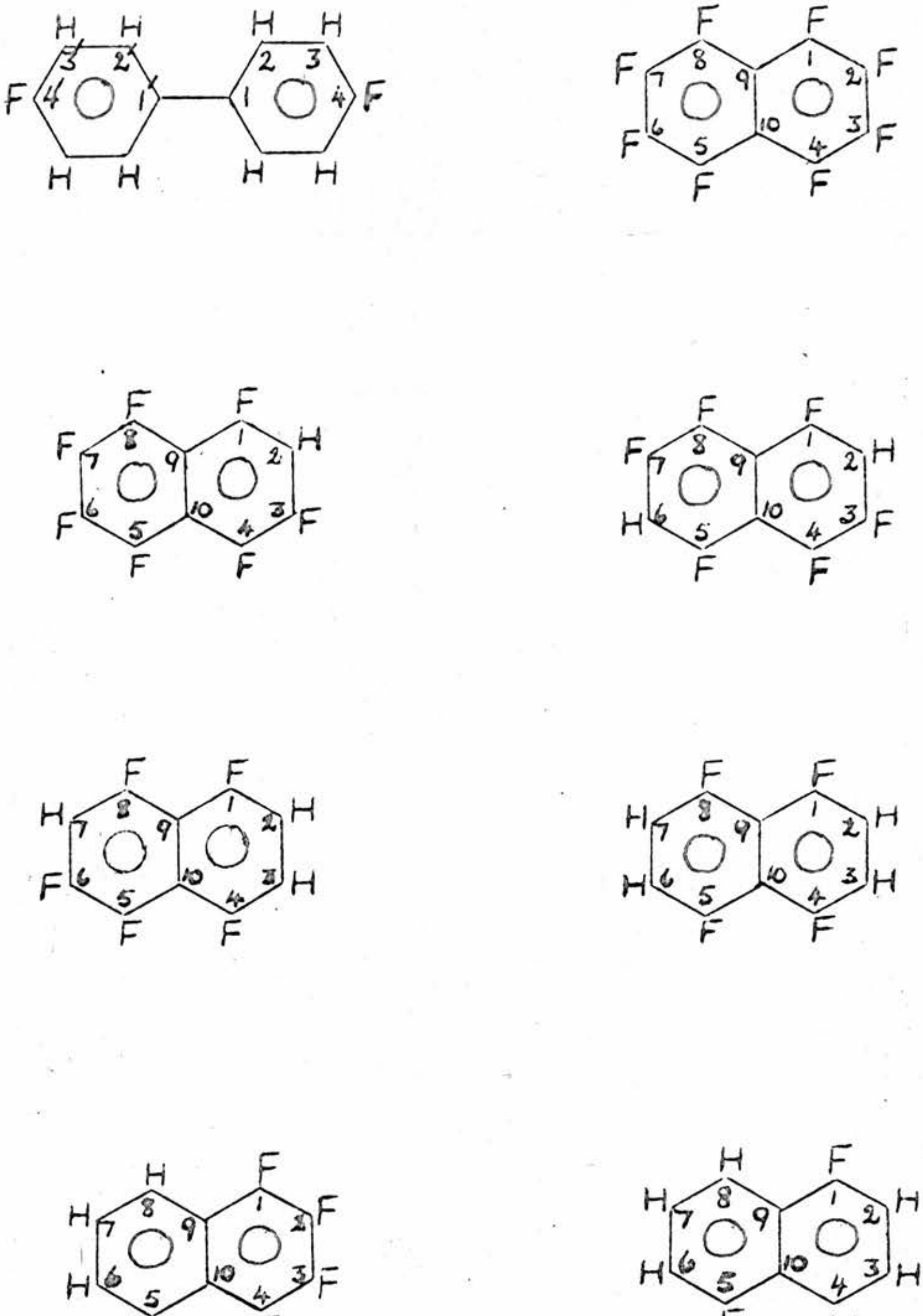


Fig. 35

densities were evaluated using h = 2.0, k = 0.70, except where stated otherwise. In addition, a value of λ = 1.2 was used throughout.

(i) $C_{10}F_8$ (table 8)

The ratio of the McLachlan densities ρ_{C_1}/ρ_{C_2} = 3.90 is in excellent agreement with the ratio a_{F_1}/a_{F_2} = 4 (p.60) and implies that the values of Q_{eff}, and therefore K, for the 1,2 positions are constant. This is in excellent agreement with the values found for those parameters. By contrast, the ratio ρ_{C_1}/ρ_{C_2} = 2.61 predicted by the Hückel spin densities suggests a value of Q_{eff} for position one which is much greater than that for position two: paradoxically, K is predicted to be constant. The Hückel values of K are larger than the McLachlan values. This arises mainly because of large percentage increases in ρ_F. Bazhin et alia[65] have also performed Hückel calculations on $C_{10}F_8^+$, using h = 2.0, k = 1 and obtain values of Q_{eff} = 97,86.6 gauss for the 1,2 positions respectively. This value of k is probably too large, however (p.115).

(ii) $C_{10}F_6H_2$ (table 9)

Experimentally, the hyperfine splittings from positions 1,4 are equivalent to within the linewidth (250 - 700 milligauss). The McLachlan density ρ_{C_4}, however, exceeds ρ_{C_1} by 0.03. With Q_{eff} = 97 gauss (see below), this is equivalent to a difference

TABLE 8 : $C_{10}F_8$ (Fig.35)

Position	McLachlan Spin Densities ρ_C	ρ_F	$K=\rho_F/\rho_C$[1]	Q_{eff}[2]	Hückel Spin Densities ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	a_F (gauss)
1,4,5,8	0.195	0.018	0.092	97.5	0.154	0.027	0.175	123.4	19.01
2,3,6,7	0.050	0.006	0.120	95.6	0.059	0.010	0.169	81.0	4.78

[1,2] See equation (26)

TABLE 9 : $C_{10}F_6H_2$ (Fig. 35)

Position	McLachlan Spin Densities				Hückel Spin Densities				ρ_C (Expt.)[1]	$a_{F,H}$ (gauss)
	ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}		
1,5	0.171	0.015	0.088	104.6	0.138	0.025	0.181	129.6		17.89
2,6	0.018				0.041				0.011	0.29
3,7	0.099	0.011	0.111	103.9	0.090	0.016	0.178	114.33		10.29
4,8	0.200	0.020	0.100	89.5	0.159	0.029	0.182	112.5		17.89

1 Calculated using (13) and $Q^H_{CH} = -28$ gauss

of 2.7 gauss in the corresponding hyperfine splittings which is considerably larger than the linewidths. The most accurate value of Q_{eff} is therefore obtained by taking the average value for those positions which equals 97.1 gauss in excellent agreement with the McLachlan values for the 1,2 positions of $C_{10}F_8^+$. The value of Q_{eff} for position 3 is slightly larger but also in very good agreement with those values.

As for $C_{10}F_8^+$, the Hückel values of ρ_C at the α positions are smaller than the corresponding McLachlan values and result in larger values for Q_{eff}. Unlike $C_{10}F_8^+$, however, the Hückel spin density at the β position shows a slight decrease over the McLachlan value resulting in a value of Q_{eff} for position 3 which is in slightly better agreement with the average Hückel values for positions 1,4. The Hückel values of K for the α,β positions are equal to those found for $C_{10}F_8^+$.

The McLachlan value of ρ_{C_2} is in better agreement with 'experiment' than the Hückel value which is almost 4 times as large. The 'experimental' value could be reproduced almost exactly by the use of k = 0.85, resulting in values of Q_{eff} for the α,β positions of $C_{10}F_6H_2^+$ which respectively increased and decreased by about 10%.

It seems that the McLachlan values of Q_{eff} and K are approximately constant for the α,β positions of $C_{10}F_8^+$, $C_{10}F_6H_2^+$ but the constant Hückel values of K are not in good agreement with the small value of Q_{eff} obtained for position 2 of $C_{10}F_8^+$.

(iii) $C_{10}F_5H_3$ (table 10)

The hyperfine splittings from positions 1,4,8 are equivalent to within the linewidths. Although the McLachlan values for ρ_{C_4}, ρ_{C_8} are the same, they, however, exceed ρ_{C_1} by 0.017. With Q_{eff} = 94.9 gauss (see below), this is equivalent to a difference of 1.61 gauss for a_{F_4} which is larger than the linewidths (950 milligauss). As for $C_{10}F_6H_2^+$, the most accurate values of Q_{eff} and K are obtained by taking averages for those three positions and are respectively found to be 94.9 gauss and 0.094, in excellent agreement with the McLachlan values for the α,β positions of $C_{10}F_8^+$ and $C_{10}F_6H_2^+$. The McLachlan value for ρ_{C_5} exceeds the average of ρ_{C_1}, ρ_{C_4} and ρ_{C_8} by 0.054 and, with Q_{eff} = 94.9 gauss, suggests a value of a_{F_5} which differs by 5.1 gauss. This is much larger than the sum total of the observed hyperfine splitting difference and the linewidth, even after allowance is made for errors in a_{F_1}, a_{F_5}. The lower value of Q_{eff} for position 5 therefore arises from an erroneously high value of ρ_{C_5}. In addition, ρ_{C_5} is completely insensitive to variation of h,k. This might arise from the fact that fluorine 5 is the only α fluorine which is ortho to another fluorine atom and this is also the case for the 4,8 positions of $C_{10}F_6H_2^+$ (p.117). Errors in the spin densities predicted by McLachlan's method may therefore arise where there exists some degree of molecular assymetry. The value of Q_{eff} for position 6 is lower than those obtained for the β fluorines of $C_{10}F_8^+$ and $C_{10}F_6H_2^+$

TABLE 10 : $C_{10}F_5H_3$ (Fig. 35)

Position	McLachlan Spin Densities ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	Hückel Spin Densities ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	ρ_C (Expt.)	$a_{F,H}$ (gauss)
1	0.159	0.015	0.094	101.3	0.133	0.025	0.188	121.1		16.1
2	0.081				0.081				0.150	4.19
3	0.056				0.066				0.078	2.18
4	0.176	0.016	0.091	91.5	0.147	0.027	0.184	109.5		16.1
5	0.224	0.023	0.103	75.0	0.174	0.032	0.184	96.6		16.8
6	0.092	0.012	0.130	77.3	0.084	0.016	0.190	84.6		7.11
7	0.027				0.048					
8	0.175	0.017	0.097	92.0	0.139	0.026	0.187	115.8		16.1

and may, for similar reasons, also arise from an erroneously high value for ρ_{C_6}. Paradoxically, the value of K for this position is larger

Although the McLachlan value for ρ_{C_3} is in fairly good agreement with the 'experimental' value, the agreement for ρ_{C_2} is poor. Unlike the more symmetrical $C_{10}F_6H_2^+$, use of k = 0.85 results in only slightly better agreement and this may also be an effect of molecular assymetry. With k = 0.7, the Hückel value for ρ_{C_3} is in slightly better agreement with 'experiment' but the value predicted for ρ_{C_7} would result in a value of a_H greater than the linewidth whereas no splitting is observed from this the proton at this position. It seems that the Hückel method is less accurate than the McLachlan method for small spin densities. Values of ρ_F, and hence K, calculated by this method are therefore highly suspect.

The Hückel densities ρ_{C_5}, ρ_{C_6} are smaller than the corresponding McLachlan values and result in values of Q_{eff} which are in better agreement with the average McLachlan value for positions 1,4,8. The Hückel values of Q_{eff} for those latter α positions show the usual increase over the McLachlan values.

<u>(iv) $C_{10}F_4H_4$ (table 11)</u>

Use of Q_{CH}^{H} = -28 gauss and the hypothetical splitting of 4.04 gauss (p.81) for the monomer cation results in a value of 0.576 for the total β spin density. The total calculated negative

TABLE 11 : $C_{10}F_4H_4$ (Fig.35)

Position	McLachlan Spin Densities ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	Hückel Spin Densities ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	ρ_C (Expt.)	$a_{F,H}$ (gauss)
1,4,5,8	0.191	0.011	0.058	84.6	0.157	0.000	very small	102.9		16.16
2,3,6,7	0.068				0.075				0.144	4.04

spin density at the 9,10 positions is −0.082 so that the spin density in any of the four α C–F bonds = (1−0.576+0.082)/4 i.e. 0.124. The calculated value of K = 0.058 and, neglecting overlap spin density, ρ_{C_1} = 0.117. This results in an 'experimental' value of Q_{eff} = 138.1 which is in poor agreement with those obtained from the Hückel and McLachlan values for ρ_{C_1}. In addition, the calculated values of ρ_{C_2} are only about 50% of the 'experimental' values and use of k = 0.85 presents little improvement. The McLachlan values of K for both α,β positions of $C_{10}F_8^+$, $C_{10}F_6H_2^+$ and $C_{10}F_5H_3^+$ are approximately constant: for this species, however, the value of K shows an approximate decrease of 40% over those latter values. Furthermore, the Hückel value for ρ_{F_1} is 0, suggesting a minute value of K. Those anomalous trends might suggest incorrect assignments for the observed hyperfine splittings but it is difficult to see how this could arise (see p. 85).

(v) iso. $C_{10}F_4H_4$ (table 12)

The McLachlan value for ρ_{C_5} is in good agreement with the 'experimental' value but this is not the case for ρ_{C_6} which is twice as large. Unlike ρ_{C_2} of $C_{10}F_6H_2^+$ (p.120), which is of comparable magnitude, use of k = 0.85 results in a value for ρ_{C_6} = 0.039 which is still too high. Like the erroneously high value for ρ_{C_2} of $C_{10}F_5H_3^+$, this may be an effect of molecular assymetry. This value of k, however, reproduces the 'experimental'

TABLE 12 : iso.$C_{10}F_4H_4$ (Fig.35)

Position	McLachlan Spin Densities				Hückel Spin Densities				ρ_C (Expt.)
	ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	
1,4	0.273	0.029	0.106	71.5	0.206	0.042	0.204	94.8	
2,3	0.055	0.007	0.127	118.4	0.067	0.014	0.209	97.2	
5,8	0.118				0.111				0.085
6,7	0.042				0.053				0.021

$a_{F,H}$ (gauss)
19.53
6.51

value for ρ_{C_5} almost exactly.

'Experimental' values for Q_{eff} may be obtained in a manner similar to that obtained for $C_{10}F_4H_4$ (p.125). The total spin density associated with the proton splittings (0.212) and the 9,10 positions (-0.048) is 0.164. This leaves a total spin density of 0.836 to be distributed amongst the four C-F bonds. Now the 'accurate' McLachlan values of Q_{eff} for the α,β fluorines of the same ~~anion~~ cation seem to be constant (c.f. $C_{10}F_8^+$ and $C_{10}F_6H_2^+$). Assuming this to be the case for iso.$C_{10}F_4H_4$, $\rho_{C_1}/\rho_{C_2} = a_{F_1}/a_{F_2} = 3$. The spin density in either of the α C-F bonds is therefore $^3/8 \times 0.836 = 0.314$. Using the average value of K = 0.117 for the 1,2 positions, $\rho_{C_1} = 0.218$. This results in a value of Q_{eff} ('experimental') = 69.4 in very good agreement with that obtained from the McLachlan value for ρ_{C_1} but in much poorer agreement with the higher value of Q_{eff} obtained from ρ_{C_2}. The McLachlan value of ρ_{C_2} is thus probably erroneous (c.f. ρ_{C_6} of $C_{10}F_5H_3^+$). It is significant that the McLachlan value of Q_{eff} for position 1 is considerably lower than those obtained for the corresponding positions of $C_{10}F_8^+$, $C_{10}F_6H_2^+$ yet K is unchanged. This is further evidence for the marked dependance of this quantity on the Hückel parameters employed (see p.28). Different predicted values of K probably arise from erroneous values of ρ_{C_n}. Hence the apparent paradox that a ~~smaller~~ larger value of K for position 6 of $C_{10}F_5H_3^+$ (p.121) gives rise to a ~~larger~~ smaller value of Q_{eff} for this position.

The larger Hückel value for ρ_{C_2} results in a value of Q_{eff}

which is in better agreement with 'experiment' than the McLachlan value for this position.

The experimental splittings for the radical cations of 1,5-difluoronaphthalene and 4,4'- difluorobiphenyl, prepared by Fischer and Zimmermann,[58] have also been included in the correlation:-

(vi) $C_{10}F_2H_6$ (table 13)

Experimentally the spin densities at positions 2,3 are equivalent but, although the McLachlan value for ρ_{C_2} is in fairly good agreement with 'experiment', that for ρ_{C_3} is about 50% too low and use of a value of k = 0.85 presents little improvement. On the other hand, ρ_{C_4} is too high and is insensitive to variations in h as well as in k (c.f. ρ_{C_5} of $C_{10}F_5H_3^+$, p.121).

Calculation of an experimental value for Q_{eff} in the manner discussed above results in a value of 73.2 gauss which is not in good agreement with the calculated Hückel and McLachlan values and suggests an erroneously low McLachlan value for ρ_{C_1}, in agreement with the erroneously high value for ρ_{C_4}. This 'experimental' value is almost the same as that found for iso. $C_{10}F_4H_4$.

(vii) $C_{12}F_2H_8$ (table 14)

The McLachlan value for ρ_{C_2} is in slightly better agreement with 'experiment' than the Huckel value. In addition, the McLachlan

TABLE 13 : $C_{10}F_2H_6$ (Fig. 35)

Position	McLachlan Spin Densities ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	Hückel Spin Densities ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	ρ_C (Expt.)	$a_{F,H}$ (gauss)
1,5	0.180	0.017	0.094	94.3	0.153	0.034	0.222	110.0		16.98
2,6	0.091				0.082				0.071	1.98
3,7	0.035				0.061				0.071	1.98
4,8	0.218				0.169				0.147	4.12

TABLE 14 : $C_{12}F_2H_8$ (Fig.35)

Position	McLachlan Spin Densities				Hückel Spin Densities				ρ_C (Expt.)	$a_{F,H}$ (gauss)
	ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}	ρ_C	ρ_F	$K=\rho_F/\rho_C$	Q_{eff}		
2,2'	0.085				0.073				0.098	2.73
3,3'	0.003				0.032					
4,4'	0.175	0.024	0.137	110.2	0.141	0.035	0.248	136.7		19.28

Note:

Since the benzene rings forming the biphenyl molecule are inclined at ca. 45° to each other,[127] the radical cation of its 44'-difluoro derivative may also be non-planar. This would result in reduced resonance interaction between the rings and necessitate the use of a smaller value of β_{CC} (p.109) for the bond between the rings, in order that accurate spin densities may be obtained. Accordingly, k was varied between 0.5 and 0.7 but this did not improve the agreement between calculated and 'experimental' values for ρ_{C_2} whereas the McLachlan values for ρ_{C_4} were changed only slightly. The cation may therefore be planar and the usual value of $\beta_{CC}=1$ was used.

value of Q_{eff} is in good agreement with an 'experimental' value of ca. 115 gauss but this latter value is subject to more uncertainty than usual because of difficulties in allowing for the spin densities associated with the meta proton splittings which are less than the linewidth (900 milligauss). The increased value of Q_{eff} is in agreement with an increased value of K over those found for the fluorinated naphthalene cations. It seems therefore that the values of K vary from one type of fluorine substituted aromatic nucleus to another.

The anion of 44'-difluorobiphenyl[75] has also been prepared (p.22) and a fluorine splitting of 3.13 gauss observed (table I). Use of the McLachlan value of ρ_{C_4} = 0.208 found for the anion results in a value of Q_{eff} = +14.6 gauss. This value of Q_{eff} is in poor agreement with the other values found for fluorinated anions e.g. +57 gauss (p.27) and +54.4 gauss (p.36). It is difficult to see how this can be explained other than by an erroneously low quoted value for a_F. The comments made on p.24 concerning pronounced 'charge effects' are still, however, valid.

It is apparent from the discussion given above that for those α,β positions of $C_{10}F_8^+$, $C_{10}F_6H_2^+$, $C_{10}F_5H_3^+$ where the McLachlan values of ρ_{C_n} are most likely to be accurate, values of Q_{eff} (ca. 95 gauss) and K which are approximately constant are obtained. Where this is not so, the errors in ρ_{C_n} can be ascribed to effects of 'molecular assymetry'. The 'experimental' values of Q_{eff} for the α,β positions of $C_{10}F_2H_6^+$ and iso.$C_{10}F_4H_4^+$ are much smaller (ca. 70 gauss) but, of the calculated McLachlan values, only that for position 1 of iso.$C_{10}F_4H_4^+$ is in good agreement, indicating errors in ρ_{C_1} of the former and ρ_{C_2} of the latter. This is confirmed by the poorer agreement of the calculated and 'experimental' spin densities associated with the proton splittings. Of the data obtained for those latter species, therefore, only that for position 1 of iso.$C_{10}F_4H_4$ will be used in the least squares fit. The lower value of Q_{eff} found for this position is not in good agreement with a value of K which is approximately the same as those for the α, β positions of $C_{10}F_8^+$, $C_{10}F_6H_2^+$ and this is further evidence for the strong dependence of this latter quantity on the Hückel parameters h,k employed. The McLachlan value of Q_{eff} for position 4 of $C_{12}F_2H_8$ is in good agreement with 'experiment' and suggests an accurate value of ρ_{C_4}. Furthermore, the larger value of K is in agreement with the larger value of Q_{eff} indicating that K does vary from one type of substituted aromatic nucleus to another.

The hyperfine splitting and spin density data used in performing the least squares fits is given in table 15.

Least squares fits of this data to the one and two parameter equations result in values of Q_{eff} = +93.1 gauss, Q^F_{CC} = +63.3 gauss and Q^F_{FF} = +298.9 gauss which are much larger than the corresponding values[86] obtained for fluorinated anions (p.36) viz. Q_{eff} = +54.5 gauss, Q^F_{CC} = +48.1 gauss and Q^F_{FF} = +146 gauss. Now Fischer[86] shows that Q^F_{FF} is very sensitive to the McLachlan

TABLE 15 : Data for fluorinated cations used in performing least squares fits to (24), (25).

Cation	Position[1]	ρ_C	ρ_F	a_F
$C_{10}F_8$	1	0.195	0.018	19.01
	2	0.050	0.006	4.78
$C_{10}F_6H_2$	1,4	0.186[2]	0.018[2]	17.89
	3	0.099	0.011	10.29
$C_{10}F_5H_3$	1,4,8	0.170[2]	0.016[2]	16.1
iso. $C_{10}F_4H_4$	1	0.273	0.029	19.53
$C_{10}F_2H_6$	4	0.175	0.024	19.28

[1] See p.116.

[2] Average values (see p.121)

values of ρ_F whereas Q^F_{CC} is not. The least squares fit values of Q^F_{CC} for both cations and anions are therefore reasonably accurate and, although an increase of 15.2 gauss is found for this term, the very large increase in Q_{eff} (38.6 gauss) is also due to a very large increase of 23.4 gauss in the term K Q^F_{FF}. The contribution to Q_{eff} from this term is 3.7 times as large for the cations as for the anions (6.4 gauss). This order of magnitude increase results in part from values of K which are about twice as large as those found by Fischer for the fluorinated anions (p. 35), and also implies an increase of ca. 80 - 90% in Q^F_{FF} which is very similar to that found. The smaller values of K for anions result from the presence of strongly electron-withdrawing groups tending to decrease the spin density on fluorine.

The larger hyperfine splittings in fluorinated cations (25) thus result from

(1) An increase of ca. 30% in Q^F_{CC} which is twice as large as the corresponding increase in Q^H_{CH} (p. 14).

(2) Increased values of ρ_F, although this might not be the case if the corresponding anions did not contain strongly electron-with drawing groups.

(3) A very large increase (ca. 100%) in the atomic term Q^F_{FF}. e.g. the contribution of $Q^F_{FF}\,\rho_F$ to the α splitting of the octa-fluoronaphthalene cation is about half that of $Q^F_{CC}\rho_C$.

In C attempts are made to show how those large increases in Q^F_{CC}, Q^F_{FF} arise.

C. Spin Polarisation Parameters

The term Q_{CC}^{F} is almost certainly positive in sign. This is apparent, both from the theory of Pople and Santry[78] (p.28) and from the two parameter least squares fits for cations and anions (p.132). Furthermore, use of a three parameter equation (p.36) to correlate experimental splittings with calculated spin densities results in values of Q_{CC}^{F} and Q_{FF}^{F} which are probably erroneous. This value for Q_{FF}^{F} is very large and positive and is similar to those obtained by earlier workers[55,64,77] on the basis of negative values for Q_{CC}^{F}. Those large values for Q_{FF}^{F} are in very poor agreement with those obtained from the most accurate calculations of the total fluorine 1s,2s spin densities at the nucleus,[87,88] based on the assumption that the fluorine atom in a C-F fragment behaves as if it had zero orbital angular momentum. It seems, therefore, that the values of Q_{CC}^{F} are +48.1 gauss and +63.3 gauss for anions and cations respectively (p.132) and that those values are reasonably accurate. Although the absolute values of Q_{FF}^{F} are less certain owing to the uncertainties in ρ_F, an increase of about 100% in this term is observed for cations. It now remains to explain this large increase and that of Q_{CC}^{F}.

An obvious way of doing so is to attempt to perform accurate calculations of the terms both for cations and anions. As discussed extensively in chapter I, Murrell and Hinchliffe[80] have attempted to calculate Q_{CC}^{F} for anions but the value of -11 gauss (p.33) which they obtain is in poor agreement with that quoted above. Although those authors have made a number of other significant approximations (p.34) in calculating this term and other terms Q^{F}_{AB}, the largest errors are likely to arise from three sources

1) Inaccuracies in the calculated atomic orbital coefficients a_{kn}, a_{rn}' (p.34).

2) Inaccuracies arising from the fact that (28) is accurate only to a first order in perturbation theory.

3) Inaccuracies arising from omission of contributions to the terms Q^{F}_{AB} from many of the excited configurations $\Psi_k \rightarrow \Psi_r$.

Now the calculation of Q^{H}_{CH} has been extended to second order in perturbation theory[28] and a contribution found which was approximately equal to 25% that of the first order (18). This additional contribution is equal to

$$-2\, Q^{H}_{CH} \Delta E^{-1} \iint \phi_B(1)\phi_A(2) \left| e^2/r_{12} \right| \phi_B(2)\phi_A(1)\, dT_1\, dT_2 \qquad (58)$$

where the terms are defined on p.9. It is easily seen from (28) that the corresponding second order contribution to Q^{F}_{CC} is equal to

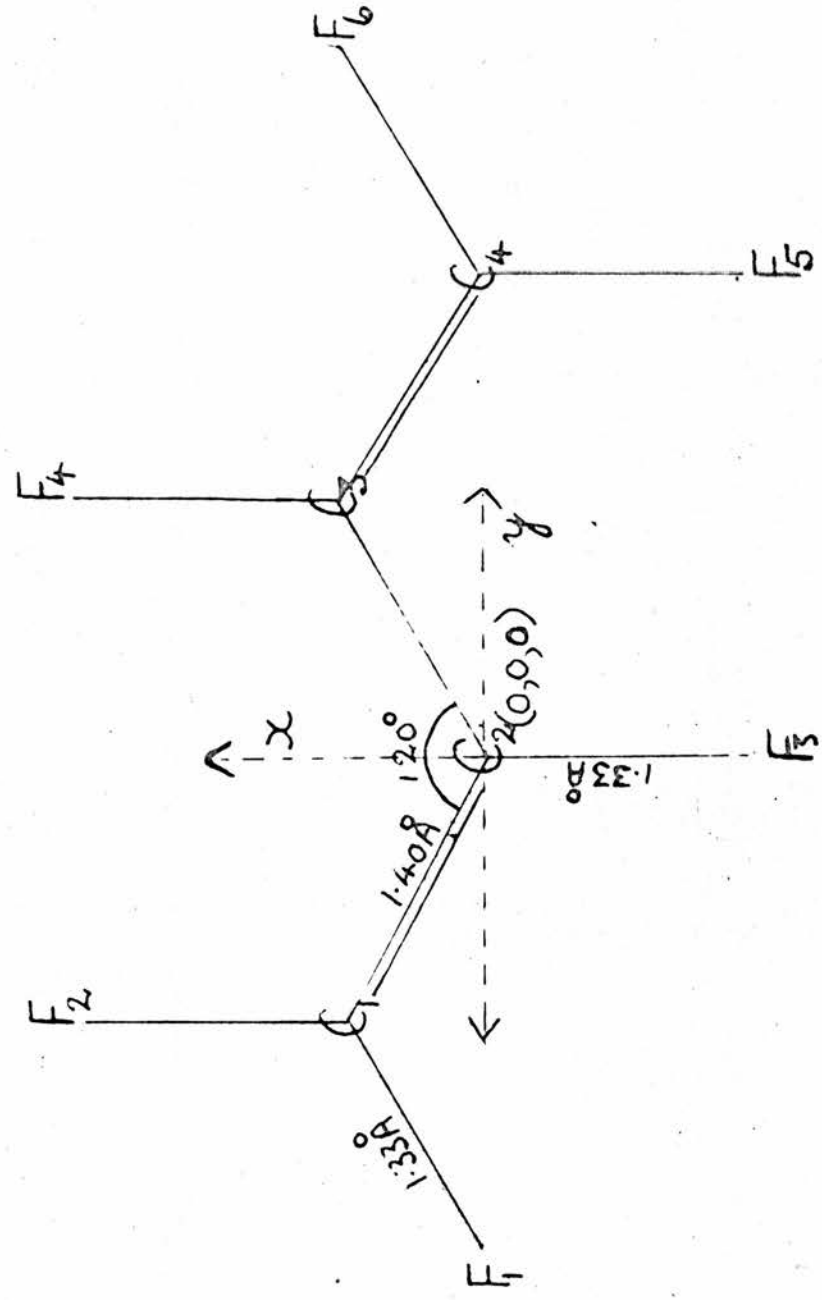
$$2\, Q^{F}_{CC} \sum_k \sum_r E^{-1}_{kr} \iint \Psi_k(1)\Psi_r(2) \left| e^2/r_{12} \right| \Psi_k(2)\Psi_r(1)\, dT_1\, dT_2 \qquad (59)$$

and the total expression for Q^{F}_{CC} is therefore obtained by addition of this term to the right hand side of the latter equation. This expression has been used by the author in an attempt to calculate Q^{F}_{CC} for cations and anions. In order to do so, however, it was first necessary to obtain σ orbitals Ψ_k, Ψ_r for both positive and negative C–F aromatic fragments. This was accomplished by performing CNDO calculations (p.111) on the hypothetical radical cation and anion of perfluorobutadiene, using the configuration shown in fig. 36. The bonds between C_2 and F_3 and C_3 and F_4 simulate such fragments and the carbon and fluorine 2s and $2p_{x,y,z}$ valence shell atomic orbital coefficients a_{kn}, a_{rn} (29) of the σ orbitals are easily obtained from the CNDO output data. Since only valence shell atomic orbitals can be used in CNDO calculations, the carbon and fluorine 1s atomic orbitals must be regarded as non-bonding. Since CNDO is an approximate SCF method taking into account electronic repulsion in an approximate manner, the atomic orbital coefficients are more accurate than those obtained by Murrell.[80] Furthermore, by performing calculations on both anion and cation, allowance is made for the effects of 'excess charge' on the magnitudes of those coefficients. Unfortunately, the output data indicates a large number of σ orbitals having significant C_2 and F_3 atomic orbital coefficients. Any accurate calculation of Q^F_{CC} must include all configurations corresponding to all transitions $\Psi_k \rightarrow \Psi_r$ between such orbitals.

$$\begin{aligned} \text{If } \Psi_k &= a_{k1}C_{2s}+a_{k2}C_{2px}+a_{k3}C_{2py}+a_{k4}F_{2s}+a_{k5}F_{2px}+a_{k6}F_{2py} \\ \text{and } \Psi_r &= a_{r1}C_{2s}+a_{r2}C_{2px}+a_{r3}C_{2py}+a_{r4}F_{2s}+a_{r5}F_{2px}+a_{r6}F_{2py} \end{aligned} \qquad (60)$$

the molecular exchange integral in (28) is equal to

Fig.36



$$a_{k1}a_{r1}\langle C_{2s}(1)\pi_C(2)|\pi_C(1)C_{2s}(2)\rangle + a_{k1}a_{r2}\langle C_{2s}(1)\pi_C(2)|\pi_C(1)C_{2px}(2)\rangle$$

$$+a_{k1}a_{r3}\langle C_{2s}(1)\pi_C(2)|\pi_C(1)C_{2py}(2)\rangle + \ldots a_{k6}a_{r6}\langle F_{2py}(1)\pi_C(2)|\pi_C(1)F_{2py}(2)\rangle \quad (61)$$

and the corresponding integral in (59) is equal to

$$a_{k1}^2 a_{r1}^2 \langle C_{2s}(1)C_{2s}(2)|C_{2s}(1)C_{2s}(2)\rangle + a_{k1}^2 a_{r1}a_{r2}\langle C_{2s}(1)C_{2s}(2)| C_{2s}(1)C_{2px}(2)\rangle$$

$$+a_{k1}^2 a_{r1}a_{r3}\langle C_{2s}(1)C_{2s}(2)|C_{2s}(1)C_{2py}(2)\rangle + \ldots a_{k6}^2 a_{r6}^2 \langle F_{2py}(1)F_{2py}(2)|F_{2py}(1)F_{2py}(2)\rangle \quad (62)$$

where the atomic integral

$$\langle X_n(1)\pi_C(2)|\pi_C(1)X_{n'}(2)\rangle = \iint X_n(1)\pi_C(2)| e^2/r_{12} |\pi_C(1)X_{n'} d\tau_1 d\tau_2 \quad (63)$$

It can be seen from those expressions that 21 different atomic integrals are required to evaluate the first order contribution to Q^F_{CC} arising from the excitation $\Psi_k \rightarrow \Psi_r$ but that many more integrals (actual number = 210) are required to evaluate the second order contribution. Those atomic integrals are mainly coulomb and hybrid[128] with only a few exchange type integrals. Although a computer programme was available for evaluating the exchange integrals, there was no such programme for evaluating the hybrid integrals, and the coulomb integrals would need to be calculated by interpolation from Roothaan's tables.[129] It would also be necessary to write a computer programme to sum the products $a_{kn}a_{rn'}$ (61) and $a_{kn}^2 a_{rn'}^2$ (62) over all significant excited configurations. This procedure would have to be carried out both for cation and anion. It is therefore apparent that performing accurate calculations of Q^F_{CC} is a large task which the author could not undertake in the time available. Furthermore, the task may not be worth the effort involved since the advent of the INDO method (p.112) enables hyperfine splittings to be directly evaluated and makes spin polarisation parameters of academic interest only.

An alternative way of explaining the difference in Q^F_{CC} is to show in which parts of the calculation the changes occur. From previous discussions (ps.34, 35), it is clear that those changes result from effects of excess charge on the atomic orbital coefficients a_{kn}, a_{rn}, (61) and the atomic integrals (63). To show this, let us consider only the most important contribution to Q^F_{CC} viz. that arising from the transition between the highest and lowest bonding and anti-bonding σ orbitals, ϕ'_B, ϕ'_A, of the $(C-F)^{\pm}$ fragments. Those orbitals are obtained from the appropriate C_2 and F_3 (Fig.36) atomic orbital coefficients, assuming sp^2 hybridisation for the former and sp for the latter, and are given in table 16.

Although small changes in the other atomic orbital coefficients of ϕ'_B are also observed between $(C-F)^+$ and $(C-F)^-$, the fluorine 2s coefficient for $(C-F)^-$ is numerically twice as large as for $(C-F)^+$. This is also the case for the fluorine 2s coefficients of ϕ'_A but, in addition, large percentage changes are observed in some of the other coefficients. The product of the 2s fluorine

TABLE 16 : CNDO atomic orbital coefficients of ϕ'_A, ϕ'_B for $(C-F)^{\pm}$

Atom	$(C-F)^+$		$(C-F)^-$	
	ϕ'_B	ϕ'_A	ϕ'_B	ϕ'_A
C_{2s}	0.039	0.382	0.027	0.438
C_{2px}	0.007	0.035	0.006	-0.128
C_{2py}	0.387	-0.051	0.418	-0.001
F_{2s}	0.004	-0.068	0.008	-0.138
F_{2px}	0.041	-0.152	0.049	-0.271

bonding and antibonding coefficients is thus algebraically 4 times smaller for $(C-F)^-$ as for $(C-F)^+$. The density at the fluorine nucleus $\delta(\vec{r}_i - \vec{r}_F)\phi_B'(i)\phi_A'(i)$ (p. 30) is therefore also algebraically 4 times smaller for $(C-F)^-$. Since this term multiplies the whole sum in (61), it can be seen that those changes in the fluorine 2s coefficients are very significant indeed. Less significance can be attached to changes in the other coefficients without first evaluating all the atomic integrals in (61), (62) and comparing with the contributions from other excited configurations.

Only 3 of the 15 atomic integrals associated with the first order contribution to Q_{CC}^F from the excited configuration $\phi_B' \rightarrow \phi_A'$ are exchange integrals. One of those has been evaluated to show the changes occurring between cation and anion. It seemed appropriate to select the integral $\langle F_{2s}(1)\pi_C(2)|\pi_C(1)F_{2s}(2)\rangle$ (60) since, by analogy with the coefficients and with the work of Vincow (p. 11) the changes might be greatest for integrals involving F_{2s} atomic orbitals. Unfortunately energy minimised carbon and fluorine atomic orbital exponents for the $(C-F)^{\pm}$ fragments do not exist. Hijikata[130] has, however, obtained energy minimised exponents for F^+ and F^- in the atomic structures FF^+ and FF^- and those were used in conjunction with similar exponents for C^+ and C^- obtained from the data of Krauss.[131] The integrals were evaluated using a programme due to Bernardi and Paiusco (see appendix) and are given in table 17.

TABLE 17 : Values of the integral $\langle F_{2s}(1)\pi_C(2)|\pi_C(1)F_{2s}(2)\rangle$ in $(C-F)^{\pm}$ fragments

Atom	$(C-F)^+$ Exponents	$(C-F)^+$ Integral(a.u.)[1]	$(C-F)^-$ Exponents	$(C-F)^-$ Integral(a.u.)
F_{2s}	2.620	0.306×10^{-2}	2.530	0.420×10^{-2}
π_C	1.80		1.567	

[1] atomic units

Although $\left[Q^{F}_{CC}\right]^{-}$ is algebraically less than $\left[Q^{F}_{CC}\right]^{+}$, the value of this integral associated with $(C-F)^{-}$ is algebraically greater than that associated with $(C-F)^{+}$ by about 35%. This arises from the fact that both carbon and fluorine orbital exponents in the $(C-F)^{+}$ fragment are larger than in the $(C-F)^{-}$ fragment. The other two exchange integrals associated with the excited configuration $\phi'_B \rightarrow \phi'_A$ would probably be greater for $(C-F)^{-}$ also. This is the order found by Bolton[21] for the corresponding exchange integral for $(C-H)^{\pm}$ viz. $\langle s(1)\pi(2)|\pi(1)s(2)\rangle$ (11). By contrast, the other integral in this equation, $\langle \sigma(1)\pi(2)|\pi(1)\sigma(2)\rangle$, which is the sum of two coulomb integrals, was found to be larger for $(C-H)^{+}$. By analogy with this, the coulomb and possibly the hybrid integrals may be also larger for $(C-F)^{+}$ and the overall effect of excess charge on the integrals, as distinct from the coefficients, may be to increase $\left[Q^{F}_{CC}\right]^{+}$. There is little point, however, in premature speculation and more work is necessary before any such statement can be made with certainty. It has been shown that significant changes in both coefficients and integrals occur between $(C-F)^{-}$ and $(C-F)^{+}$.

The term Q^{F}_{FF} cannot be directly evaluated in Murrell and Hinchliffe's calculation.[80] This is due to the fact that the most important excited configurations contributing to this term (p.32) involve transitions from the fluorine 1s orbital which is not included in their atomic orbital basis set for the C-F fragment. Furthermore, there is no way of allowing for the infinity of the fluorine s orbitals in the transitions $F_{1s} \rightarrow F_{ns}$. On the other hand, Fischer and Colpa,[86] who include the 1s orbital, maintain that the contributions to Q^{F}_{FF} from those transitions and from the transitions $\sigma_B \rightarrow F_{ns}$, are probably small and consider only the contribution from the single transition $F_{1s} \rightarrow \sigma_A$. They found, however, that the molecular integral $\langle F_{1s}(1)\pi_F(2)|\pi_F(1)\sigma_A(2)\rangle$ (28) associated with this transition is very sensitive to the detailed form of the basis set used to construct the bonding and anti-bonding orbitals, σ_B and σ_A. A negative contribution could in fact be obtained. It is therefore apparent that the differences existing in $\left[Q^{F}_{FF}\right]^{\pm}$ cannot be explained by direct calculation.

Nevertheless, it is significant that the experimental value of $\left[Q^{F}_{FF}\right]^{-}$ = +146 gauss, although possibly inaccurate (p.36) is not too far removed from the most accurate value of +70 gauss (p.35), calculated on the assumption that a fluorine atom in a C-F fragment behaves as if the orbital angular momentum were completely quenched. Now this latter value was obtained from the total 1s,2s spin densities at the nucleus of a free fluorine atom using highly accurate spin polarisation wave functions[88] which make allowance for a large degree of electron correlation. It would be more appropriate to calculate $\left[Q_{FF}\right]^{-}$ from the total spin density at the nucleus of the F^{-} ion since the difference between theory and experiment may result from effects of 'excess charge'. Unfortunately spin polarisation wave functions for

F^+, F^- are not yet available so that the total spin density at the nuclei of those ions cannot be calculated. It appears, however, that this presents the best way of explaining the very large difference in Q^F_{FF} occurring between radical anions and cations.

CONCLUSION

It has been found possible to prepare the radical cations of octafluoronaphthalene and of some β H-substituted derivatives. The single parameter equation

$$a_F = Q_{eff}\rho_C$$

where $Q_{eff} = Q^F_{CC} + KQ^F_{FF}$ varies as $K = \rho_F/\rho_C$, has been used to correlate the hyperfine splittings in the E.S.R. spectra with McLachlan spin density calculations of ρ_C, ρ_F. For those α, β positions of $C_{10}F_8^+$, $C_{10}F_6H_2^+$, $C_{10}F_5H_3^+$, at which the predicted values of ρ_C are most likely to be accurate, the values of Q_{eff} (ca. 95 gauss) and K (ca. 0.1) are approximately constant. Those values of K were found to be highly dependant on the Hückel parameters employed as shown for position 1 of iso. $C_{10}F_4H_4$ (p.127) where the lower value of Q_{eff} is not in agreement with a predicted value of K which is approximately the same as those found for $C_{10}F_8^+$, $C_{10}F_6H_2^+$. The larger value of Q_{eff} for the 4,4' positions of the radical cation of 44'-difluorobiphenyl is, however, in agreement with an increased value of K indicating that this quantity varies from one type of substituted aromatic nucleus to another. A least squares fit of a_F to ρ_C results in a value of Q_{eff} = +93.1 gauss which is much larger than the corresponding value of +54.5 gauss obtained by Fischer[86] for fluorinated anions.

It has also been shown that the hyperfine splitting data is best accommodated by the two parameter equation

$$a_F = Q^F_{CC}\rho_C + Q^F_{FF}\rho_F$$

with a positive value for Q^F_{CC} and that use of the three parameter equation

$$a_F = Q^F_{CC}\rho_C + (Q_{CF} + Q_{FC})\rho_{CF} + Q^F_{FF}\rho_F$$

to correlate the values of a_F with calculated spin densities results in values of Q^F_{CC} and Q^F_{FF} which are probably erroneous. The very large value of Q^F_{FF} (ca.931 gauss) so obtained[86] is similar to those found by earlier workers who assumed Q^F_{CC} was negative, by analogy with Q^H_{CH}. Although the value of Q^F_{CC} = +63.3 gauss obtained from a least squares fit to the two parameter equation shows an approximate increase of 35% over the corresponding value of +48.1 gauss for fluorinated anions,[86] the value of Q^F_{FF} = +289.9 gauss has increased by about 100%. Since the values of K also show an overall increase of about 100%, the large hyperfine splittings in fluorinated cations are due to a large increase (ca.4) in the term $Q^F_{FF}\rho_F$.

Attempts have been made to show that the increases in Q^F_{CC} and Q^F_{FF} result from effects of 'excess charge' on certain terms used in their calculation.

APPENDIX

1. McLachlan Spin Density Programme

McLachlan spin density calculations were performed on an IBM 1620 computer using a programme written by D. H. Levy[132] in Fortran II, for an IBM 7090 and modified for the 1620 by Dr. C. Thomson. The programme calculates both Hückel and McLachlan spin densities from input data consisting of the constant λ and the non-zero elements of the initial secular determinant.

2. CNDO Programme

CNDO calculations were performed on an IBM 360/44 computer using a programme, written by Segal in Fortran IV for an IBM 7090, obtained through the Quantum Chemistry Program Exchange. The programme was modified for the 360 series by Dr.C. Thomson. The input data consists of the geometry of the radical specified as the atomic numbers and cartesian co-ordinates of the atoms and also the multiplicity of the state. Output data includes the interatomic distances, overlap matrices, SCF eigenvalues, eigenvectors and bond orders with separate listings for the α and β electrons of an open-shell system.

3. Integral Programme

The two centre exchange integrals were evaluated using a programme written in Fortran IV by F. Bernardi and G. Paiusco for an IBM 7094 computer and modified for the IBM 360/44 by Dr. C. Thomson. The input parameters are those needed to specify the four orbitals, the corresponding species of basic charge distributions and the interatomic distances. In addition, it is necessary to provide the matrix of the co-efficients w_{sq} and w''_{sq}.[133] Output data consists of the values of the integrals.

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