NMR STUDIES OF

SOME ACYL FLUORIDES

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By

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SCOPE AND CONTENTS:

The conformational preferences and carbon-fluorine coupling constants in a number of simple acyl and diacyl fluorides have been studied by means of ^{1}H and ^{19}F nuclear magnetic resonance spectroscopy.

One and two bond carbon-fluorine coupling constants were obtained by observing the ^{13}C satellites in the ^{19}F spectra of the compounds studied. Conformation analysis was performed by observing the temperature variation of coupling constants. In this way, it was possible to show that oxalyl fluoride is most probably in a trans-planar conformation while malonyl fluoride and the succinyl halides are hindered rotators.

The n.m.r. spectral cases ABX, AA'BB', AA'BB'X and AA'A''A'''XX' are discussed and utilized.

The previously unreported compounds succinyl chloridefluoride and 3,3,3-trifluoropropionyl fluoride have been identified by means of their n.m.r. spectra.

The observed coupling constants and conformational preferences are discussed in terms of a mechanism for carbon-fluorine coupling.

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CHAPTER I

Introduction

Nuclear Magnetic Resonance [1,2]

In general nuclear magnetic resonance (n.m.r.) spectra and the n.m.r. parameters, chemical shift and coupling constant, are of considerable use in the solution of the chemical problems of structure, stereochemistry, hindered internal rotation, molecular conformation and chemical exchange. Nuclear magnetic resonance has its origin in the magnetic properties of the nucleus. Any nucleus having a non-zero spin I has an associated magnetic moment μ given by

$$\mu = \gamma I h$$

where γ is a constant, called the magnetogyric constant, for a given nucleus. When the nucleus is placed in a static magnetic field, it can then take up any of the 2I + 1 orientations specified by the quantum number m_I where

$$m = I, I - 1, \ldots\ldots, - I$$

That is, the observable magnetic moment along any specified direction (here defined as the z-axis, along which the magnetic field is applied) is given by

$$\mu_z = \frac{m}{I} \mu$$

Now the energy of interaction between the applied field and the nuclear moment is $-\mu_z H_o$, H_o being the intensity of the static magnetic field applied along the z-axis. Hence the energy of any particular quantum state is

$$E_m = -\frac{m}{I} \mu H_o$$

Recalling $\mu = \gamma I h$, as given above, we obtain

$$E_m = -mh\gamma H_o$$

for the energy of the nucleus in the field.

Application of electromagnetic radiation to the above system will result in transitions between the states if the condition

$$\Delta E = h\nu$$

is met. The selection rule is $\Delta m = \pm 1$; hence transitions

occur only between adjacent levels and

$$\Delta E = [-(m-1) + m]\, h\gamma H_o$$

$$= h\gamma H_o$$

Therefore

$$h\nu = h\gamma H_o$$

and

$$\nu = \frac{\gamma H_o}{2\pi}$$

for resonance. For nuclear moments, and the usual magnetic field strengths employed ($\simeq 10^4$ gauss) this frequency is in the r.f. region. The above theory shows that the resonance frequency is proportional to the applied magnetic field. It should be noted that the case $I = \frac{1}{2}$ is particularly simple; there are two energy levels separated by an energy of $h\gamma H_o$, $m = +\frac{1}{2}$ corresponding to parallel alignment of the nuclear moment with H_o and $m = -\frac{1}{2}$ corresponding to antiparallel alignment. Both ^1H and ^{19}F nuclei have $I = \frac{1}{2}$. The natural abundance of these nuclei and the high relative intensities of their n.m.r. absorptions make them the most highly favoured of all nuclei for nuclear resonance studies; by far the most work has been done using them. In contrast the abundant isotopes of carbon and oxygen, ^{12}C and ^{16}O, have no nuclear spin and hence no resonance. Organic and

fluorinated organic compounds are therefore studied by means of ^{1}H and ^{19}F resonance. In a 10 kilogauss field the proton resonance frequency is 42.577 Mc/sec; that of ^{19}F is 40.055 Mc/sec.

In practise an oscillator of fixed frequency ν_o is used and the magnetic field is swept until resonance occurs. If this is done under high enough resolution, that is with sufficiently stable instrumentation, for liquid samples it is found that different compounds do not resonate at a single value of magnetic field, but rather at different values over a range which is about 10^{-5} of the applied field for protons, the range increasing for the nuclei of heavier atoms. This phenomenon is known as chemical shift. The spectrum of a molecule containing a particular nucleus in several different chemical environments usually consists of several peaks, one for each environment. As an example, consider the spectrum of ethanol at 30.5 Mc/sec under moderate resolution[3], shown in Figure 1.1(a). A separate peak is obtained for each group of chemically equivalent protons in the molecule. It should be noted that the intensities are approximately in the ratio 3 : 2 : 1, allowing the identification of each peak; in general in n.m.r. the integrated intensities are proportional to the number of nuclei present.

Chemical shifts have their origin in the local field arising from the circulation of the electrons surrounding the nucleus when H_o is applied. The local field will be proportional to, and oppose,

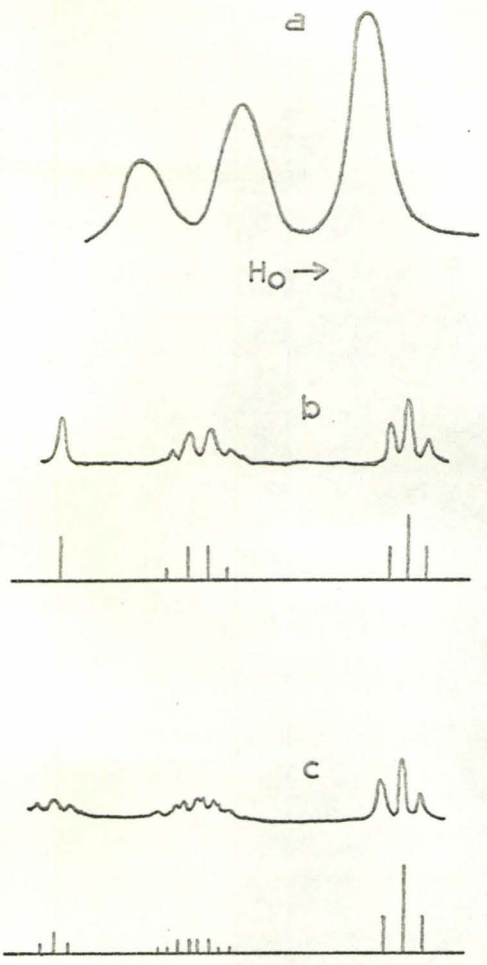


Fig. 1.1 30.5 Mc/sec Proton Spectra of Ethanol Samples. (a) Under Moderate Resolution, Showing Chemical Shift Effect. (b) High Resolution Spectrum of Acidified Ethanol Showing Ethyl Group Splitting. (c) High Resolution Spectrum of Pure Ethanol Showing Coupling to the Hydroxyl Proton. Theoretical First Order Spectra are Shown under (b) and (c)

the applied field H_o. Hence the net field experienced by the nucleus is

$$H = (1 - \sigma) H_o$$

where σ is a constant, called the screening constant, independent of H_o but dependent on the chemical environment. Chemical shifts are therefore expressed in terms of a fraction of applied field, usually parts per million (ppm). Since the position of the unshielded resonance is not exactly known, the chemical shift parameter, δ, is used to give the chemical shift between the resonance of interest and another resonance, often that of a reference compound. Hence

$$\delta = \left(\frac{H-H_r}{H}\right) 10^6$$

in ppm, where H is the resonance field and H_r is the resonance field for the reference compound. Alternately, δ may be expressed in terms of frequency differences as

$$\delta = \left(\frac{\nu-\nu_r}{\nu_o}\right) 10^6$$

This is a useful expression, since the magnetic field is in practice calibrated in terms of frequency units by means of frequency modulation at an audio frequency, giving frequency differences as the actual experimental measurements. Chemical shifts may alternately be quoted in frequency units (c/sec) if the oscillator frequency is specified.

Under higher resolution, the spectra of compounds comtaining more than one resonance often show the splitting of several resonances into multiplets. Figure 1.1(b) shows the n.m.r. spectrum[3] of an acidified sample of ethanol at 30.5 Mc/sec under higher resolution. It is seen that, while the hydroxyl proton resonance remains a single peak, the resonances of the methyl and methylene protons are split into three and four peaks respectively. The splitting has its origin in the coupling of nuclear spins through bonding electrons. This interaction, expressed in terms of the spin-spin coupling constant J, is field independent and is usually quoted in c/sec.

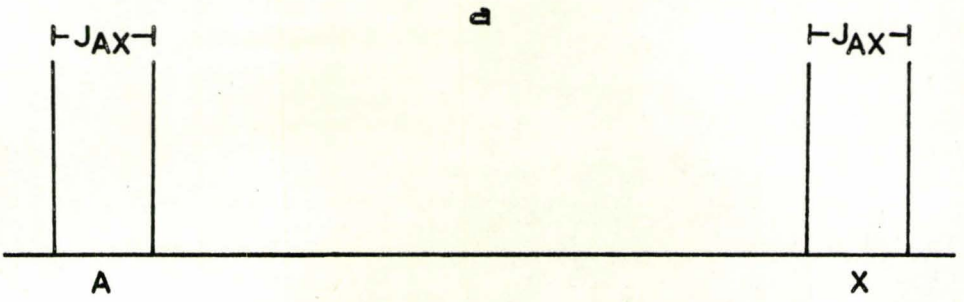
The simplest case of multiplet splitting encountered is that in the so-called AX spectrum, that is, two spin $I = \frac{1}{2}$ nuclei having a spin-spin coupling constant J_{AX} and a chemical shift $\nu_o\delta_{AX}$ (in frequency units) between them which is much larger than J_{AX}. Alternately the two nuclei may be of different spins, for

example ^{1}H and ^{19}F. In the limit $\nu_o \delta_{AX} \gg J_{AX}$, the effect of the coupling is simply to shift the resonance of each nucleus by mJ_{AX}, where m is the expectation value for the spin coupled to the nucleus being resonated. Since $m = \pm \frac{1}{2}$ for both the A and X nuclei, the resonance of each spin is split by the other into two lines J_{AX} apart, giving the four line spectrum shown in Figure 1.2(a). The more general case where one group of p chemically equivalent spin $I = \frac{1}{2}$ nuclei is coupled to another group of n chemically equivalent nuclei which also have spin $I = \frac{1}{2}$ can be designated $A_p X_n$. In this case the A resonance is split into n + 1 lines spaced J_{AX} apart with relative intensities given by the binomial coefficients for n; the X resonance is split into p + 1 lines also spaced J_{AX} apart with relative intensities given by the binomial coefficients for p. This occurs simply because n spins each having $m = \pm \frac{1}{2}$ can add together to give n + 1 different values of $F_z(X)$, the expectation value of total spin for the X nuclei, that is

$$F_z(X) = \sum_x m_x$$

$$= \frac{n}{2}, \quad \frac{n}{2} - 1, \ldots, -\frac{n}{2}$$

A total of n + 1 equally spaced lines then occurs for the spectrum of the A nuclei, the effect of coupling on the A spectrum being to



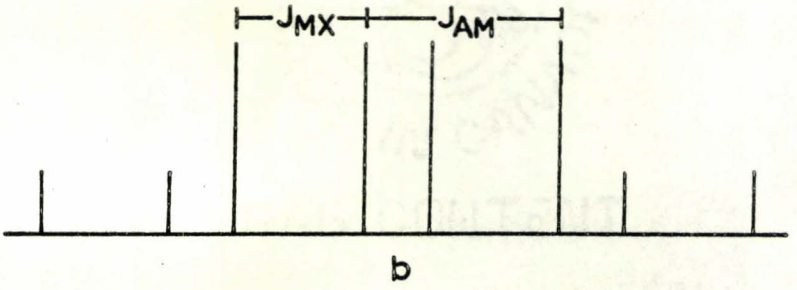


Fig. 1.2 First Order Multiplets.

(a) The AX Case. (b) Splittings in the M Multiplet of the A_3M_2X Case; $J_{AX} = 0$, $J_{AM} > J_{MX}$.

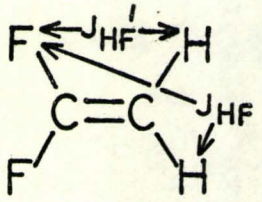
shift the resonance position by $F_z(X)\ J_{AX}$. The relative probability of a particular F_z value, and hence the relative intensity of a particular line in the multiplet, depends on the number of nuclei causing the splitting. This can perhaps best be seen by considering a particular case, for example, the spectrum of acidified ethanol already mentioned. The methyl and methylene protons are coupled. Now the spins of the two methylene protons can add in the following way

F_z	Relative Probability
1	1
0	2
-1	1

Hence the methyl resonance is split into three equally spaced lines of relative intensities 1 : 2 : 1 by the methylene protons, the splitting between adjacent lines being J. Similar considerations give a 1 : 3 : 3 : 1 quartet with the same splitting for the methylene resonance. Multiplet intensities in general may be found from the table of binomial coefficients for values of n up to 6 given below

n	Coefficients
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1
5	1 5 10 10 5 1
6	1 6 15 20 15 6 1

The theoretical A_3X_2 spectrum is shown under the observed spectrum in Figure 1.1(b) and agrees reasonably well with it. Under very high resolution further splittings are observed. These arise because $J/\nu_o\delta = 0.095$ for the ethyl group in ethanol at 30.5 Mc/sec; hence the spectrum calculated assuming $\nu_o\delta \gg J$ is valid only to a first approximation. The complete treatment involves a quantum mechanical analysis. Such a treatment for the spectrum of acidified ethanol would be designated A_3B_2, the use of alphabetically adjacent letters being a convention employed to indicate "strong coupling", that is, that the assumption $\nu_o\delta \gg J$ is no longer made. Methods for such analyses are well known, and may be found in Chapter 6 of reference 1 and also in Chapter 8 of reference 2. It should also be noted that the simple first order theory given above is valid only if all the A-X coupling constants are identical. For certain molecular symmetries this may not be the case; for example, 1,1-difluoroethylene is planar and hence two H-F coupling constants are required to describe the coupling between protons and fluorine in this molecule.



In this case the protons or fluorines are said to be chemically equivalent (same chemical shift) but magnetically non-equivalent. The spectrum of the above molecule, designated either as A_2X_2 ($J \neq J'$) or as AA'XX' to indicate magnetic non-equivalence, depends upon the values of the four coupling constants J_{HF}, $J_{HF'}$, J_{HH} and J_{FF}, no longer has a simple first order appearance, and requires a quantum mechanical treatment for its analysis.

The spectrum of acified ethanol shown in Figure 1.1(b) shows no observable coupling between the hydroxyl and other protons; the hydroxyl resonance is a single line. This situation occurs because rapid exchange of the hydroxyl proton averages out any such coupling. If, however, the spectrum of highly purified ethanol is obtained, coupling is observed. Figure 1.1(c) shows such a spectrum[3]; both the methylene and hydroxyl resonances are split by coupling between the methylene and hydroxyl protons. There appears to be no coupling between the methyl and hydroxyl protons; in general couplings between protons four or more bonds apart are too small to be observed. A first order spectrum may be calculated by extension of the principles given above by assuming $\nu_o \delta >> J$ for both the methyl-methylene and methylene-hydroxyl couplings. The spectrum is then designated as A_3M_2X where A = methyl protons, M = methylene protons, and X = the hydroxyl proton. Taking $J_{AX} = 0$ as discussed above we expect the methyl resonance to be a 1 : 2 : 1 triplet, splitting J_{AM}, and the hydroxyl resonance to be

a 1 : 2 : 1 triplet as well, but with splitting J_{MX}. The methylene resonance we expect to be an eight line multiplet, since the 1 : 3 : 3 : 1 quartet with splitting J_{AM} due to coupling with the methyl protons will have each line split into a doublet of equal intensity, splitting J_{MX}, by coupling with the hydroxyl proton. This expected first order spectrum is shown below the observed spectrum in Figure 1.1(c) and also, giving the multiplet structure in greater detail in Figure 1.2(b). The first order spectrum of any number of groups of magnetically equivalent nuclei may be calculated by similar means. It should be noted that coupling constants can be positive or negative, but that first order spectra give only the magnitude of the coupling, and not its sign.

Couplings to nuclei having $I > \frac{1}{2}$ are somewhat harder to observe because such nuclei have electric quadrupole moments which interact strongly with the molecular electric field gradient at the nuclear site. This interaction causes rapid transitions between the $2I + 1$ spin states of the quadrupolar nucleus, hence any spin-spin coupling to such a nucleus is averaged out unless the quadrupolar nucleus is in an environment of high symmetry. The abundant isotopes of chlorine and bromine have $I = 3/2$; the stable isotope of iodine has $I = 5/2$. Hence in organic halides R - X (X = Cl, Br, I) the asymmetrical environment of the halogen nucleus and its quadrupole moment combine to average out any spin-spin coupling and the proton

or fluorine spectrum behaves as though the halogen nucleus were non-magnetic.

One special case of spin-spin coupling between nuclei having $I = \frac{1}{2}$ is that of the coupling between ^{13}C and either protons or fluorine nuclei. The ^{13}C-^{1}H and ^{13}C-^{19}F coupling constants are on the order of several hundred c/sec in magnitude and are generally obtained from the proton or fluorine spectrum of the molecule with ^{13}C in natural (1.1%) abundance. In such a spectrum coupling to ^{13}C results in the appearance of the so-called ^{13}C satellites, that is small peaks above and below the main resonance. The origin of these satellites may be seen by considering the ^{19}F spectrum[4] of oxalyl chloridefluoride, ClOCCOF, shown in Figure 1.3. The main peak is the resonance of the isotopically normal molecule, that is, one with the non-magnetic ^{12}C in both positions. A small proportion of molecules will, however, have ^{13}C in one or the other position. Coupling between carbon and fluorine then results in splitting of the fluorine resonance of the ^{13}C containing molecule into two peaks. If the ^{13}C is directly bonded to fluorine, the splitting is $J(^{13}CF)$, the one bond carbon-fluorine coupling constant. If the ^{13}C is in the other position, the splitting is $J(^{13}CCF)$, the smaller two bond coupling constant. Hence four peaks, the intensity of each

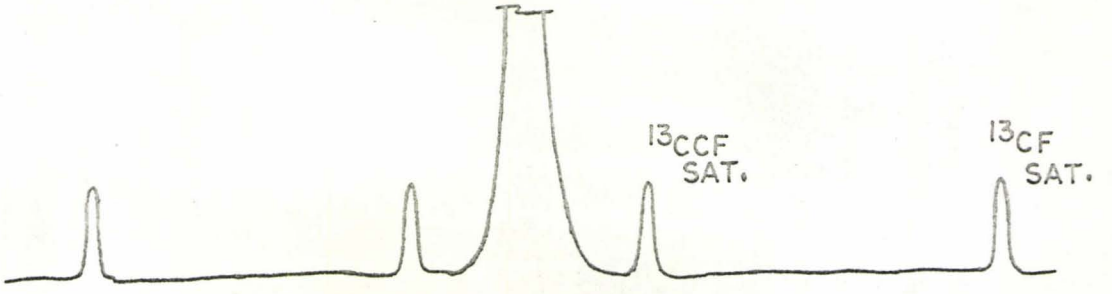


Fig. 1.3 ^{19}F Spectrum of Oxalyl Chloridefluoride at High Gain Showing ^{13}C Satellites.

being approximately ½ of 1% of that of the main peak, are found about the main peak. The variation of ^{13}C coupling constants from molecule to molecule is of considerable interest in bonding studies; in particular, $J(^{13}CH)$ the one bond ^{13}C-^{1}H coupling constant, has been found to be proportional to the s-character of the C-H bond, that is,

$$J_{CH} = J_o \, a_H^2$$

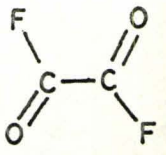
where a_H^2 is the s-character of the C-H hybrid orbital described by the wave function

$$\Psi_{CH} = a_H s + b_H p$$

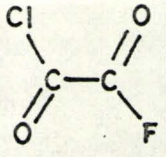
and $J_o \approx 500$ c/sec.

N.m.r. and Fluorine Double Bonding

An earlier study[4] of oxalyl fluoride (I) and oxalyl chloridefluoride (II) in this laboratory showed the magnitude of the direct



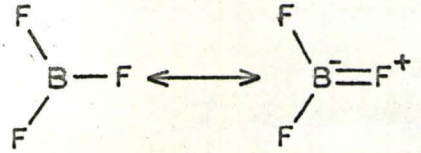
I



II

values of $J(^{13}CF)$ might be expected to occur for them as well. Such double bonding has also been used to explain the unexpected deshielding of the fluorine nucleus in acyl fluorides and tetrahalomethanes.

Considerable evidence exists that fluorine does double bond, despite its high electronegativity. For instance, we might expect the ^{11}B chemical shifts of the boron trihalides, BX_3, to be in the order $BI_3 > BBr_3 > BCl_3 > BF_3$, that is, to parallel the electronegativities of the halogens since a more electronegative halogen would presumably remove some of the electron density from the boron atom and hence deshield it. In fact, the observed chemical shifts[6] are in the expected order for BI_3, BBr_3 and BCl_3, but the chemical shift of BF_3 is between those observed for BI_3 and BBr_3. In other words, the boron atom in BF_3 is not as deshielded as expected. This has led to the suggestion[6] that the boron-fluorine double bonding previously invoked as an explanation for the anomalously short B-F bond distance[7] in BF_3 and for the observed order of Lewis acidities in the boron trihalides[7,8] also affects the ^{11}B chemical shift. The transfer of electron density back to the boron atom by the delocalization of a fluorine lone pair into the empty 2p orbital of boron reshields the boron atom. Hence contributions from resonance structures similar to Vb



Va Vb

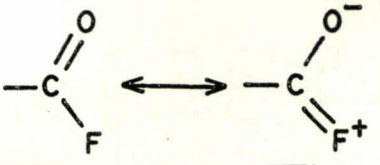
shift the ^{11}B resonance to a higher field than that expected from electronegativity considerations alone. Good and Ritter[9] separated the boron trihalide ^{11}B chemical shifts into a σ-bonding contribution, δ_σ, and a π-bonding contribution, δ_π. Simple l.c.a.o.-molecular orbital calculations gave π-bonding energies which were proportional to the values of δ_π obtained from the observed chemical shifts. The extent of π-bonding calculated was greatest in BF_3.

Gillespie[10] has considered bond angles in the group V trihalides. While the bond angle increases slightly with each member in the series $AsCl_3$, $AsBr_3$, AsI_3, the bond angles in both PF_3 and AsF_3 are anomalously large, in fact, larger than those for all the other members of the same series. Gillespie attributed this to partial double bonding in the fluorides followed by an increased repulsion between the bonding electrons and hence a larger bond angle. Other evidence that resonance structures similar to VIb are more

VIa VIb.

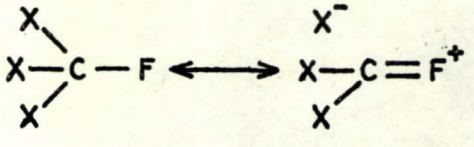
important in PF_3 than in the other phosphorus trihalides is the observed order of ^{31}P n.m.r. chemical shifts[11] in the phosphorus trihalides,

carbon-fluorine coupling constants to be 365.9 c/sec and 376.5 c/sec respectively. Unlike the case of the direct carbon-proton coupling, no simple correlation between the magnitude of the carbon-fluorine coupling constant and a single bond property such as s-character has been found. However, most direct $J(^{13}CF)$ coupling constants fall within the range 200-300 c/sec. The much larger values obtained for the oxalyl halides led Bacon and Gillespie[4] to suggest a contribution to $J(^{13}CF)$ from partial double bond character in the C-F bond, that is from resonance structure IIIb.



IIIa IIIb

Muller and Carr[5] obtained $J(^{13}CF)$ for three other acyl fluorides and a number of tetrahalomethanes, CF_nX_{n-4} Compounds in both of these classes gave unusually large couplings, which fact led Muller and Carr to independently propose C-F partial double bond character for the acyl fluorides. Muller and Carr also noted that since partial fluorine double bonding is also expected for the tetrahalomethanes, owing to contributions from resonance structures similar to IVb, larger

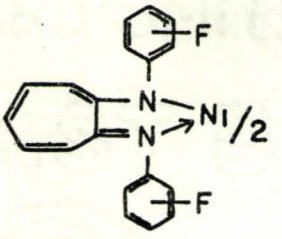


IVa IVb

$PF_3 > PI_3 > PCl_3 > PBr_3$. We see that the PCl_3 and PF_3 shifts are anomalous as far as electronegativity considerations are concerned, that of PCl_3 being shifted slightly and that of PF_3 greatly in the direction expected if double bonding is present.

Eaton and coworkers[12] postulated conjugation between the fluorine atoms and the phenyl rings in nickel (II) N,N'-di (fluorophenyl) aminotroponeimineates (VII) in order

VII



to explain the ^{19}F n.m.r. contact shifts observed. Using the ^{1}H contact shifts, Eaton and his coworkers obtained the electron spin-density at each carbon in the aromatic system in the usual manner[13], that is, the proton hyperfine interaction constant a_N for each ring position was calculated from the observed proton contact shifts and the spin density obtained from the relationship

$$a_N = Q \rho_C$$

where ρ_C is the electron spin density on the ring carbon concerned. The constant Q is -22.5 gauss for a proton directly attached to an aromatic ring. A similar analysis of ^{19}F contact shifts in the

three di(fluorophenyl) derivatives gave fluorine hyperfine constants a_F for fluorine in the ortho, meta or para position of the phenyl ring. The values of a_F found could not be related to the spin densities ρ_C (found from the ^1H contact shifts) by the expected relationship

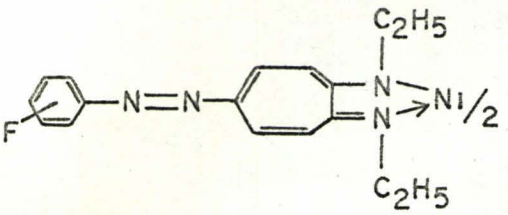
$$a_F = Q\rho_C$$

where Q would be a constant for the C-F bond. Application of this relationship gave values for Q of +44.1 gauss, +4.0 gauss, and +47.2 gauss for fluorine in the ortho, meta and para positions respectively. Eaton and his coworkers therefore suggested a transfer of spin density from the ring carbon to the fluorine by means of $p\pi$-$p\pi$ double bonding between the carbon and fluorine. Such transfer would result in a hyperfine interaction given by the expression

$$a_F = (Q + Q'AP_{CF})\ \rho_C$$

where P_{CF} is the π bond character of the C-F bond, $0<P_{CF}<1$, and Q,Q' and A are constants which are the same for all fluorines bonded to aromatic systems. Using this relationship and values of P_{CF} obtained from simple l.c.a.o.-molecular orbital calculations values

of Q = -147 gauss and Q'A = +848 gauss were obtained. Subsequent work[14] by the same authors on the Y-(fluorophenylazo)-N,N'-diethylaminotroponeiminates (VIII) has led to similar results and a refinement of the values of Q and Q'A.



VIII

Fluorine contact shifts would appear to indicate, therefore, that considerable double bonding occurs between fluorine and the aromatic system in these chelates.

It can therefore be seen that considerable physical evidence exists showing fluorine double bonding to be a fairly common occurence. In boron trifluoride, the empty boron 2p orbital is filled by the donation of a fluorine lone pair. In the phosporus and arsenic trifluorides the incomplete valency shell on the central atom permits double bond formation. The work of Eaton et al. strongly suggests conjugation between a phenyl ring and fluorine attached to it. Hence carbon-fluorine double bonding probably occurs in the acyl fluorides and tetrahalomethanes as well, and the larger values of $J(^{13}CF)$ obtained for these compounds[4,5] may well reflect this double bond character.

Conformation of Oxalyl Halides and Related Molecules

The earlier study on carbon-fluorine coupling in the oxalyl halides[4] also showed the magnitude of the two bond coupling constant, $J(^{13}CCF)$ to be 103.2 c/sec for oxalyl fluoride and 97.0 c/sec for oxalyl chloridefluoride. These are the largest $^{13}C-C-F$ coupling constants known, the two bond coupling constants known for other molecules[4,5,15] having a magnitude $\leq$ 61.0 c/sec. The much larger magnitude of $J(^{13}CCF)$ in the oxalyl halides is rather striking, particularly since Hencher and King[16,17] have concluded from the infrared (vapour) and Raman (liquid) spectra that the oxalyl halides exist only in the trans-planar configuration. It is tempting to attribute the increase in $J(^{13}CCF)$ in the oxalyl halides to this planarity, perhaps by postulating a coupling mechanism operating through a C-C bond having partial double bond character.

The structures of a number of molecules related to the oxalyl halides have been investigated in the solid, liquid, and gas phases by various techniques. The oxalate ion, $C_2O_4^{=}$ nitrogen tetroxide, N_2O_4 and boron tetrafluoride, B_2F_4, are all formally isoelectronic with oxalyl fluoride. Boron tetrachloride, B_2Cl_4, can be considered similar to oxalyl chloride. X-ray diffraction shows that nitrogen tetroxide, boron tetrafluoride and boron tetrachloride all have planar structures in the solid[18].

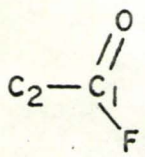
The crystal structures of oxalate salts contain either planar oxalate ions (e.g. $Na_2C_2O_4$) or oxalate ions which have one $-CO_2^-$ group twisted out of plane (e.g. $(NH_4)_2\ C_2O_4.H_2O$, angle of twist $\approx 28^\circ$) depending on the cation[18]. A comparison of the infrared and Raman spectra of N_2O_4 indicates that N_2O_4 retains its planar structure in the liquid and gas phases; the mutual exclusion rule does not appear to be violated and there are no gross differences between the solid, liquid and gas phase spectra[19]. However, recent work[20] has shown that rapid condensation of N_2O_4 results in the trapping of unstable N_2O_4 isomers in the solid phase. One of these isomers appears to be the V_d, or 90° staggered, form of $O_2N\text{-}NO_2$. It appears therefore that small quantities of non planar N_2O_4 may exist in the gas phase along with the planar form.

The retention of planar structure by the N_2O_4 molecule in the liquid and gas phases is in marked contrast to the behaviour of the oxalate ion and the boron tetrahalides. Recently obtained infrared and Raman spectra[21] of the oxalate ion in aqueous solution indicate V_d symmetry, that is, that the planes of the two $-CO_2^-$ groups are at an angle of 90° to each other. Three coincidences between infrared and Raman frequencies would seem to rule out the planar form, yet not enough lines appear to support

a symmetry lower than V_d, hence a 90° angle of stagger is most likely. Gayles and Self[22] have obtained the infrared spectra of B_2F_4 in the gas and the solid states. Band contours in the spectrum of the gas indicate a non-planar conformation. Changes in the spectrum upon solidification probably reflect a change to the planar form observed by X-ray diffraction. It should be noted that Finch et al.[23] have suggested free rotation in gaseous B_2F_4, using an argument based on infrared intensity considerations. Mann and Fano[24] have analyzed the infrared (gas) and Raman (liquid) spectra of B_2Cl_4 and concluded the molecule has V_d symmetry in the liquid and gas phases. A recent electron diffraction study[25] of B_2Cl_4 compares the experimental curve to those expected for V_d symmetry, V_h symmetry, and a freely rotating molecule, showing B_2Cl_4 to have V_d symmetry. In summary, it would appear that the oxalate ion and the boron tetrahalides are all definitely non-planar in the liquid and gas phases, boron tetrachloride having the two $-BCl_2$ groups held staggered at 90° and boron tetrafluoride possibly being free-rotating.

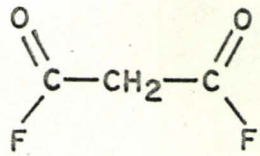
The division of the isoelectronic molecules considered above into two classes, planar (N_2O_4 and the oxalyl halides) and non-planar ($C_2O_4^{=}$ and the boron tetrahalides), together with the

anomalously large two bond carbon coupling constants previously obtained for oxalyl fluoride and oxalyl chloridefluoride suggests a new n.m.r. study of acyl and diacyl fluorides might be revealing. This work reports such a study. Carbon-13 satellites in the ^{19}F spectra of a number of simple acyl fluorides $R_nCH_{3-n}COF$ (R = methyl, ethyl) were observed to obtain, first, more values of $J(^{13}CF)$ for the -COF group and, second and more important, values of $J(^{13}CCF)$ under circumstances where the C_1-C_2 bond (IX) is expected to

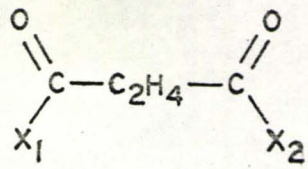


IX

be single. Since J_{HH}, J_{HF} and J_{FF} are generally temperature dependent in molecules which exist in more than one rotational conformer[2], n.m.r. spectra of oxalyl fluoride, malonyl fluoride (X) and several succinyl



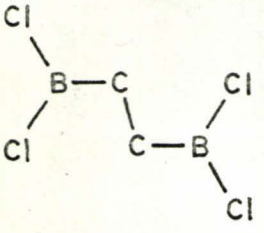
X



XI

halides (XI) were obtained at various temperatures and analysed with a view towards obtaining evidence for or against rotation in

the molecule. The higher diacyl fluorides were included mainly because ethylenebis(dichloroborine), $Cl_2BC_2H_4BCl_2$, has been shown[26] by X-ray diffraction to have nearly a planar form in the solid with the boron and carbon atoms arranged in a zig-zag line (XII), and this



XII

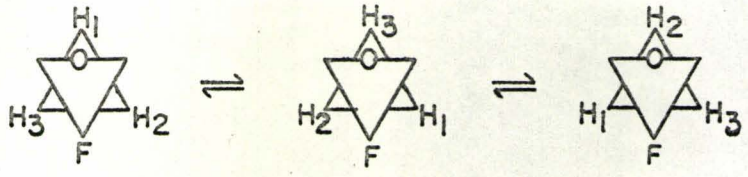
molecule is similar to succinyl chloride. Carbon-fluorine coupling constants were also obtained for the diacyl fluorides to determine if there is, in fact, any correlation between $J(^{13}CCF)$ and the presense or absence of planarity. The results obtained were considered in the light of theoretical mechanisms for $J(^{13}CF)$ and $J(^{13}CCF)$ and the results of simple molecular orbital calculations on some acyl fluorides.

CHAPTER 2

^{19}F Spectra of the Simple Acyl Fluorides

Spin-Spin Coupling in the Acyl Fluorides

The ^{19}F spectra of the acyl fluorides studied, $R_nCH_{3-n}COF$ (R = Me, Et), depend on two types of spin-spin coupling, that between the fluorine and the α-protons, and that between the fluorine and ^{13}C one or two bonds removed. The proton-fluorine coupling constant, J_{HF}, might be expected to vary markedly from member to member in the series, since it is the result of averaging over the three possible rotational conformers. Acetyl fluoride, CH_3COF, has been shown[27] by microwave spectroscopy to have a methyl proton trans to fluorine in its equilibrium conformation, analogous to acetaldehyde[28]. Hence any given methyl proton has one of three equally probably orientations with respect to the fluorine atom, as shown (I).



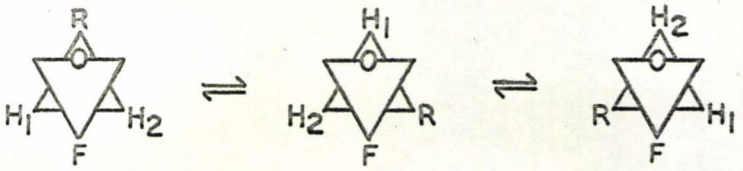
Ia Ib Ic

For sufficiently low barrier heights, rapid interconversion occurs, resulting in an averaged H-F coupling constant given by

$$J_{HF} = (2J_g + J_t)/3$$

where J_t is the coupling for a proton when <u>trans</u> to fluorine and J_g that for a proton in the <u>gauche</u> position. Since rotational averaging results in equal H-F coupling constants, a first order spectrum results.

Substitution at the α-position results in one conformation being more or less stable than the other two. By analogy with propionaldehyde, the conformations of which have been found by microwave[29] and n.m.r.[30], we might expect the conformations shown (II) for an α-monosubstituted acetyl fluoride, IIb and IIc being of equal population.

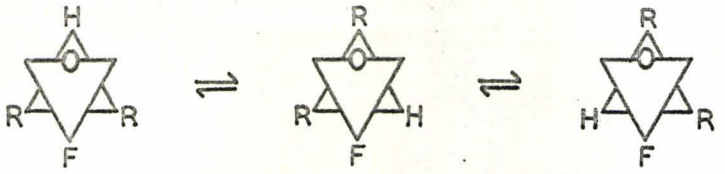


IIa IIb IIc

Taking p as the fractional population of IIa, IIb and IIc each have population (1-p)/2 and the average H-F coupling constant is therefore

$$J_{HF} = pJ_g + (1 - p)(J_g + J_t)/2$$

Disubstitution gives similar conformers (III), and an



IIIa ⇌ IIIb ⇌ IIIc

average coupling constant

$$J_{HF} = pJ_g + (1 - p) J_t$$

where (1 - p) is the fractional population of IIIa. Karabatsos and Hsi[30] have shown by n.m.r. temperature studies that for propionaldehyde, CH_3CH_2CHO, the conformation with the methyl group trans to the aldehyde proton is more stable by 800 cal/mole and for iso-butyraldehyde, $(CH_3)_2CHCHO$, the conformations with one methyl group trans are more stable by 500 cal/mole. By analogy we might expect conformation IIa to be favoured in the case of propionyl fluoride and IIIb and IIIc in that of iso-butyryl fluoride. Substitution at the α-position would therefore favour J_g, the gauche coupling, which might result in a substantial change in J_{HF} upon α-substitution if J_g and J_t are substantially different, as well as temperature variation of the observed H-F coupling.

The ^{19}F resonance of the isotopically normal acyl fluoride molecule should therefore consist of a multiplet of binomial intensities with splitting J_{HF} given by the appropriate expression above. The presence of ^{13}C at either the carbonyl position or the α-position splits this resonance by $J(^{13}CF)$ or $J(^{13}CCF)$ respectively. Owing to isotope effects, caused by differences in zero point energies[1,2], the chemical shift of the ^{13}C containing molecule is increased by a small amount (≤ 0.2 ppm) from that of the isotopically normal molecule. If we use the symbol $\Delta\delta_F$ for these isotope shifts, then the high and low field ^{13}C satellites occur at $\Delta\delta_F + \frac{1}{2} J(^{13}C..F)$ and $\Delta\delta_F - \frac{1}{2} J(^{13}C..F)$ respectively, from the resonance of the isotopically normal molecule. Since all the coupling is first order, any splitting in the resonance of the isotopically normal molecule due to H-F coupling will also be repeated in each of the ^{13}C satellites.

Observed Coupling in the ^{19}F Spectra

The ^{19}F spectrum of acetyl fluoride at high gain, shown in Figure 2.1, gives $J_{HF} = 7.13 \pm 0.11$ c/sec and the values of ^{13}C coupling constants and isotope effects shown in Table 2.1.

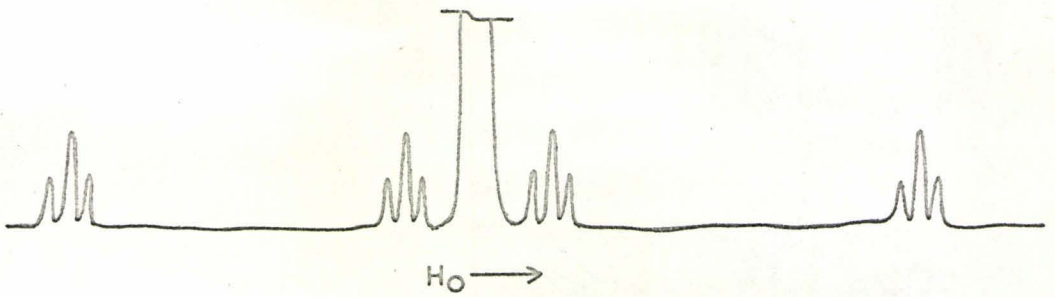


Fig. 2.1 ^{19}F Spectrum of Acetyl Fluoride at High Gain Showing ^{13}C Satellites.

TABLE 2.1

^{13}C Coupling Constants and Isotopic Shifts in Acyl Fluorides

Compound	$J(^{13}CF)$ c/sec	$\Delta\delta$ ppm $(^{13}CF)-(^{12}CF)$	$J(^{13}CCF)$ c/sec	$\Delta\delta$ ppm $(^{13}CCF)-(^{12}CCF)$
CH_3COF[a]	352.8 ± 0.2	+0.133 ± 0.002	59.4 ± 0.3	+0.023 ± 0.003
CH_3CH_2COF	358.2 ± 0.2	+0.128 ± 0.002	53.9 ± 0.2	+0.021 ± 0.004
$CH_3CH_2CH_2COF$	359.6 ± 0.3	+0.129 ± 0.003	50.7 ± 0.3	+0.023 ± 0.004
$(CH_3)_2CHCOF$	365.6 ± 0.2	+0.125 ± 0.002	50.4 ± 0.2	+0.015 ± 0.003
$(CH_3)_3CCOF$	372.0 ± 0.4	+0.122 ± 0.003	46.2 ± 0.3	+0.016 ± 0.003

[a] J_{HF} = 7.13 ± 0.11 c/sec. Muller and Carr (ref.5) have also measured $J(^{13}CF)$ and $J(^{13}CCF)$ for acetyl fluoride

The α-substituted acetyl fluorides studied give no measurable H-F coupling, suggesting either that substitution results in a preponderence of conformers with small H-F coupling or that J_g and J_t are of opposite sign and substitution results in conformer populations at room temperature which give an average coupling constant close to zero. In the next chapter, analysis of the ^1H and ^{19}F spectra of 3,3,3-trifluoropropionyl fluoride, CF_3CH_2COF, yields the values of J_{HF} for this compound at four temperatures over the range -65 to 37°c shown in Table 2.2. These values can be used to obtain J_g and J_t in a fairly simple manner. Referring back to the discussion above on rotational averaging in α-monosubstituted acetyl fluorides, we recall p was taken to be the fractional population of the conformer with the substituent trans to the fluorine. If we take this conformer to be ΔE in energy below the other two, then the fractional populations are given by

$$p : (1-p)/2 = \exp(\Delta E/RT) : 1$$

Hence

$$\Delta E = RT \ln [2p/(1-p)]$$

$$= 2.303\ RT \log [2p/(1-p)]$$

TABLE 2.2

Temperature Dependence of J_{HF} in
3,3,3-Trifluoropropionyl Fluoride

T °C	J_{HF} c/sec
37	0.87 ± 0.03
0	1.68 ± 0.07
-31	2.67 ± 0.10
-65	3.68 ± 0.11

Recalling that

$$J_{HF} = pJ_g + (1 - p)(J_g + J_t)/2$$

it can readily be shown that

$$\Delta E = 2.303RT \log [(J_t + J_g - 2J_{HF})/(J_{HF} - J_g)]$$

A positive ΔE indicates the conformer with the substituent group trans to the fluorine is more stable. A similar derivation gives

$$\Delta E = 2.303\ RT \log [(J_t - J_{HF})/2(J_{HF} - J_g)]$$

for the disubstituted case. In this case a positive ΔE indicates the conformers with one substituent trans to the fluorine are more stable.

In practice, ΔE, J_g and J_t are unknowns, while J_{HF} is known at several temperatures. For CF_3CH_2COF the experimental data was treated in the following way; first of all, since four experimental points are hardly enough to determine three unknowns accurately, the number of unknowns was reduced to two by assuming J_g and J_t the same for all acetyl fluorides.

Since in acetyl fluoride itself $J_{HF} = \frac{1}{3}(2J_g + J_t) = 7.13$ c/sec, therefore $J_t = 21.39 - 2J_g$ c/sec was assumed for CF_3CH_2COF. Substitution of this in the expression for ΔE then gave

$$\Delta E = 2.303RT \log [(21.39 - J_g - 2J_{HF})/(J_{HF} - J_g)]$$

Substitution of the observed J_{HF} at each of the four temperatures into this equation then gave four expressions for ΔE in terms of J_g. Since J_{HF} is of unknown sign, it was first necessary to determine its sign relative to $(2J_g + J_t)$. We note from Table 2.2 that the absolute value of J_{HF} decreases as the temperature is raised to room temperature. Since at high temperatures J_{HF} must tend to $\frac{1}{3}(2J_g + J_t) = 7.13$ c/sec, it is apparent that J_{HF} in CF_3CH_2COF is negative at and below room temperature. Therefore, the values of J_{HF} substituted in the expression for ΔE were taken to be negative with respect to $(2J_g + J_t)$. The value of J_g was then varied until all four calculated values of ΔE were at minimum deviations from each other. Use of this method gave a negative value of J_g for convergence to a positive ΔE. The values obtained were $\Delta E = 950$ cal/mole, $J_g = -7.3$ c/sec and $J_t = 35.9$ c/sec. Convergence to a negative ΔE can also be

obtained; in this case ΔE = -450 cal/mole, J_g = 45.5 c/sec and J_t = -69.6 c/sec. While it is impossible to distinguish between the two assignments on spectroscopic grounds alone, a positive ΔE seems more likely by analogy with the corresponding aldehydes.[29,30]

The values of J_g and J_t obtained for both assignments were used to set limits on the energy differences between the conformers of propionyl fluoride, butyryl fluoride and iso-butyryl fluoride. This was done by assuming J_{HF} to lie in the range $-0.5 \leq J_{HF} \leq 0.5$ for these compounds. Substitution of $J_{HF} = \pm 0.5$ and the values of J_g and J_t obtained above in the appropriate expressions for ΔE gave the limits shown in Table 2.3. The values obtained for assignment 1 are close to those obtained for the corresponding aldehydes[30].

Table 2.1 also includes values for the carbon-fluorine coupling constants and isotope shifts in the other acyl fluorides studied, that is, propionyl fluoride, CH_3CH_2COF, butyryl fluoride, $CH_3CH_2CH_2COF$, iso-butyryl fluoride, $(CH_3)_2CHCOF$, and pivalyl fluoride, $(CH_3)_3CCOF$. The isotope shifts for ^{13}C in both positions are of the same magnitudes as those previously observed[4,5] for fluororganic compounds. It can readily be seen that substitution of methyl groups at the α-position increases the absolute

TABLE 2.3

Energy Differences Between Rotational Conformers Calculated for Various Acyl Fluorides

Compound	ΔE cal/mole Assignment 1	Assignment 2
CH_3CH_2COF	760 to 880	-350 to -440
$CH_3CH_2CH_2COF$		
$(CH_3)_2CHCOF$	490 to 590	-150 to -170
CF_3CH_2COF	960	-450

Assignment 1 : $J_g = -7.3$ c/sec, $J_t = 35.9$ c/sec

Assignment 2 : $J_g = 45.5$ c/sec, $J_t = -69.6$ c/sec

value of $J(^{13}CF)$ and decreases that of $J(^{13}CCF)$. Moreover, all the values of $J(^{13}CF)$ measured are abnormally large, as in the previous studies of acyl fluorides considered in the introduction. The variation of $J(^{13}CF)$ with increasing number of methyl groups sbustituted is of considerable interest, and is discussed in terms of the C-F double bond characters expected from inductive and hyperconjugative effects in the last chapter of this work. The values of $J(^{13}CCF)$ observed suggest strongly that the $\approx$100 c/sec values obtained for oxalyl fluoride and oxalyl chloridefluoride are anomalous. This is also discussed in the last chapter.

CHAPTER 3

Temperature Studies on the Spectra of Oxalyl Fluoride and Malonyl Fluoride

Oxalyl Fluoride

The reported ^{19}F spectrum[4] of oxalyl fluoride, $(COF)_2$, shows a single strong line arising from the isotopically normal species and an eight line ^{13}C satellite spectrum as shown in Figure 3.1. The presence of eight lines in the ^{13}C satellites arises from fluorine-fluorine coupling, which splits each satellite into two lines. In terms of the notation introduced in Chapter 1, the ^{13}C satellite spectrum is the AB portion of an ABX type spectrum, where A represents the nucleus of one fluorine atom, say that directly bonded to the ^{13}C atom, B represents the other fluorine nucleus, and X represents the ^{13}C nucleus. The resonance frequency of each fluorine nucleus differs from that of the main peak by the isotope effect, that is

$$\nu_A = \nu_o \, \delta \, [(^{13}CF) - (^{12}CF)]$$

$$\nu_B = \nu_o \, \delta \, [(^{13}CCF) - (^{12}CCF)]$$

The observed spectrum depends on $\nu_A - \nu_B$, J_{AB}, J_{AX} and J_{BX} Analytical expressions for line positions and intensities are given in the literature[1,2].

... equivalent, but simpler approach to analysis is the effective frequency method.[31,32] In the ABX case, the effective frequency method consists of the introduction of two sets of effective frequencies given by

$$\nu_a = \nu_A \pm J_{AX}$$

$$\nu_b = \nu_B \pm J_{BX}$$

The use of lower case subscripts follows the notation of Diehl et al.[33], that is, indicates effective frequencies. Calculation of an AB spectrum for each set of effective frequencies given above using J_{AB} as coupling constant gives all eight lines of the ABX spectrum. We, therefore, say the AB part of the ABX spectrum has been factored into two ab subspectra. Since an AB spectrum can be readily identified and interpreted, the subspectra can be quickly found and all spectral parameters obtained from them. Using this method, Bacon and Gillespie[4] were able to completely interpret the ^{19}F spectrum of oxalyl

fluoride at room temperature, obtaining J_{FF}, $J(^{13}CF)$, $J(^{13}CCF)$ and both isotope effects, as well as showing $J(^{13}CF)$ and $J(^{13}CCF)$ to have opposite signs.

Reference to the literature[1] shows that J_{AB} appears twice in an AB spectrum, regardless of the magnitude of J_{AB} relative to $\nu_o\delta$. Hence the splitting J_{FF} will appear four times in the ^{13}C satellites of oxalyl fluoride, each satellite being split by this amount. The value of J_{FF} can therefore be obtained directly from the spectrum. Since any rotational isomerism in the molecule should affect J_{FF}, a temperature study of this splitting was undertaken. Table 3.1 shows the values of J_{FF} obtained from the splittings in the ^{13}C satellites at four temperatures over the range -72 to 29°C. It is immediately apparent that J_{FF} is virtually temperature independent, the observed variation being only 1.2% over a temperature range of 101°C. Therefore, oxalyl fluoride, unlike the other molecules studied in this work, does not exist in several interconverting conformers. The temperature independence of fluorine-fluorine coupling indicates that this molecule exists solely in one conformation, presumably the <u>trans</u> planar form,[17] or alternately that the molecule has completely free rotation about the carbon-carbon bond.

TABLE 3.1

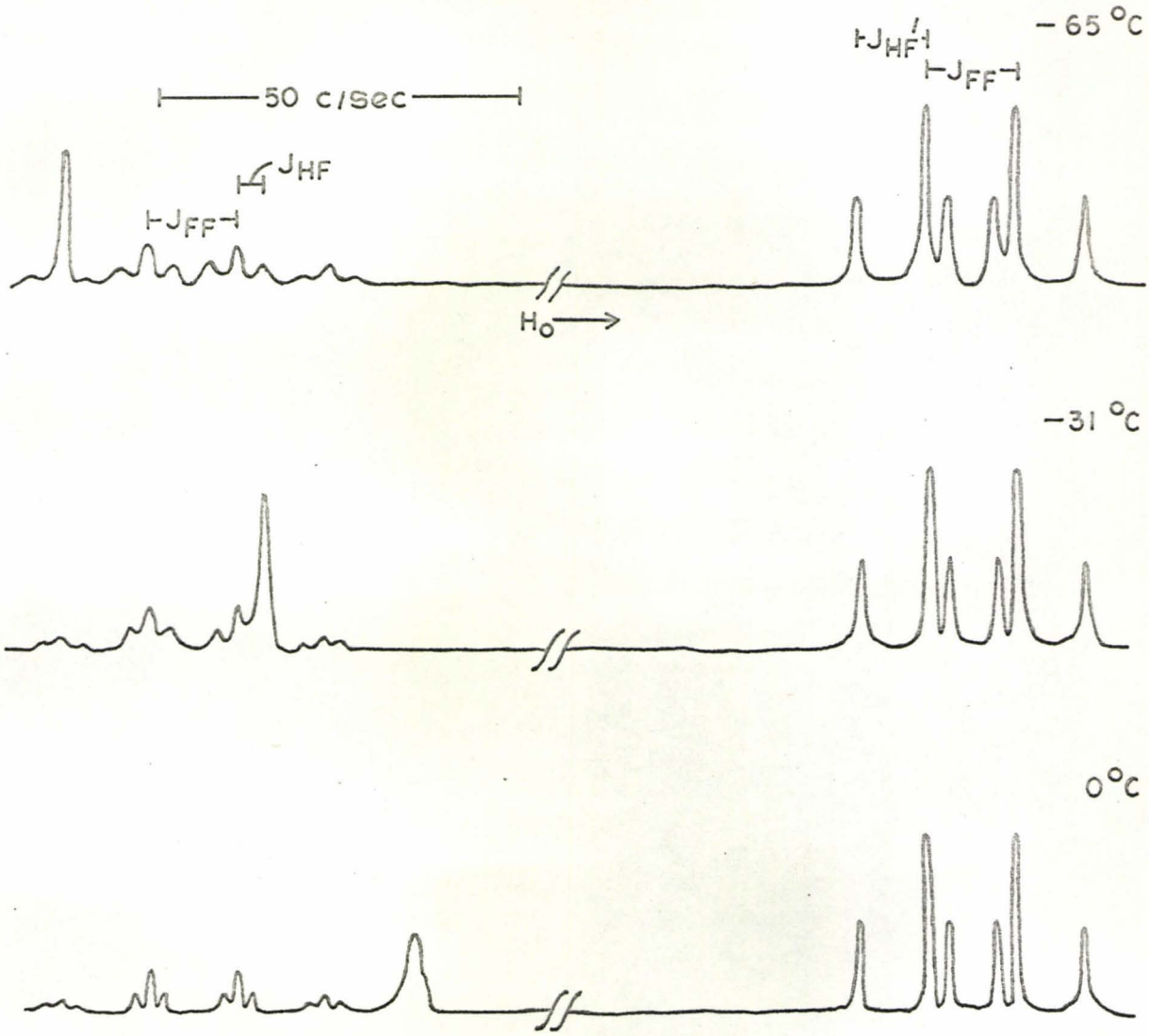
Temperature Dependence of Fluorine-Fluorine Coupling in Oxalyl Fluoride

T°C	J_{FF} c/sec
29	46.75 ± 0.39
-2	47.15 ± 0.33
-43	47.12 ± 0.39
-72	47.31 ± 0.36

Malonyl Fluoride Samples

The ^{19}F spectrum at - 65°C of a sample of the product of the fluorination of malonic acid by sulfur tetrafluoride is shown at the top of Figure 3.2. It is immediately apparent that the sample is not pure, several compounds being present. The low field group of peaks occurs in the chemical shift region associated with acyl fluorides. The group of six peaks at high field is obviously a spin-spin multiplet. Closer examination shows it to be a doublet with J = 12.23 ± 0.28 c/sec, each component of which is split into a triplet with J = 9.41 ± 0.30 c/sec. Examination of the low field group of resonances shows it to consist of another spin-spin multiplet, this time a quartet with J = 12.28 ± 0.26 c/sec, each component of which is split into a triplet having J = 3.68 ± 0.11 c/sec and an additional resonance showing no structure. This additional resonance overlaps the lower component of the quartet.

Hasek, Smith and Englehardt[34] have shown that reaction of a carboxylic acid with sulfur tetrafluoride proceeds in two steps. Under mild conditions the acyl fluoride is formed, while under more vigourous reaction conditions another molecule of sulfur tetrafluoride reacts with the acyl fluoride resulting in the replacement of the carbonyl oxygen.



3.2 ^{19}F Spectrum at Various Temperatures of a Sample Containing Malonyl Fluoride and CF_3CH_2COF

$$RCOOH + SF_4 \longrightarrow RCOF + HF + SOF_2$$

$$RCOF + SF_4 \longrightarrow RCF_3 + SOF_2$$

In the case of a difunctional acid the possibility arises that under intermediate reaction conditions one carbonyl oxygen only will be replaced. For malonyl fluoride this would result in the production of 3,3,3-trifluoropropionyl fluoride, as follows

$$CH_2(COF)_2 + SF_4 \longrightarrow CF_3CH_2COF + SOF_2$$

This compound should give rise to a fluorine resonance of two spin-spin multiplets, a quartet and a doublet, with splitting J_{FF} in each case. Further splitting of each component of these multiplets into triplets by the two protons would also be expected, the splitting being J_{HF} for the quartet and J_{HF}' for the doublet. Considering Figure 3.2 again, it is obvious that a considerable amount of CF_3CH_2COF is present. The high field resonance is assigned to the trifluoromethyl group and the low field resonance to the -COF group. The coupling constants obtained are $J_{FF} = 12.24 \pm 0.27$ c/sec, $J_{HF} = 3.68 \pm 0.11$ c/sec and $J_{HF}' = 9.41 \pm 0.30$ c/sec. The value of J_{HF}' obtained compares favourably to those of 8.0, 8.4, 8.9 and 9.2 given by Elleman, Brown and Williams[35,36] for the proton-fluorine coupling in the $-CH_2CF_3$ group in CF_3CH_2F, CF_3CH_2Cl,

CF_3CH_2Br and $CF_3CH_2CF_3$ respectively. The preparation and identification of CF_3CH_2COF has not previously been reported.

The remaining resonance in the acyl fluoride region is assigned to malonyl fluoride, an assignment which is confirmed by the observation of a simple 1 : 2 : 1 triplet in both the ^{19}F and ^{1}H spectra at higher temperatures (see below). This is the A_2X_2 spectrum expected for malonyl fluoride. Carbon-13 satellites of the malonyl fluoride resonance were also observed at -65°C. Both high and low field satellites were observed for the one bond carbon-fluorine coupling, giving $J(^{13}CF) = 331.03 \pm 0.56$ c/sec and $\Delta\delta = 0.136 \pm 0.005$ ppm. Only the low field satellite could be observed for the two bond coupling, that at high field being overlapped by the quartet. The low field satellite occurred at 30.7 ± 0.95 c/sec below the malonyl fluoride main peak, which, assuming a two bond isotope effect of 0.02 ppm, is equivalent to $J(^{13}CCF) = 63.8 \pm 1.9$ c/sec. This value of $J(^{13}CCF)$ is only slightly larger than those obtained for the α-substituted acetyl fluorides in the previous chapter.

Additional fluorine spectra were obtained at -31 and 0°C and are also shown in Figure 3.2. Figure 3.3 shows the proton spectrum obtained at 37°C with a sample from a second synthesis. The four spectra show J_{HF} in malonyl fluoride

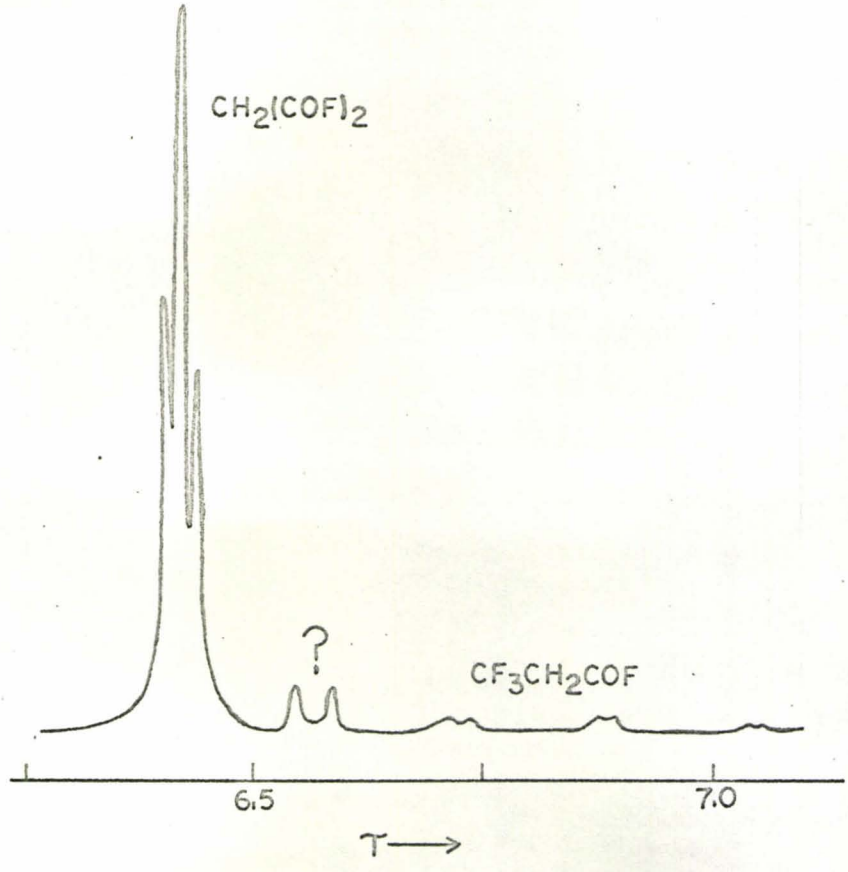


Fig. 3.3 ^1H Spectrum at 37°C of a Sample Containing Malonyl Fluoride and CF_3CH_2COF

increases from a value of close to zero at -65°C to a value of 0.96 ± 0.07 c/sec at 37°C. Where splitting is observed both the ^{1}H and ^{19}F spectra are simple triplets. This clearly indicates that the molecule is undergoing hindered rotation, rather than being held in a planar configuration. Taking $J_g = -7.3$ c/sec and $J_t = 35.9$ c/sec as determined for the acyl fluorides of the previous chapter the expression

$$\Delta E = 2.303\ RT \log [(J_t + J_g - 2J_{HF})/(J_{HF} - J_g)]$$

gives $\Delta E = 730$ cal/mole if J_{HF} is assumed positive, that is, of the same relative sign as J_{HF} in acetyl fluoride. This is likely since the observed J_{HF} in malonyl fluoride increases with temperature. The value $\Delta E = 730$ cal/mole is in quite good agreement with the values obtained for the α-monosubstituted compounds of the previous chapter.

Coupling constants and ^{19}F chemical shifts for CF_3CH_2COF were also measured from each of the four spectra. The values obtained are given in Table 3.2. Chemical shifts are quoted relative to the malonyl fluoride resonance. There is little variation in J_{HF}', but considerable change in J_{HF} with temperature. The value of J_{HF}' should be temperature independent, since all three conformations of the $-CF_3$ group

TABLE 3.2

Temperature Dependence of Coupling Constants and ^{19}F Chemical Shifts in 3,3,3-Trifluoropropionyl Fluoride

T°C	$\nu_o\delta(COF)$ ppm	$\nu_o\delta(CF_3)$ ppm	$J_{F_1F_2}$ c/sec	J_{HF} c/sec	J_{HF}' c/sec
37[a]	-	-	-	0.87±0.03	9.67±0.01
0	-0.547±0.006	111.60±0.01	11.95±0.27	1.68±0.07	9.44±0.22
-31	-0.164±0.007	111.64±0.01	12.15±0.30	2.67±0.10	9.42±0.21
-65	0.340±0.010	111.71±0.02	12.24±0.27	3.68±0.11	9.41±0.30

[a] Coupling Constants taken from ^1H spectrum

are equal in energy. The values of J_{HF} obtained have been used in the previous chapter to obtain values of ΔE, J_g and J_t in α-substituted acetyl fluorides.

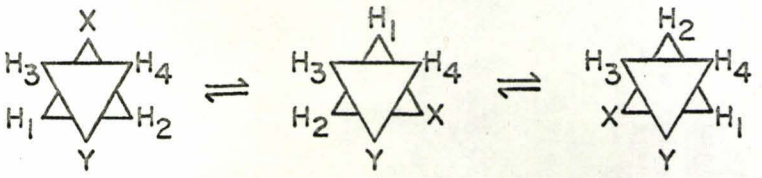
The proton spectrum obtained at 37°C contains two resonances in addition to that of malonyl fluoride. One, a quartet split into doublets, J = 9.67, 0.87 c/sec respectively, is assigned to CF_3CH_2COF. The other resonance consists of two peaks of equal intensity separated by 2.55 c/sec, probably a doublet arising from spin-spin coupling with fluorine. Malonyl fluoride appears to decarbonylate quite readily at room temperature; a gas is given off which collects as a liquid in a trap at liquid nitrogen temperature (-196°C), vaporizes at dry ice temperature (-79°C) and burns with a blue flame, hence carbon monoxide (M.p. -199°C, B.p. -192°C). The unidentified doublet in the proton spectrum may be the resonance of a product of the decarbonylation.

CHAPTER 4

The Succinyl Halides

Proton-Proton Coupling in the Succinyl Halides

Spin-spin coupling between the protons of any succinyl halide can best be understood through consideration of the molecule as a 1,2-disubstituted ethane, XCH_2CH_2Y. Coupling in disubstituted ethanes and the resulting n.m.r. spectra have been considered by a number of authors, notably Sheppard and Turner[37] and Abraham and Pachler[38]. For a substituted ethane, three conformations exist, as shown (I)



Ia Ib Ic

Rapid interconversion between these conformations leads to an averaging of coupling constants, but two coupling constants are in general still required to describe the vicinal coupling.

Taking p as the fractional population of the trans isomer and J_g and J_t as the spin-spin coupling constants for two protons gauche or trans to each other respectively leads to the following average coupling constants

$$J_{13} = J_{24} = J = pJ_g + (1 - p)\,(J_g + J_t)/2$$

$$J_{14} = J_{23} = J' = pJ_t + (1 - p)\,J_g$$

In general J and J' are equal only if the three conformers are equally probable, that is if $p = \frac{1}{3}$, when

$$J = J' = (2J_g + J_t)/3$$

This occurs only for elevated temperatures, or cases where the energy difference between the trans and gauche conformers is zero. Since p is a function of both the energy difference and the temperature, J and J' will in general be temperature and solvent dependent.

The spectrum obtained when J and J' are not equal can be designated AA'BB', or alternately $A_2B_2(J \neq J')$. The analysis of such a spectrum will be discussed in the next section of this

chapter. Analysis does not yield J and J' directly, but rather the absolute values of the sum and difference of J and J', that is of the quantities N and L defined by

$$N = J + J'$$

$$L = J - J'$$

When the spectrum under consideration is that of a 1,2-disubstituted ethane, N and L can be expressed in terms of p, J_g and J_t as

$$N = \frac{1}{2}(3J_g + J_t) + \frac{p}{2}(J_t - J_g)$$

$$L = \frac{1}{2}(1 - 3p)(J_t - J_g)$$

N and L will in general be temperature and solvent dependent. The range of values which J_g and J_t can be expected to take is fairly well known from the literature. Sheppard and Turner[37] obtained the spectra of several 1,2-disubstituted ethanes in the pure liquid and in solution and analyzed them for N and L. Conformer populations were then obtained from infra-red intensity measurements and used to calculate J_t and J_g from the experimental values of N and L. It was found for various compounds that J_t varied over the range 9-18 c/sec while J_g varied from 1.2 to 3.5 c/sec, both couplings having the same relative sign. Other

empirical data and theoretical calculations confirm[39] J_t to be considerably greater than J_g. The quantity $(J_t - J_g)$ appearing in the expression for L can therefore be taken as positive. Hence if the trans conformer is more stable ($\frac{1}{3} \leq p \leq 1$), L is negative; if the gauche conformer is more stable ($0 \leq p \leq \frac{1}{3}$), L is positive. The absence of any information in the A_2B_2 spectrum on the sign of L can be rectified by an elegant rule due to Abraham and Pachler[38]. From the expression for N and L it can be seen that

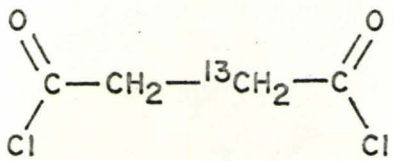
$$(3N + L)/2 = 2J_g + J_t$$

The quantity $(3N + L)/2$ should therefore be independent of temperature or solvent variation within the experimental error if the correct sign of L has been taken. Applying this rule to the values of N and L obtained by solvent variation, Abraham and Pachler were able to show the trans conformation to be the more stable isomer of 1-chloro-2-bromoethane and the gauche isomers to be favoured for 2-chloroethanol and 2-bromoethanol.

Succinyl Chloride

The proton spectrum of isotopically normal succinyl chloride, $ClOCCH_2CH_2COCl$, is a single sharp line ($\tau = 6.63$)

since all four protons have the same chemical shift. However, observation of the ^{13}C satellites in the proton spectrum will yield information on proton-proton coupling, since the two unequal carbon-proton coupling constants (II)



II

introduce an effective chemical shift between the two pairs of protons, resulting in an AA'BB'X spectrum. Since carbon-proton isotope effects are relatively small[2], they can be neglected in the analysis of this spectrum, and the effective frequencies relative to the main peak are therefore given by

$$\nu_a = \pm J(^{13}CH)/2$$

$$\nu_b = \pm (J^{13}CCH)/2$$

and the effective chemical shift is

$$\nu_o \, \delta_{ab} = [J(^{13}CH) - J(^{13}CCH)]/2$$

Since $J(^{13}CCH)$ is generally quite small in ethanic systems, ≈ 4 c/sec, it can be neglected, giving

$$\nu_b \approx$$

$$\nu_o \delta_{ab} \approx J(^{13}CH)/2$$

The AA'BB' part of an AA'BB'X spectrum breaks down into two aa'bb' subspectra. Each ^{13}C-H satellite in the succinyl chloride spectrum is therefore half of an aa'bb' subspectrum having the effective chemical shift and frequencies given above.

The high-field portion of the ^{13}C satellite spectrum of succinyl chloride at three different temperatures is shown in Figure 4.1. In order to interpret these spectra, a computer program was written for the AA'BB' case. First order theory does not apply, since $J \neq J'$. In addition, the condition $\nu_o \delta \gg J$ does not hold since $J(^{13}CH)/2 \approx 65$ c/sec for sp^3-hybridized carbon atoms while N≈10-16 c/sec for 1,2-disubstituted ethanes. The analysis of the AA'BB' case is given in great detail in standard texts[1,2] and in a paper by Grant, Hirst and Gutowsky[40]. The spectrum consists at most of twenty-eight lines, four of which are "combination lines". Hence the A or B portion of the spectrum consists of a maximum of fourteen lines. The spectrum is a function of the chemical shift, N,L, and two further parameters K and M defined by

$$K = J_{AA} + J_{BB}$$

$$M = J_{AA} - J_{BB}$$

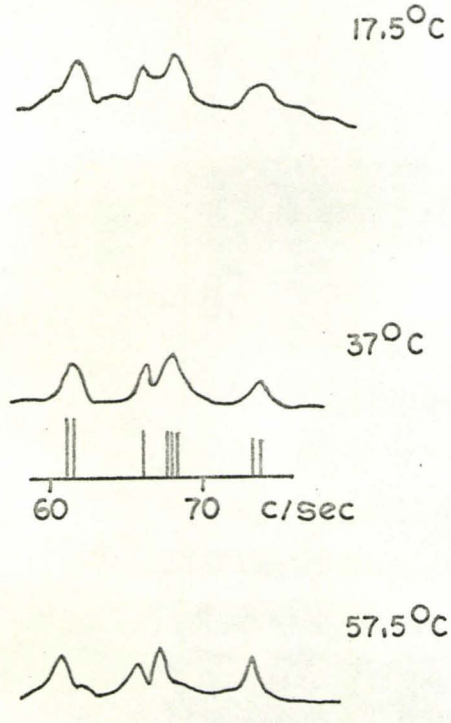


Fig. 4.1 The High Field ^{13}C Satellite in the Proton Spectrum of Succinyl Chloride at Various Temperatures.

The signs of L and M have no effect on the spectrum, while the relative sign of K and N does[40]. Explicit expressions for the frequencies and intensities of all the transitions in the AA'BB' case are not given in the literature, since the solution of a 4 x 4 matrix is involved for some of them. It was therefore necessary in the course of this work to first obtain expressions for the frequencies and intensities of these transitions in terms of the eigenvalues and eigenvectors of the 4 x 4 matrix. Table 4.1 gives the transition frequencies and intensities for all 14 A transitions including the combination lines. The transition numbering is that of Grant, Hirst and Gutowsky[40]. The energies E_i and the coefficients C_{ji} are the eigenvalues and corresponding eigenvectors obtained by numerical solution of the 4 x 4 matrix. The computer program written accepts values of ν_o δ, K, L, M and N, solves the 4 x 4 matrix and calculates line positions and intensities using the expressions in Table 4.1.

For succinyl chloride $J_{AA} = J_{BB}$ of necessity and hence M = 0. As reference to Table 4.1 will show, this reduces the number of lines by two, lines 9 and 10 coinciding, as do lines 11 and 12. The experimental spectrum at 37°C was the first to be fitted. Examination of this spectrum shows that it consists

TABLE 4.1

Frequencies and Intensities for the A Transitions in the AA'BB' Case

Transition	Frequency Relative to $1/2(\nu_A+\nu_B)$	Intensity
1	$1/2\,[(\nu_o\delta)^2+N^2]^{1/2}+N/2$	$1-\sin 2\phi$
2	$-1/2\,[(\nu_o\delta)^2+N^2]^{1/2}-E_1$	$[(c_{11}+c_{31})\cos\phi-(c_{21}+c_{31})\sin\phi]^2$
3	$1/2\,[(\nu_o\delta)^2+N^2]^{1/2}-N/2$	$1+\sin 2\phi$
4	$-1/2\,[(\nu_o\delta)^2+N^2]^{1/2}+E_2$	$[(c_{12}+c_{32})\sin\phi+(c_{22}+c_{32})\cos\phi]^2$
5	$1/2\,[(\nu_o\delta)^2+N^2]^{1/2}-E_3$	$[(c_{13}+c_{33})\sin\phi+(c_{23}+c_{33})\cos\phi]^2$
6	$1/2\,[(\nu_o\delta)^2+N^2]^{1/2}+E_4$	$[(c_{14}+c_{34})\cos\phi-(c_{24}+c_{34})\sin\phi]^2$
7	$1/2\,[(\nu_o\delta)^2+N^2]^{1/2}-E_4$	$[(c_{14}+c_{34})\sin\phi+(c_{24}+c_{34})\cos\phi]^2$
8	$1/2\,[(\nu_o\delta)^2+N^2]^{1/2}+E_3$	$[(c_{13}+c_{33})\cos\phi-(c_{23}+c_{33})\sin\phi]^2$
9	$1/2\,[(\nu_o\delta+M)^2+L^2]^{1/2}+1/2(M^2+L^2)^{1/2}$	$\sin^2(\theta_a-\psi_+)$
10	$1/2\,[(\nu_o\delta-M)^2+L^2]^{1/2}+1/2(M^2+L^2)^{1/2}$	$\cos^2(\theta_a+\psi_-)$
11	$1/2\,[(\nu_o\delta+M)^2+L^2]^{1/2}-1/2(M^2+L^2)^{1/2}$	$\cos^2(\theta_a-\psi_+)$
12	$1/2\,[(\nu_o\delta-M)^2+L^2]^{1/2}-1/2(M^2+L^2)^{1/2}$	$\sin^2(\theta_a+\psi_-)$
13	$1/2\,[(\nu_o\delta)^2+N^2]^{1/2}-E_1$	$[(c_{11}+c_{31})\sin\phi+(c_{21}+c_{31})\cos\phi]^2$
14	$1/2\,[(\nu_o\delta)^2+N^2]^{1/2}+E_2$	$[(c_{12}+c_{32})\cos\phi-(c_{22}+c_{32})\sin\phi]^2$

The angles are defined by the relationships

$$\cos 2\phi : \sin 2\phi : 1 = \nu_o\delta : N : [(\nu_o\delta)^2+N^2]^{1/2}$$

$$\cos 2\psi_\pm : \sin 2\psi_\pm : 1 = (\nu_o\delta \pm M) : L : [(\nu_o\delta \pm M)^2+L^2]^{1/2}$$

$$\cos 2\theta_a : \sin 2\theta_a : 1 = M : L : (M^2+L^2)^{1/2}$$

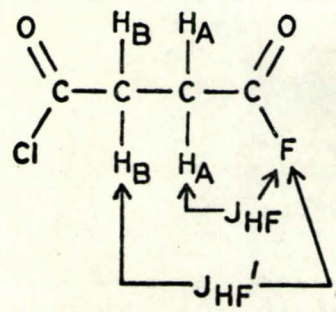
of four peaks at average positions (obtained by the statistical analysis of a number of spectra) 61.51, 66.25, 68.09 and 73.74 c/sec above the resonance of the isotopically normal molecule. A trial theoretical spectrum was calculated assuming ν_a = 65 c/sec, K = -25 c/sec, L = 2 c/sec and N = 12 c/sec. The values of the later three parameters are similar to those obtained by Hirst and Grant[44] for a number of 1,2-disubstituted ethanes. From the trial spectrum it was obvious that only eight lines contribute significantly to the spectrum, lines 3 and 4 overlapping to give the peak at 61.51 c/sec, lines 1 and 2 overlapping to give the peak at 73.74 c/sec, while lines 5, 8 and 10 make up the peak at 68.09 c/sec The remaining peak, at 66.25 c/sec is line 11. Since, from Table 4.1, the splitting between lines 1 and 3 is N and that between lines 10 and 11 is L, fairly accurate estimates of N and L could be made from the observed spectrum. The approximate values of ν_a, N and L were refined by recalculating the spectrum on a trial and error basis and averaging the positions of overlapping lines until the agreement between calculated and observed peak positions was well within the experimental error. It was found that the spectrum was insensitive to changes in K, therefore all spectra were calculated using the arbitrary values -25, -30, -35 and -40 c/sec for K, all four values of K giving the same spectrum to better than $\pm$ 0.01 c/sec. The final fit for the 37°C spectrum used the values N = 12.29, L = 2.40, ν_a = 67.33 c/sec. The theoretical

spectrum so calculated is shown beneath the experimental spectrum in Figure 4.1. The other spectra were fitted in a similar manner.

Table 4.2 shows the values of $J(^{13}CH)$, N and L obtained at each temperature. The temperature variation of N and L indicates that rotation about the central C-C bond is occuring. The last two columns of Table 4.2 show the quantities $(3N + L)/2$ and $(3N - L)/2$. The near invariance of $(3N + L)/2$ with temperature indicates that L is positive and hence the gauche conformers are favoured. In theory an analysis for ΔE, J_g and J_t similar to that done for the substituted acetyl fluorides of Chapter 2 could be carried out. This was attempted, but the experimental variation in N and L is not great enough to give meaningful results.

Succinyl Chloridefluoride

The proton spectra at 35°C of a number of succinyl chloridefluoride (III) samples are shown in Figure 4.2. Although none



III

TABLE 4.2

Spectral Parameters for Succinyl Chloride at Several Temperatures

T°C	$J(^{13}CH) = 2\nu_a$	N	L	(3N+L)/2	(3N-L)/2
17.5	134.7	12.13	2.55	19.47	16.92
37	134.5	12.29	2.40	19.65	17.24
57.5	134.6	12.47	1.90	19.65	17.76

of the three samples used was completely free of succinyl chloride or succinyl fluoride, it was possible to obtain the positions and intensities of most of the peaks in the spectrum of the chloridefluoride by refering to all three of the spectra shown. The spectrum of isotopically normal succinyl chloride-fluoride is another example of the AA'BB'X case, and hence the proton spectrum consists of two aa'bb' subspectra. For the chloridefluoride, the effective frequencies are given by

$$\nu_a = \nu_A \pm J_{AX}/2 = \nu_A \pm J_{HF}/2$$

$$\nu_b = \nu_B \pm J_{BX}/2 = \nu_B \pm J_{HF'}/2$$

and the effective chemical shifts are

$$\nu_o \, \delta_{ab} = (\nu_A - \nu_B) \pm (J_{HF} - J_{HF'})/2$$

$$= \nu_o \, \delta_{AB} \pm (J_{HF} - J_{HF'})/2$$

It is possible to obtain the relative signs of J_{HF} and $J_{HF'}$ from the proton spectrum. Since J_{AX} and J_{BX} are small compared to $\nu_o \, \delta_{AB}$ in the case of succinyl chloridefluoride, the two subspectra overlap considerably. The spectrum

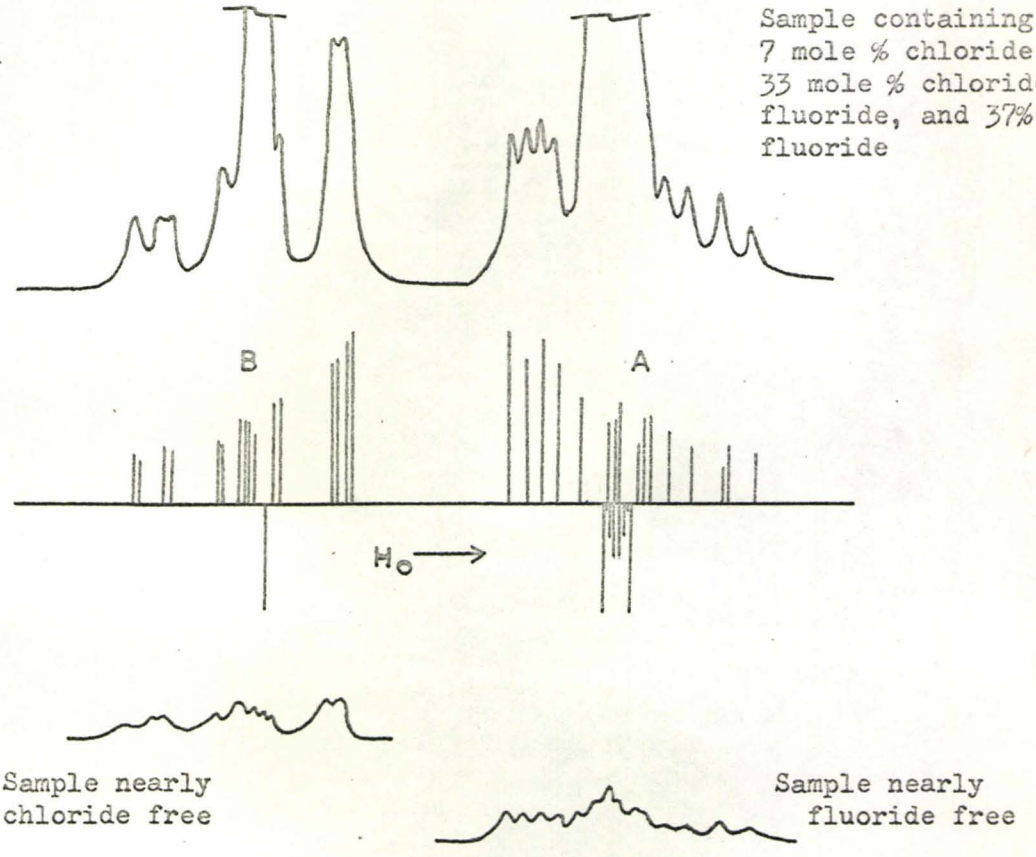


Fig. 4.2 ^1H Spectra of Succinyl Chloridefluoride Samples at 35°C

The Theoretical Spectrum Shown is that calculated for $\nu_o\delta_{AB} = 23.16$, $J_{HF} = 2.22$, $J_{HF}' = -0.30$, $K = -45$, $L = 2.15$, $M = 0$ and $N = 12.86$ c/sec. The Negative Lines Shown in the Theoretical Spectrum are those Arising from Trace Amounts of the Chloride or Fluoride.

was analyzed in a manner similar to that already outlined for the succinyl chloride case. A trial spectrum, consisting of two subspectra, was calculated using appropriate values of $\nu_o\ \delta_{ab}$, K, L and N. The values of $\nu_o\ \delta_{ab}$ and N used for the trial spectrum were estimated from the experimental spectrum. M was taken as zero. Both values of $\nu_o\ \delta_{ab}$, and those of K, L and N were varied by trial and error until the deviations between the observed and calculated spectra were minimized. For most lines the deviations were as small as 0.01 c/sec. From a comparison of the calculated and experimental spectra it was obvious that small amounts ($\approx$2 mole%) of the chloride and fluoride were present in the "chloride-free" and "fluoride-free" samples respectively. Allowance was made for this in the analysis.

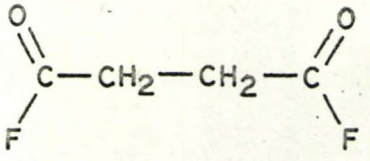
The best fit obtained, shown in Figure 4.2, has $\nu_o\ \delta_{AB}$ = 23.16, J_{HF} = 2.22, J_{HF}' = -0.30, L = 2.15, M = 0 and N = 12.86 c/sec. The value of K chosen has a moderate effect on the spectrum. Close agreement between observed and calculated spectra was obtained for K = -35, -40 and -45 c/sec, K = -45 giving the closest agreement. This is a larger negative value for K than is usually encountered for substituted ethanes[41], presumably due to the presence of two carbonyl groups in this

molecule; several authors[42,43] have shown experimentally and theoretically that J_{gem} becomes more negative when a π-system is attached to the methylene group under consideration. In the succinyl halides K is the sum of two such geminal coupling constants and hence might be expected to have a much larger negative value than usual.

In the AA'BB'X spin system it is theoretically impossible to distinguish between the A and B resonances. However, the larger H-F coupling constant for the resonance at higher field implies that it is the resonance of the protons α to the $-C\lessgtr^{O}_{F}$ group. Moreover, the chemical shift obtained for the resonance at lower field is the same, to 0.01 ppm, as that of succinyl chloride. The high and low-field resonances can therefore be assigned to the protons α and β to the $-C\lessgtr^{O}_{F}$ group, respectively. On the τ-scale the chemical shifts are $\tau_A = 7.01$, $\tau_B = 6.62$. Succinyl chloridefluoride has not previously been reported.

Succinyl Fluoride

The proton spectrum of succinyl fluoride (IV) at 35°C



IV

is shown in Figure 4.3. The main feature of this spectrum is the three intense peaks, which are separated by 0.88 c/sec and centred on τ = 7.02. The spectrum is not a simple 1 : 2 : 1 triplet, since the height of the central peak is about the same as that of the other two. This situation arises because the protons are unequally coupled to the two fluorines, resulting in a more complex spectrum. The central peak actually arises from a number of overlapping lines. The spin system of the isotopically normal molecule is one usually termed AA'A"A"'XX', and involves fifteen coupling constants. As in the case of succinyl chloride, the six proton-proton coupling constants are

$$J_{13} = J_{24} = J$$

$$J_{14} = J_{23} = J'$$

$$J_{12} = J_{34} = J_{gem} = K/2$$

There are eight proton-fluorine coupling constants, four of which are given by J_{AX}, the other four being given by J_{AX}'. It should be noted that each group of methylene protons is

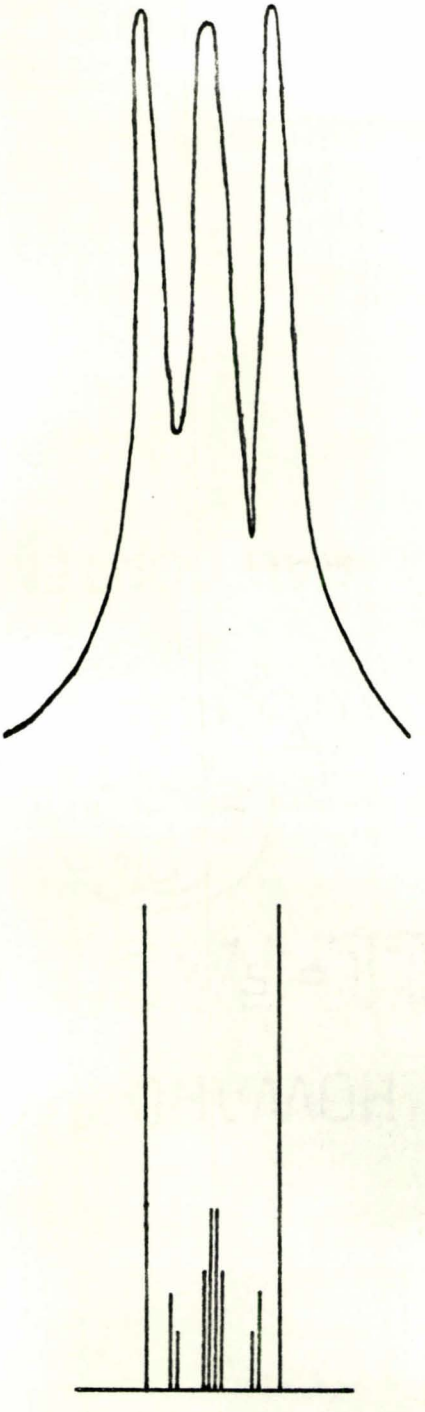


Fig. 4.3 ^{1}H Spectrum of Succinyl Fluoride at 35°C and Theoretical AA'A"A"' XX' Spectrum

coupled J_{AX} to one fluorine and J_{AX}' to the other. The last of the fifteen coupling constants is that between the two fluorines J_{XX}.

The AA'A"A"'XX' case was first considered by Lynden-Bell, who analyzed the spectra of diphosphine[44] and 1,2-^{13}C ethylene[45], which are both of this type. Lynden-Bell has also published the matrix elements for this case and discussed the spectrum[46]. The most prominent feature of the A spectrum is two strong lines centred on ν_A and separated by $|J_{AX} + J_{AX}'|$, that is, occuring at frequencies

$$\nu_a = \nu_A \pm (J_{AX} + J_{AX}')/2$$

The intensity of each of these lines is one-quarter that of the entire A spectrum. Lynden-Bell also found that the positions of sixteen other lines in the A spectrum could be given explicitly. These resonances occur at frequencies

$$\nu_A \pm \{\tfrac{1}{2}\,[(J_{AX}-J_{AX}')^2 \pm (N + J_{XX})^2]^{1/2} \pm \tfrac{1}{2}\,(N+J_{XX})\}$$

$$\nu_A \pm \{\tfrac{1}{2}\,[(J_{AX}-J_{AX}')^2 \pm (N - J_{XX})^2]^{1/2} \pm \tfrac{1}{2}\,(N-J_{XX})\}$$

$$\nu_A \pm \{\tfrac{1}{2}\,[(J_{AX} - J_{AX}')^2 \pm (L - J_{XX})^2]^{1/2} \pm \tfrac{1}{2}\,(L - J_{XX})\}$$

$$\nu_A \pm \{\tfrac{1}{2}\,[(J_{AX} - J_{AX}')^2 \pm (L + J_{XX})^2]^{1/2} \pm \tfrac{1}{2}\,(L + J_{XX})\}$$

where N and L are as previously defined, that is,

$$N = J + J'$$

$$L = J - J'$$

(A different set of parameters was used by Lynden-Bell). Neglecting combination lines, thirty-two transitions remain. Half of these involve the solution of one 4 x 4 matrix; the other half that of another 4 x 4 matrix. The solutions must be performed numerically.

An attempt to further simplify the AA'A"A"'XX' case was made by Diehl[47]. Although the effective frequency method, used several times in this work, breaks down for two unequally coupled X spins, it has been shown[33] that the additional introduction of effective coupling constants often permits the factoring of a spectrum of this type into several sub-spectra. In this manner the ABB' part of the ABB'XX' spectrum

of pyridine has been shown[33,47] to consist of two ab_2 and two abc subspectra. Diehl reported[47] that the A part of the AA'A"A"'XX' spectrum is composed of two a_4 subspectra, that is, single lines, at effective frequencies

$$\nu_a = \nu_A \pm (J_{AX} + J_{AX'})/2$$

and two aa'bb' subspectra, each having effective resonance frequencies

$$\nu_a = \nu_A + (J_{AX} - J_{AX'})/2$$

$$\nu_b = \nu_A - (J_{AX} - J_{AX'})/2$$

and chemical shift

$$\nu_o \delta_{ab} = (J_{AX} - J_{AX'})$$

The effective coupling parameters in the subspectra were said by Diehl to be

$$k = K \mp 2 J_{XX}$$

$$l = L \mp J_{XX}$$

$$m = 0$$

$$n = N \pm J_{XX}$$

the upper signs being taken for one subspectrum and the lower signs for the second. Recently this has been questioned in the literature[48], and it appears that Diehl was in error. During the course of this work an attempt was made to check Diehl's subspectral analysis by using it to calculate the proton spectrum of diphosphine reported by Lynden-Bell[44]. Substitution of the diphosphine spectral parameters reported by Lynden-Bell into Diehl's subspectral expressions gave a calculated spectrum which was in gross disagreement with both the experimental and calculated spectra of Lynden-Bell. It was therefore concluded that Diehl's subspectral transformations for this spin case were invalid, and a computer program was written for the AA'A"A"'XX' case following Lynden-Bell's approach.

Rather than use the matrix elements given by Lynden-Bell[46], matrix elements were calculated for a different set of basis wave functions. These wave functions were simple linear combinations, within a given sub-matrix, of those used by Lynden-Bell. The basis functions used here therefore give different matrix elements, but have the same symmetry properties and lead to the same solutions as those used by Lynden-Bell. A different set of basis functions was chosen

in this work to better consider the analogy with the AA'BB' case. The basis functions and matrix elements obtained for the $F_z(X) = 0$ states of A_1 symmetry are shown in Table 4.3. The matrix elements for the $F_z(X) = 0$ states of B_2 symmetry can be obtained from Table 4.3 by replacing J_{XX} with $-J_{XX}$. The transition frequencies involving states of A_2 and B_1 symmetry and those having $F_z(X) = \pm 1$ have already been given in explicit form by Lynden-Bell[46]. Two properties of the spin system can be noted here, namely that the number of transitions is the same as for two a_4 and two aa'bb' subspectra, and that if $J_{XX} = 0$ the spectrum consists of the two strong peaks separated by $|J_{AX} + J_{AX'}|$, plus one aa'bb' subspectrum with subspectral parameters

$$\nu_a = \nu_A + (J_{AX} - J_{AX'})/2$$

$$\nu_b = \nu_A - (J_{AX} - J_{AX'})/2$$

$$\nu_o \delta_{ab} = (J_{AX} - J_{AX'})$$

$$k = K$$

$$l = L$$

$$m = 0$$

$$n = N$$

TABLE 4.3

$F_z(X) = 0$ A_1 Basis Functions and Matrix Elements for the $AA'A''A'''XX'$ Case

$F_z(A)$	No.	Wave Function	Diagonal Matrix Elements *	Off-Diagonal Matrix Elements
2	1	$(\alpha\alpha\alpha\alpha\alpha\beta+\alpha\alpha\alpha\alpha\beta\alpha)/\sqrt{2}$	$2\nu_A + (N+J_{XX})/2$	
1	1	$(\alpha\beta\alpha\alpha\alpha\beta+\beta\alpha\alpha\alpha\alpha\beta+\alpha\alpha\alpha\beta\beta\alpha+\alpha\alpha\beta\alpha\beta\alpha)/2$	$\nu_A - (J_{AX} - J_{AX}')/2$	$H_{12} = (N+J_{XX})/2$
	2	$(\alpha\alpha\alpha\beta\alpha\beta+\alpha\alpha\beta\alpha\alpha\beta+\alpha\beta\alpha\alpha\beta\alpha+\beta\alpha\alpha\alpha\beta\alpha)/2$	$\nu_A + (J_{AX} - J_{AX}')/2$	
0	1	$(\beta\beta\alpha\alpha\alpha\beta+\alpha\alpha\beta\beta\beta\alpha)/\sqrt{2}$	$-(J_{AX} - J_{AX}') - N/2$	$H_{12} = J_{XX}/2$
	2	$(\alpha\alpha\beta\beta\alpha\beta+\beta\beta\alpha\alpha\beta\alpha)/\sqrt{2}$	$(J_{AX} - J_{AX}') - N/2$	$H_{13} = H_{23} = N/2$
	3	$(\alpha\beta+\beta\alpha)(\alpha\beta+\beta\alpha)(\alpha\beta+\beta\alpha)/2\sqrt{2}$	$J_{XX}/2$	$H_{14} = H_{24} = L/2$
	4	$(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)(\alpha\beta+\beta\alpha)/2\sqrt{2}$	$J_{XX}/2 - K$	$H_{34} = -L/2$
-1	1	$(\alpha\beta\beta\beta\alpha\beta+\beta\alpha\beta\beta\alpha\beta+\beta\beta\alpha\beta\beta\alpha+\beta\beta\beta\alpha\beta\alpha)/2$	$-\nu_A + (J_{AX} - J_{AX}')/2$	$H_{12} = (N+J_{XX})/2$
	2	$(\alpha\beta\beta\beta\beta\alpha+\beta\alpha\beta\beta\beta\alpha+\beta\beta\alpha\beta\alpha\beta+\beta\beta\beta\alpha\alpha\beta)/2$	$-\nu_A - (J_{AX} - J_{AX}')/2$	
-2	1	$(\beta\beta\beta\beta\alpha\beta+\beta\beta\beta\beta\beta\alpha)/\sqrt{2}$	$-2\nu_A + (N+J_{XX})/2$	

* For convenience, $(K-J_{XX})/4$ is subtracted from all diagonal matrix elements. This makes no difference in calculating transition energies.

The total intensity of the aa'bb' subspectrum in this case is one-half that of the entire A spectrum.

The computer program incorporating the theory discussed above was first checked by calculating the diphosphine spectrum. Reference to the spectrum of Figure 4.3 indicates $|J_{AX} + J_{AX}'| = 1.76$ c/sec for succinyl fluoride. The remainder of the theoretical spectrum was calculated using $|J_{AX} - J_{AX}'| = 2.36$, $K = -40$, $L = 1.9$, $N = 13.4$ and $J_{XX} = 0$ c/sec. The stronger lines of the spectrum so calculated are shown below the experimental spectrum in Figure 4.3. The parameters used above are about the values that would be expected from comparison with the other succinyl halides studied. They have no great significance, other than to show that the height of the central peak in the spectrum observed is accounted for by theory.

Proton spectra obtained for five temperatures over the range -33 to 92°C are shown in Figure 4.4. It can readily be seen that $|J_{AX} + J_{AX}'|$ varies markedly with temperature, from 2.67 ± 0.02 c/sec at the lowest temperature to 0.92 ± 0.03 c/sec at the highest. This can only mean that the molecule is experiencing hindered rotation and that the conformer populations change with temperature. Therefore, succinyl fluoride, like succinyl chloride, occurs in more than one rotational conformer.

Analysis of the ^{13}C satellites in the ^{19}F spectrum gives $J(^{13}CF) = 357.3 \pm 0.4$, $J(^{13}CCF) = 58.1$ c/sec.

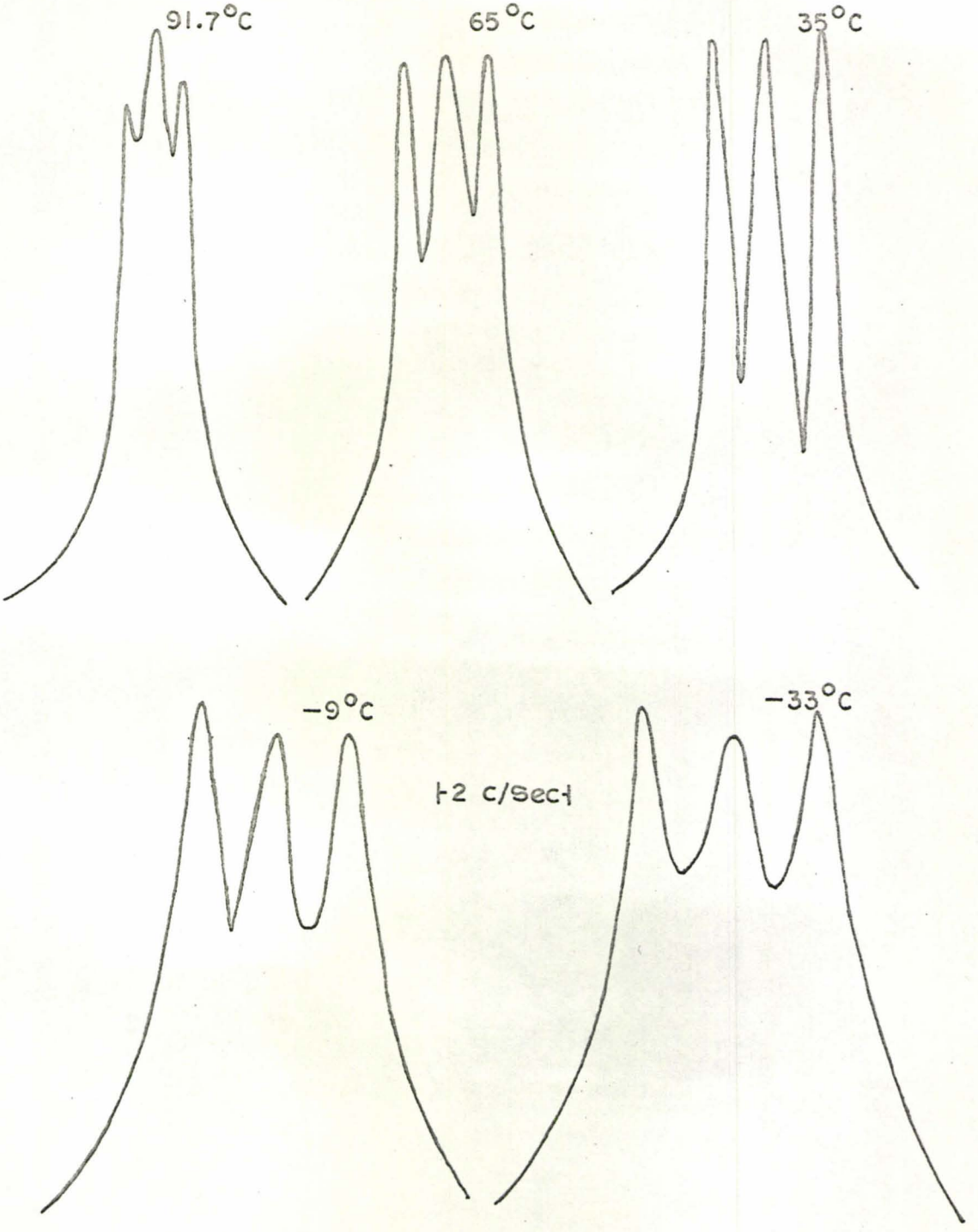


Fig. 4.4 ^{1}H Spectra of Succinyl Fluoride at Various Temperatures

CHAPTER 5

Compound Preparation and N.M.R. Technique

Compound Preparation

Succinyl chloride was obtained commercially and purified by distillation under vacuum. Acetyl fluoride, propionyl fluoride, butyryl fluoride and pivalyl fluoride were obtained from Dr. G. Olah, Dow Chemical of Canada Limited, Sarnia, Ontario. Malonyl fluoride was prepared by fluorinating malonic acid with sulfur tetrafluoride[34]. The remaining compounds studied were prepared by metathesis of the acid chloride with sodium fluoride[49]. The details of the preparations done in the laboratory are given below.

Isobutyryl Fluoride

A mixture consisting of 12.1 gm. (0.114 moles) isobutyryl chloride and 9.2 gm. (0.219 moles) sodium fluoride dissolved in 10.3 ml. of N,N-dimethyl formamide was refluxed for 90 minutes. The isobutyryl fluoride produced was then allowed

to distill out of the reaction mixture, giving 5.55 gm. (53% yield) of $(CH_3)_2$ COF.

Oxalyl Fluoride

A mixture consisting of 8.3 ml (0.097 moles) oxalyl chloride and 16.2 gm (0.386 moles) sodium fluoride dissolved in 28.0 ml of acetonitrile was placed in a stainless steel autoclave. The sealed autoclave was placed in a mechanical shaker for 3 1/2 hours, during which time the temperature was gradually raised from 70°C to 128°C. The autoclave was then connected to a vacuum line and carbonyl fluoride removed by distillation with the autoclave held at dry ice temperature. Oxalyl fluoride was then distilled out with the autoclave surrounded by an ice water bath. After purification by re-distillation, oxalyl fluoride was distilled into an n.m.r. tube and the tube sealed off under vacuum.

Malonyl Fluoride

19.72 gm (0.190 moles) of dry malonic acid was placed in a stainless steel autoclave which was then connected to a vacuum line. 24.0 ml (0.433 moles) of sulfur tetrafluroide which had

been bubbled through a mercury trap to remove impurities was then distilled into the autoclave. The sealed autoclave was placed in a mechanical shaker for 16 hours at 40 - 45°C. The HF and SOF_2 produced were removed by vacuum distillation with the autoclave held at dry ice temperature. Malonyl fluoride was then distilled out with the autoclave at room temperature and sealed into a glass n.m.r. tube. The extreme tendency of malonyl fluoride to undergo decarbonylation and hydrolysis made it impossible to obtain a reliable measure of the yield. 3,3,3-trifluoropropionyl fluoride was also produced in this synthesis. A second synthesis gave similar results.

Succinyl Fluoride

7.8 ml (0.071 moles) of succinyl chloride and 11.8 gm (0.281 moles) of sodium fluoride dissolved in 30 ml of acetonitrile were refluxed under reduced pressure (≈350 mm) at 80 - 90°C for four hours. At the end of this time the product and solvent were distilled out of the reaction mixture under reduced pressure. The acetonitrile was removed by distillation at reduced pressure through a column packed with glass rings, leaving 4.3 gm (50% yield) of succinyl fluoride. The product was identified by its ^{1}H and ^{19}F spectra. The proton spectrum showed the product to contain

approximately 30 mole % acetonitrile, corresponding to a true succinyl fluoride yield of 44%.

Succinyl Chloridefluoride

The procedure used to prepare and purify succinyl fluoride was repeated using 8.5 ml (0.077 moles) of succinyl chloride and 5.94 gm (0.141 moles) of sodium fluoride dissolved in 25 ml of acetonitrile. 6.4 gm of product was collected. The ^{1}H spectrum of a sample of the product showed it to be 23 mole % acetonitrile, 7 mole % succinyl chloride, 33 mole % succinyl chloridefluoride and 37 mole % succinyl fluoride. This corresponds to yields of 25% for the chloridefluoride and 28% for the fluoride.

A sample free of the chloride was obtained by redistillation. A sample free of the fluoride was obtained using a reaction mixture of 12.0 ml (0.108 moles) succinyl chloride and 2.26 gm (0.054 moles) sodium fluoride in 25 ml of acetonitrile and repeated distillation. A sample free of both the chloride and the fluoride could not be obtained with any reasonable number of distillations, presumably because the three boiling points are too close. The boiling point of succinyl chloridefluoride lies between those of the fluoride and the chloride.

N.m.r. Spectra

The compounds studied were sealed in 5 mm o.d. precision glass n.m.r. sample tubes. All the difunctional acyl fluorides studied were degassed and sealed under vacuum to remove any HF present, which might otherwise promote fluoride ion exchange. Fluorine spectra were obtained at 56.445 Mc/sec using a Varian Associates DP-60 spectrometer. Proton spectra were obtained at 60.000 Mc/sec using a Varian Associates A-60 spectrometer. Fluorine spectra were calibrated by generating audio sidebands using a Muirhead-Wigan D-890-A Decade Oscillator. As many as twenty spectra were recorded and a statistical analysis performed on the results, enabling line positions to be found to a standard deviation equal to, or less than, 0.3 c/sec. Proton spectra were calibrated using the A-60 chart scale. In the case of the succinyl chloride satellite spectra, six to eight spectra were recorded at each temperature and a statistical analysis performed to avoid the effects of random noise on the spectrum. A standard deviation of 0.1 c/sec was achieved in this manner. Fluorine temperature studies were performed using a Varian Associates Model V4340 Variable Temperature Probe Assembly and THR Insert. Temperatures were measured using a Leeds and Northrup No.8692 Temperature Potentiometer connected to a copper-constantan thermocouple. Proton temperature studies

employed a Varian Associates V6040 Variable Temperature Controller. Temperatures on the V6040 Controller were checked using the temperature dependence of the chemical shift in the spectra of ethylene glycol and methanol.

Computer programs were written in FORTRAN IV language and run on the IBM 7040 computer in the McMaster Computer Centre.

CHAPTER 6

Conclusions

Summary of Experimental Results

Table 6.1 gives a summary of the one and two bond carbon-fluorine coupling constants obtained during the course of this work. It appears from the previous chapters of this work that all the compounds listed in Table 6.1 except oxalyl fluoride undergo hindered rotation, the energy difference between rotational isomers being 1 kcal/mole or less. In the case of oxalyl fluoride, the invariance of J_{FF} with temperature indicates the molecule is held to one conformation, or else is undergoing completely free rotation. The former conclusion is in agreement with the vibrational spectra[17]. Examination of Table 6.1 shows a correlation of $J(^{13}CCF)$ with $J(^{13}CF)$ if the values for oxalyl fluoride are excluded, namely that an increase in $J(^{13}CF)$ results in a decrease in $J(^{13}CCF)$. This is shown in Figure 6.1, where $J(^{13}CCF)$ is plotted against $J(^{13}CF)$.

TABLE 6.1

Carbon-Fluorine Coupling Constants for

Compounds Studied in this Work

Compound	$J(^{13}CF)$ c/sec	$J(^{13}CCF)$ c/sec
CH_3COF	352.8 ± 0.2	59.4 ± 0.3
CH_3CH_2COF	358.2 ± 0.2	53.9 ± 0.2
$CH_3CH_2CH_2COF$	359.6 ± 0.3	50.7 ± 0.3
$(CH_3)_2CHCOF$	365.6 ± 0.2	50.4 ± 0.2
$(CH_3)_3CCOF$	372.0 ± 0.4	46.2 ± 0.3
$(COF)_2$ [a]	365.9 ± 0.4	103.2 ± 0.4
$CH_2(COF)_2$ [b]	331.0 ± 0.6	63.8 ± 1.9
$(CH_2COF)_2$	357.3 ± 0.4	58.1 ± 0.4

[a] From Reference 4

[b] At -65°C

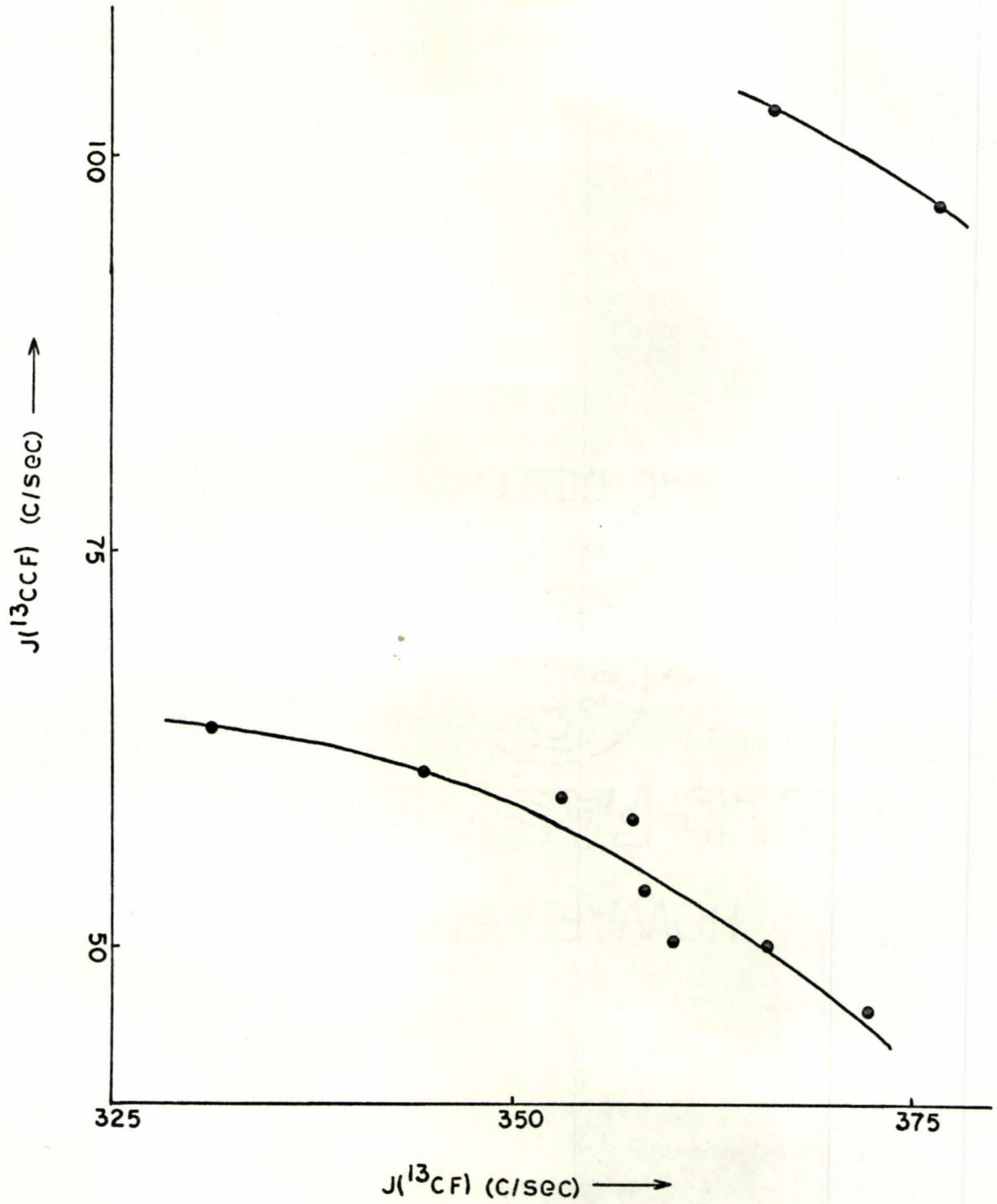


Fig. 6.1 Variation of $J(^{13}CCF)$ with $J(^{13}CF)$

The results of Muller and Carr[4] for benzoyl fluoride, C_6H_5COF ($J(^{13}CF)$ = 344 c/sec, $J(^{13}CCF)$ = 61 c/sec) have also been included in the graph. The variation of $J(^{13}CCF)$ with $J(^{13}CF)$ appears to be non-linear. A least squares fit of the data gives $J(^{13}CCF) = 56.681 - 0.507\,(J(^{13}CF) - 355) - 0.0085\,(J(^{13}CF) - 355)^2$. This line is shown in Figure 6.1. Figure 6.1 also shows the same plot for the carbon-fluorine coupling constants previously obtained[4] in oxalyl fluoride and oxalyl chloridefluoride. The same decrease in $J(^{13}CCF)$ with increased $J(^{13}CF)$ is noted, the curve having a slope similar to the curve for the other compounds studied, but lying 50 c/sec above it. Any mechanism which is advanced to explain the carbon-fluorine coupling in the acyl and diacyl fluorides must therefore give a decrease in $J(^{13}CCF)$ when $J(^{13}CF)$ increases and also account for the much larger values of $J(^{13}CCF)$ encountered in the oxalyl halides. It has already been postulated[4,5] that a considerable contribution to $J(^{13}CF)$ results from partial carbon-fluorine double bonding. If this is the case, an increase in $J(^{13}CF)$ should be accompanied by a decrease in the carbon-fluorine bond length. This is discussed in the next section.

Correlation of Direct Coupling with Bond Lengths

Accurate bond lengths are not available for the compounds listed in Table 6.1, with the exception of acetyl fluoride. However, microwave studies have been made on 1,1-difluoroethylene, formyl fluoride, carbonyl fluoride and a number of fluoromethanes and fluorohalomethanes, all compounds in which C-F double bonding might occur. Table 6.2 lists carbon-fluorine bond lengths and coupling constants obtained from the literature for a number of these compounds. A plot of $J(^{13}CF)$ vs. r_{CF} is shown in Figure 6.2(a). It is immediately apparent that there is no obvious correlation between the observed values of $J(^{13}CF)$ and r_{CF}. However, the length of the C-F bond might be expected to depend somewhat upon its s-character, since the covalent radius of carbon decreases slightly with increasing s-character[50], this decrease being reflected in the different C-H bond lengths in ethylene (r_{CH} = 1.071 A^{o}) and ethane (r_{CH} = 1.093 A^{o}). If it is assumed that this variation is due solely to a change in the covalent radius of carbon with s-character, and that the variation with s-character is linear, then any departure from 25% s-character in a particular bond will result in the lengthening of that bond by an amount Δr given by

$$\Delta r = 0.264\ (0.25 - a^2)\ A^{o}$$

TABLE 6.2

Literature Values[a] for J_{CF} and Carbon-Fluorine Bond Lengths in Various Compounds

Compound	$J(^{13}CF)$ c/sec	r_{CF} Å	a_{CF}^2	$r_{CF}-\Delta r$ Å
CF_4	259.2	1.317	0.250	1.317
CF_3H	274.3	1.332	0.174	1.311
CF_2H_2	234.8	1.358	0.131	1.327
CFH_3	157.5	1.385	0.106	1.347
CF_3Cl	299	1.328	0.236	1.324
CF_2Cl_2	325	1.335	0.250	1.335
$CFCl_3$	337	1.330	0.244	1.328
CF_3I	344	1.332	0.236	1.328
$H_2C=CF_2$	287[b]	1.323[c]	0.247	1.322
HCOF	369	1.338	0.085	1.294
COF_2	308.4	1.312	0.236	1.308

[a] Taken from Reference 51

[b] Reference 5

[c] V. W. Laurie and D. T. Pence, J. Chem. Phys. 38, 2693 (1963)

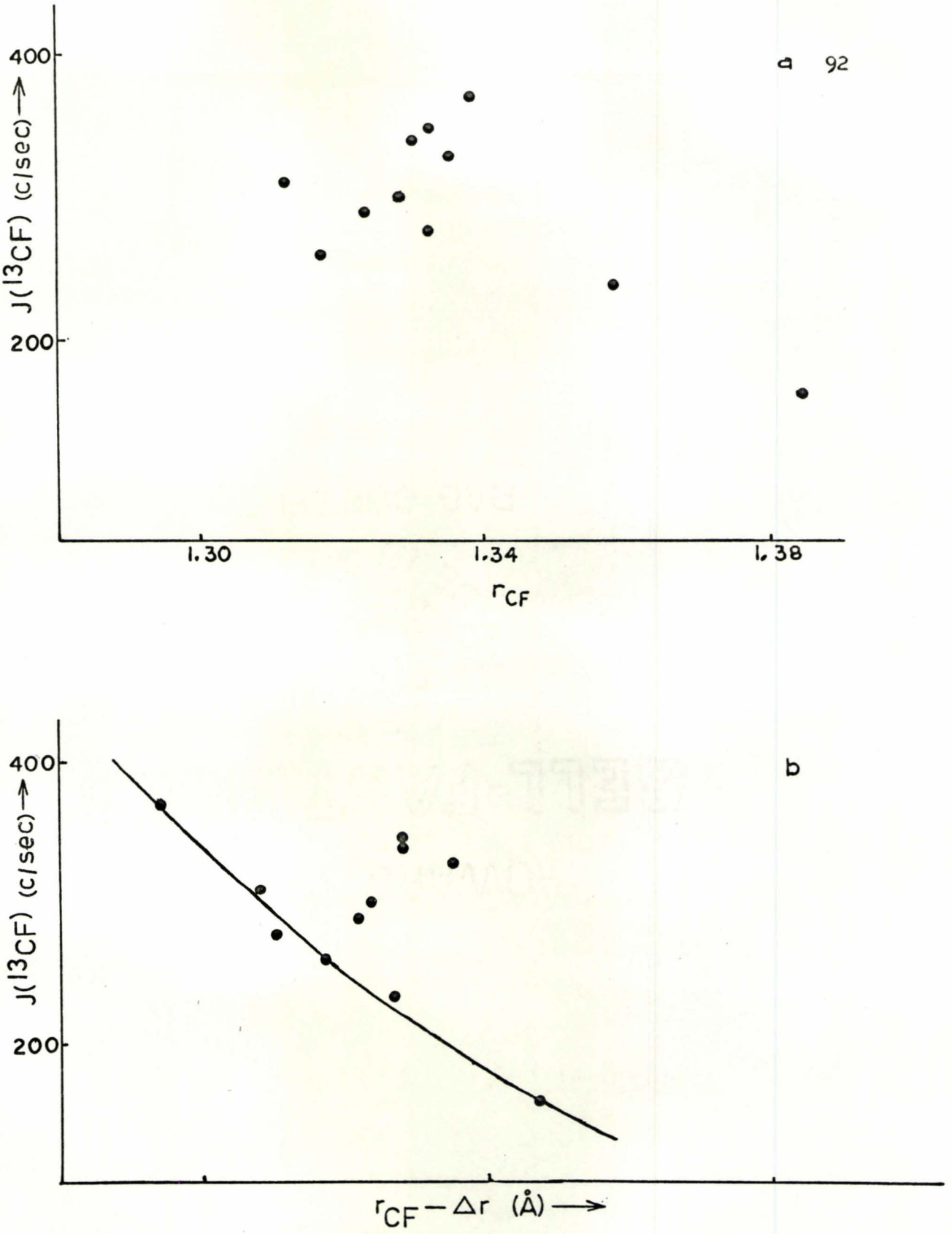


Fig. 6.2 Variation of $J(^{13}CF)$ with Carbon-Fluorine Bond Length

(a) Bond Lengths Uncorrected (b) Bond Lengths Corrected

where a^2 is the fractional s-character of the bond being considered.

The fractional s-character of the C-F bonds in the compounds of Table 6.2 were therefore calculated. For the fluoromethanes, CF_nH_{4-n}, the s-character of the C-H bonds, a_H^2, was calculated from the C-H coupling constant using the well-known relationship[1,2]

$$J(^{13}CH) = 500\ a_H^2$$

Values of $J(^{13}CH)$ were obtained from the review by Kemmitt and Sharp[51]. Since the sum over the four bonds of fractional s-character is unity, a_F^2, the s-character in the carbon-fluorine bonds, can readily be obtained by means of the relationship:

$$na_F^2 + (4 - n)\ a_H^2 = 1$$

where n is the number of fluorine atoms in the molecule. Table 6.3 summarizes the calculation of a_F^2 for the fluoromethanes. An s-character of 0.25 is assumed for CF_4.

For CF_3Cl, CF_2Cl_2, CF_3I, $H_2C = CF_2$ and COF_2, a_F^2 was calculated using the literature values for the FCF bond angles. If the carbon hybrid orbitals are represented by normalized wave functions of the form

$$\psi_i = \frac{1}{(1 + \lambda_i^2)^{1/2}} (S + \lambda_i p_i)$$

TABLE 6.3

Calculation of s-characters in the Carbon-Fluorine Bonds of Fluoromethanes from $J(^{13}CH)$

Compound	$J(^{13}CH)$ [a] c/sec	a_H^2	a_F^2
CF_4	-	-	0.250
CF_3H	239.1	0.478	0.174
CH_2H_2	184.5	0.369	0.131
CFH_3	149.1	0.298	0.106

[a] From Reference 51

where p_i is a linear combination of 2p orbitals chosen in such a way that it lies along the axis of the bond being considered, then it can be shown[52], that the condition must hold if ψ_i and ψ_j

$$\lambda_i \lambda_j = -\sec \theta_{ij}$$

are to be orthogonal, θ_{ij} being the angle between bonds i and j. If bonds i and j are both C-F bonds, then

$$\lambda_F^2 = -\sec \theta_{FCF}$$

Since the fractional s-character, a_F^2, is related to λ_F^2 by the relationship

$$a_F^2 = 1/(1+\lambda_F^2)$$

a_F^2 can readily be calculated given the FCF bond angle. Values of θ_{FCF} and calculated values of λ_F^2 and a_F^2 are given in Table 6.4.

In $CFCl_3$ the ClCCl angle is 109°40' [51]. Hence $a_{Cl}^2 = 0.252$ and $a_F^2 = 0.244$. In HCOF, the HCF bond angle is 109° [51], and therefore

$$\lambda_H \lambda_F = -\sec (109^\circ)$$
$$= 3.0716$$

For HCOF, $J(^{13}CH) = 267$ c/sec [53], hence $a_H^2 = 0.534$. Recalling

$$a_H^2 = 1/(1+\lambda_H^2)$$

TABLE 6.4

Calculation of s-characters in the Carbon-Fluorine Bonds of Various Compounds from FCF Bond Angles

Compound	θ_{FCF} [a]	λ_F^2	a_F^2
CF_3Cl	108°	3.236	0.236
CF_2Cl_2	109.5°	2.996	0.250
CF_3I	108°	3.236	0.236
$H_2C=CF_2$	109.1° [b]	3.056	0.247
COF_2	108.0°	3.236	0.236

[a] From Reference 51 except where noted

[b] V. W. Laurie and D. T. Pence, J. Chem. Phys. 38, 2693 (1963)

gives $\lambda_H^2 = 0.873$. Since, from the orthogonality condition above

$$\lambda_F^2 = (3.0716)^2/\lambda_H^2$$

$$= 10.807$$

therefore $a_F^2 = 0.085$. All the calculated values of a_F^2 are listed in the fourth column of Table 6.2. The last column of this table shows the C-F bond lengths corrected for s-character by calculating Δr using the equation given. Figure 6.2(b) shows a plot of $J(^{13}CF)$ vs $(r-\Delta r)$. In this case, the points fall reasonably close to a line of negative slope, implying that partial carbon-fluorine double bonding does increase the absolute value of $J(^{13}CF)$ in these compounds. A least squares fit gives $J(^{13}CF) = 250.91-3927.60((r-\Delta r) -1.32) + 20687.65((r-\Delta r)-1.32)^2$ if the points for CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_3I and $H_2C{=}CF_2$ are ignored. The s-characters for these last five compounds were calculated solely on the basis of interatomic angles; it may be that this is not the best criterion for s-character.

A Mechanism for Carbon-Fluorine Coupling

As noted in Chapter 2, successive α-methyl substitution in the acetyl fluorides results in a progressive increase in $J(^{13}CF)$ from 352.8 c/sec in CH_3COF to 372.0 c/sec in $(CH_3)_3CCOF$. Since $J(^{13}CF)$ = 369 c/sec in formyl fluoride, replacement of the formyl proton by a methyl group decreases $J(^{13}CF)$. The postulate that $J(^{13}CF)$ varies with carbon-fluorine partial double bond order

therefore implies that this bond order is smaller in acetyl fluoride than in formyl fluoride and increases when α-methyl groups are added. A bond order in acetyl fluoride smaller than that in formyl fluoride is consistent with either an inductive or a hyperconjugative methyl effect. However an increase in C-F bond order upon α-methyl substitution is not consistent with an inductive methyl effect, since in the presence of more methyl groups more electrons would be donated to the carbonyl carbon, making it less electronegative, hence reducing the C-F bond order, an effect opposite to that inferred from $J(^{13}CF)$. However, hyperconjugation should be less effective in the presence of α-methyl groups. Since hyperconjugation would be likely to reduce the C-F bond order, α-methyl substitution should increase $J(^{13}CF)$ if hyperconjugation occurs.

Huckel molecular orbital calculations were made on the π-electrons of the molecules of this study in order to estimate the carbon-fluorine, carbon-oxygen and carbon-carbon bond orders. The simplest form of the Huckel m.o. treatment[54] was used, namely that with formal neglect of overlap. In this treatment the π-electron wave function is taken to be the product of a number of molecular orbitals, each of which is itself a linear combination of atomic p_z orbitals centred on each of the π-centres. Each l.c.a.o.-m.o. is therefore of the form

$$\psi_i = \sum_{r=1}^{n} c_{ir} \varphi_r$$

where φ_r is the atomic p_z orbital on the rth atom and c_{ir} is the coefficient of the rth atomic orbital in the ith molecular orbital. Formal neglect of overlap between neighbouring atoms results in secular equations of the form

$$c_1(H_{11} - \epsilon) + c_2 H_{12} + \ldots\ldots + c_n H_{1n} = 0$$

$$c_1 H_{12} + c_2(H_{22} - \epsilon) + \ldots\ldots + c_n H_{2n} = 0$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$c_1 H_{1n} + c_2 H_{2n} + \ldots\ldots\ldots + c_n(H_{nn} - \epsilon) = 0$$

The coulomb integrals H_{rr} can be replaced by the symbol α_r and the resonance integrals H_{rs} by β_{rs}, yielding secular equations of the form

$$c_1(\alpha_1 - \epsilon) + c_2\beta_{12} + \ldots\ldots + c_n\beta_{1n} = 0$$

$$c_1\beta_{12} + c_2(\alpha_2 - \epsilon) + \ldots\ldots + c_n\beta_{2n} = 0$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$c_1\beta_{1n} + c_2\beta_{2n} + \ldots\ldots\ldots + c_n(\alpha_n - \epsilon) = 0$$

In general, α is different for each element and β depends on the two atoms which the bond joins. For atoms not joined by a bond, $\beta = 0$. Solution of the characteristic equation, given by

$$\begin{vmatrix} \alpha_1-\epsilon & \beta_{12} & \cdots\cdots & \beta_{1n} \\ \beta_{12} & \alpha_2-\epsilon & \cdots\cdots & \beta_{2n} \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \beta_{1n} & \beta_{2n} & \cdots\cdots & \alpha_n-\epsilon \end{vmatrix} = 0$$

and the above secular equations gives the eigenvalues (energies) and eigenvectors (coefficients) for the molecule under consideration. The available π-electrons then occupy the calculated molecular orbitals, two per orbital, starting with the orbital of lowest energy. The π-bond order, P_{rs}, for any particular bond, r-s, is given by the expression[54]

$$P_{rs} = \sum n_i c_{ir} c_{is}$$

where n_i is the number of electrons in the ith molecular orbital.

The calculations for the -COF group involve a 3x3 determinant, namely

$$\begin{vmatrix} \alpha_C-\epsilon & \beta_{CO} & \beta_{CF} \\ \beta_{CO} & \alpha_O-\epsilon & 0 \\ \beta_{CF} & 0 & \alpha_F-\epsilon \end{vmatrix} = 0$$

Calculations for the -COF group was done using the values suggested by Streitweisser[54] for oxygen and fluorine, namely

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$$\alpha_O = \alpha_C + \beta_{CC} \qquad \beta_{CO} = \beta_{CC}$$
$$\alpha_F = \alpha_C + 3\beta_{CC} \qquad \beta_{CF} = 0.7\beta_{CC}$$

Solution of the characteristic equation and secular equations gives the coefficients for the three molecular orbitals, the lower two of which are filled, one electron each coming from carbon and oxygen and two from fluorine. The calculated coefficients give $P_{CF} = 0.274$ and $P_{CO} = 0.848$. Calculations were also made for acetyl fluoride, inductive model, by changing α_C to allow for the effect of electron donation from the methyl group and recalculating using the three centre m.o. treatment given above. For acetyl fluoride, hyperconjugative model, a five centre m.o. was calculated involving the three atoms of the -COF group, the methyl carbon and an orbital representing the contribution from the carbon-hydrogen bonds in the methyl group. Six centre m.o.s were calculated for oxalyl fluoride and oxalyl chloridefluoride involving all the atoms of each molecule. For malonyl fluoride, an eight centre m.o. centred on the six atoms of the two -COF groups, the central carbon atom and the additional orbital representing the contribution from the C-H bonds was used. The ten centre m.o. used for succinyl fluoride involved the two -COF groups, the two α-carbons and the two additional orbitals representing the contributions of the αC-H bonds. In all cases, the parameters given in Chapter 5 of Reference 54 were used.

An IBM 7040 Fortran IV program was written which accepted as input the number of centres involved in the π-bonding and the parameters for the atoms involved, solved the resulting secular equations and calculated the bond orders for the bonds of interest. The calculated values of P_{CF}, P_{CO} and P_{CC} are shown in Table 6.5.

The calculations summarized in Table 6.5 show that for acetyl fluoride either a methyl inductive effect or hyperconjugation reduces the C-F bond order slightly and the C-O bond order rather more. A small C-C bond order results if hyperconjugation is allowed. In malonyl and succinyl fluoride all the calculated bond orders are very close to those obtained for acetyl fluoride (hyperconjugative model), while in the oxalyl halides P_{CC} is much greater, P_{CO} being slightly greater and P_{CF} slightly less than in the other compounds. Since the observed values of $J(^{13}CF)$ are of comparable magnitudes for all the compounds of this study but $J(^{13}CCF)$ is much greater for the oxalyl halides, the calculated π-structures parallel the coupling constant behaviour. Moreover, the only compounds which experimental data suggests are likely to be planar have the highest calculated C-C bond order.

McConnell[55] and Karplus[56] have discussed the π-contribution to spin-spin coupling. In compounds with π-structures, nuclear spins couple through the spins of the π-electrons by means of the same σ-π interactions which are responsible for electron-nuclear hyperfine

TABLE 6.5

Huckel M.O. Calculations on the Acyl Fluorides

Group or Compound	P_{CF}	P_{CO}	P_{CC}
-COF Group	0.274	0.848	-
CH_3COF (Inductive Methyl)	0.272	0.759	-
CH_3COF (Hyperconjugation)	0.267	0.805	0.214
$(COF)_2$	0.255	0.828	0.288
COCl.COF	0.254	0.826	0.297
$CH_2(COF)_2$ [a]	0.268	0.806	0.209
$(CH_2COF)_2$ [a, b]	0.267	0.806	0.212 [b]

[a] Calculations for malonyl fluoride and succinyl fluoride include the effect of hyperconjugation.

[b] Bond order given is that for C_1-C_2. For C_2 - C_3 a bond order $P_{CC} = 0.143$ is obtained.

splitting in electron spin resonance. According to McConnell, the resulting contribution to the coupling constant between nuclear spins N and N' is given by

$$J_{NN'}(\pi) = \rho^2 P^2 aa'/h\Delta E$$

where ρ is the Bohr magneton, P the π-bond order, and ΔE the average energy of excitation to a triplet state. The quantities a and a' are the electron-nuclear hyperfine interaction constants for each fragment of the excited state and are often known from the studies of free radicals of similar structure. Substitution of the known values for the Bohr magneton and Planck's constant in the above equation gives

$$J_{NN'}(\pi) = 8.10 \times 10^{-3} P^2 aa'/\Delta E$$

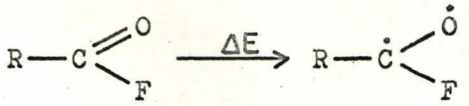
if ΔE is expressed in electron volts and the hyperfine coupling constants in gauss. The π-bond order P is that calculated from the m.o. treatment. The theory of Karplus discusses the coupling mechanism in terms of valence bond structures. Both Karplus and McConnell considered only the case where the nuclear spins concerned lay on opposite sides of the π-bond. In considering the σ-π contribution to the proton-proton coupling in acetone, Holmes and Kivelson[57] showed that if both spins under consideration are on the same side of the π-bond, then a contribution of the same magnitude

but opposite sign results.

The above theory gives a π-contribution to the one bond C-F coupling constants in the acyl fluorides of

$$J_{CF}(\pi_{CO}) = -8.10 \times 10^{-3} P_{CO}^{2} a_C a_F / \Delta E$$

if interaction with the C-O π bond (I) is considered



I

The hyperfine coupling constants desired, a_C and a_F, are that between an unpaired electron on an sp^2-hybridized carbon atom and the ^{13}C nucleus of that atom, and that between an unpaired electron on an sp^2-hybridized carbon atom and the nucleus of a directly bonded fluorine atom. Eaton et al.[14] have concluded $a_F = -83 + 580\ P_{CF}$ on the basis of a least squares fit of ^{19}F hyperfine constants obtained from the analysis of n.m.r. contact shifts involving the fragment F-C(sp^2). The hyperfine coupling between ^{13}C and the unpaired electron in the methyl radical is known to be +41 ± 3 gauss[58]. Taking these values for a_C and a_F and ΔE = 6.3 eV for the carbonyl group[57] gives

$$J_{CF}(\pi_{CO}) = P_{CO}^{2}(4.4 - 30.6\ P_{CF})$$

Theoretical calculations show[59] that the hyperfine coupling between an unpaired electron on an sp^2-hybridized carbon and the ^{13}C nucleus of a directly bonded sp^3-hybridized carbon atom to be -20.9 gauss. Hence in acetyl fluoride and the α-substituted acetyl fluorides a contribution

$$J_{CCF}(\pi_{CO}) = P_{CO}^{2}(-2.2 + 15.6\ P_{CF})$$

to the two bond carbon-fluorine coupling constant should result. For $P_{CF} > 0.144$, therefore, the proposed mechanism gives a negative contribution to $J(^{13}CF)$ and a positive contribution of similar magnitude to $J(^{13}CCF)$. Now the absolute sign of $J(^{13}CF)$ is most probably negative[60], while that of $J(^{13}CCF)$ is opposite[4,61] and hence positive. For $P_{CF} > 0.144$, the proposed mechanism therefore increases both the absolute value of $J(^{13}CF)$ and that of $J(^{13}CCF)$. The molecular orbital calculations give $P_{CF} \approx 0.27$, predicting the larger coupling constants observed in this study. Since hyperconjugation decreases both P_{CO} and P_{CF}, the observed increase in $J(^{13}CF)$ with α-substitution in the acetyl fluorides is in accord with the coupling mechanism given. Numerical values of $J_{CF}(\pi_{CO})$ calculated from the above expression are an order of magnitude too small to explain the observed variation in $J(^{13}CF)$. However, it

is well known that the simple m.o. treatment gives disproportionate weight to ionic structures, and these make no contribution to the mechanism proposed. In addition, the values of a_C and a_F chosen may be considerably in error. The usefulness of the equation derived for $J_{CF}(\pi_{CO})$ is therefore strictly qualitative, and lies in its provision of an explanation for the observed coupling constant behaviour in terms of bonding.

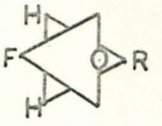
The contribution $J_{CCF}(\pi_{CO})$ to the two bond coupling will vary in the same manner as $J(^{13}CF)$, that is, be largest when hyperconjugation is smallest. Hence this mechanism alone would make $J(^{13}CCF)$ larger in $(CH_3)_3CCOF$ than in the other compounds, which is opposite to the behaviour observed for $J(^{13}CCF)$. However, the presence of a C-C partial double bond leads to another mechanism, that of coupling through the π electrons of the C-C double bond. This should give rise to a contribution given by

$$J_{CCF}(\pi_{CC}) = P_{CC}{}^2 a_C(-0.67 + 4.70\ P_{CF})/\Delta E_{CC}$$

The evaluation of the quantities a_C and ΔE_{CC} is beyond the scope of this work. However, a_C, the hyperfine coupling between the unpaired electron on the α-carbon and the ^{13}C nucleus of that atom, will be positive. Hence for $P_{CF} > 0.144$ a positive contribution is made to $J(^{13}CCF)$, increasing its absolute value. There are therefore two mechanisms contributing to $J(^{13}CCF)$, one which contributes slightly

less with hyperconjugation present and the other which is markedly dependent on C-C double bond character. It is possible therefore that small contributions (≈10 c/sec each) are made from both mechanisms in the substituted acetyl fluorides and that the net effect is the decrease in $J(^{13}CCF)$ noted with α-methyl substitution. In addition, a_C itself may change markedly from compound to compound. Calculations by Karplus and Fraenkel[62] indicate a_C should decrease from a theoretical value of +43.8 gauss in the methyl radical to one of around + 30.5 gauss in the radical $\dot{C}(C)_3$. A similar behaviour might occur for the α-carbon in the substituted acetyl fluorides, causing a much greater decrease in $J(^{13}CCF)$ on successive α-methyl substitution than would be expected on the basis of decreasing hyperconjugation alone.

The molecular orbital calculations performed in this work took no account of the effects of hindered rotation. However, carbon-hydrogen hyperconjugation to an adjacent carbonyl group should be most effective when the hydrogens involved make a dihedral angle of 60° with the C-C=O plane[63]. For an α-monosubstituted acetyl fluoride, such as propionyl fluoride, butyryl fluoride, or malonyl fluoride, this will be the conformation with the substituent group <u>trans</u> with respect to the fluorine atom (II)



II

The results of Chapter 2 indicate this conformer lies 700-900 cal/mole lower in energy than the other two. Hence a decrease in temperature should increase the fractional population of this isomer and increased hyperconjugation should result. In an α-monosubstituted acetyl fluoride, a decrease in temperature should therefore decrease $J(^{13}CF)$, and either decrease or increase $J(^{13}CCF)$ depending on which of the two mechanisms suggested for the two bond coupling predominates in the compound studied. The ^{13}C satellites in the fluorine spectrum of propionyl fluoride were therefore studied at four temperatures over the range -92 to 29°C. The values of coupling constants and isotope effects obtained are shown in Table 6.6, along with values of p, the fractional population of the <u>trans</u> isomer, calculated by taking ΔE = 820 cal/mole, the midpoint of the 760-880 cal/mole range obtained for propionyl fluoride in Chapter 2. There is a noticeable decrease in both coupling constants as the temperature decreases. The decrease in $J(^{13}CF)$ is expected from the theory given. The decrease in $J(^{13}CCF)$ implies the first mechanism suggested is the more important contributor to the two bond coupling in this molecule. However,

TABLE 6.6

Temperature Dependence of Carbon-Fluorine Coupling Constants and Isotope Effects in Propionyl Fluoride

T°C	p	$J(^{13}CF)$ c/sec	$\Delta\delta$ ppm $(^{13}CF)-(^{12}CF)$	$J(^{13}CCF)$ c/sec	$\Delta\delta$ ppm $(^{13}CCF)-(^{12}CCF)$
29	0.662	358.16 ± 0.30	0.126 ± 0.003	54.09 ± 0.21	0.021 ± 0.005
-17	0.715	357.95 ± 0.36	0.131 ± 0.003	53.64 ± 0.36	0.022 ± 0.005
-64	0.782	357.08 ± 0.44	0.133 ± 0.004	52.61 ± 0.33	0.020 ± 0.008
-92	0.830	357.04 ± 0.42	0.134 ± 0.004	-	-

some contribution from the second mechanism must be present to account for the larger two bond coupling in propionyl fluoride ($J(^{13}CCF)$=54 c/sec) where hyperconjugation is more likely than in $(CH_3)_3CCOF$ ($J(^{13}CCF)$ = 46.2 c/sec). It may be noted here that the results for malonyl fluoride give the lowest one bond and the highest, except for the oxalyl halides, two bond coupling constant of all the compounds studied. This implies extremely strong hyperconjugation in the molecule. Part of this increase in hyperconjugation is probably due to the recording of the ^{13}C satellite spectrum at -65°C where the conformational preference is for isomers where hyperconjugation is likely to be more effective, as in propionyl fluoride.

As previously discussed, the molecular orbital calculations show oxalyl fluoride and oxalyl chloridefluoride to have considerably more C-C partial double bond character than the substituted acetyl fluorides. Since the contribution from C-C double bond character depends on P_{CC}^2, the increased value of $J(^{13}CCF)$ in these two compounds may well be due to increased double bond character, as suggested in the introduction. In addition, the role played by a_C may be quite important, since $J_{CCF}(\pi_{CC})$ varies directly as a_C. For the two bond coupling constant in oxalyl fluoride, a_C is the coupling between an unpaired electron on an sp^2 carbon bonded to fluorine, oxygen and another carbon, and the ^{13}C nucleus of that sp^2

carbon. According to Karplus and Fraenkel[62] the dependence of a_C on the atoms bonded to an sp^2 carbon is given by

$$a_C = -12.7 + \sum_{i=1}^{3} Q_{CX_i}{}^{C}$$

where $Q_{CX_i}{}^{C}$ is a parameter for the ith C-X bond. According to Karplus and Fraenkel, $Q_{CC}{}^{C} = 14.4$ gauss. Experimental results have been interpreted by several authors[59,64] to give a value of $Q_{CO}{}^{C}$ in the region 9-16 gauss. An estimate of Q_{CF} can be made by employing a result of Reiger and Fraenkel[65] who showed $Q_{CN}{}^{N}$ to be proportional to $Q_{CN}{}^{C}$, the constant of proportionality being the negative of the ratio of the hyperfine splitting from a single unpaired 2s electron in a nitrogen atom with an ^{14}N nucleus to the splitting from a single unpaired 2s electron in a carbon atom with a ^{13}C nucleus. Hence in the present case $Q_{CF}{}^{C}$ should be proportional to $Q_{CF}{}^{F}$, the constant of proportionality being the negative of the ratio of the hyperfine splitting from a single unpaired 2s electron in a carbon atom with a ^{13}C nucleus to that from a single unpaired 2s electron in a fluorine atom with a ^{19}F nucleus. Theoretical calculations[62,66] give values of 1191 gauss for carbon and 1509 gauss for fluorine. Hence $Q_{CF}{}^{C} - 0.789\ Q_{CF}{}^{F}$. $Q_{CF}{}^{F}$ can be estimated from the electron-fluorine hyperfine coupling for the fragment F-C (sp^2), $a_F = -83 + 580\ P_{CF}$ gauss. Only the first term of a_F is due to σ-π interaction in the C-F bond, that is,

Q_{CF}^{F} = -83 gauss. Use of this value gives Q_{CF}^{C} = +65.5 gauss. Using Q_{CF}^{C} = 65.5 gauss, Q_{CO}^{C} = 12.5 gauss, the midpoint of the range given above, and Q_{CC}^{C} = 14.4 gauss in the equation of Karplus and Fraenkel gives a_C = 80 gauss. Hence the much higher values of $J(^{13}CCF)$ in the oxalyl halides could result from the coupling mechanism across the C-C partial double bond, made more important by this large value of a_C. A value of a_C = 80 gauss for the -COF group would also give larger values of $J_{CF}(\pi_{CO})$ for all the compounds studied, making the theory more in agreement with experiment.

One point of great interest in the consideration of two bond carbon-fluorine coupling in general is the fact that with one exception, <u>trans</u>-CFBr=CFBr[67], the two bond coupling is not anomalously large in fluoroethylenes. For instance, in $CFCl{=}CCl_2$, $J(^{13}CCF)$ = 43.7 c/sec[68]. Since the π-character of the C-C bond should be near unity, a rather large contribution to the two bond coupling might be expected. A six centre m.o. calculation involving all the atoms of $CFCl{=}CCl_2$ was therefore made as part of this work. This calculation gives P_{CC} = 0.960 and P_{CF} = 0.173. The expression

$$J_{CCF}(\pi_{CC}) = P_{CC}^{2} a_C(-0.67 + 4.70\ P_{CF})/\Delta E_{CC}$$

has already been derived. Since this approaches zero in the region $P_{CF} \approx 0.144$, the proposed mechanism actually predicts a small contribution to the two bond coupling for $CFCl{=}CCl_2$, in agreement

with the literature result.

In summary, this work establishes considerable empirical correlation between $J(^{13}CF)$ and $J(^{13}CCF)$ and π-bond character in the C-F and C-C bonds of a number of compounds. While the coupling mechanisms proposed are not entirely convincing, the discussion here presented indicates they may have a considerable effect in the compounds studied.

REFERENCES

1. J. A. Pople, W. G. Schneider, and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance. McGraw-Hill, New York, 1959.
2. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy. Pergamon Press, New York, 1965.
3. J. T. Arnold, Phys. Rev. 102, 136 (1956).
4. J. Bacon and R. J. Gillespie, J. Chem. Phys. 38, 781 (1963).
5. N. Muller and D. T. Carr, J. Phys. Chem. 67, 112 (1963).
6. W. D. Phillips, H. C. Miller, and E. L. Muetterties, J. Am. Chem. Soc. 81, 4496 (1959).
7. F. A. Cotton and G. Wilkinson. Advanced Inorganic Chemistry, 2nd ed., Interscience, New York, 1966. Chapter 10.
8. F. A. Cotton and J. R. Leto, J. Chem. Phys. 30, 993 (1959).
9. C. D. Good and D. M. Ritter, J. Am. Chem. Soc. 84, 1162 (1962).
10. R. J. Gillespie, J. Am. Chem. Soc. 82, 5978 (1960).
11. H. S. Gutowsky and D. W. McCall, J. Chem. Phys. 22, 162 (1954).
12. D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, Mol. Phys. 5, 407 (1962).
13. R. S. Drago, Physical Methods in Inorganic Chemistry. Rheinhold, New York, 1965. Pp. 298-303.

14. D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips and T. L. Cairns, J. Am. Chem. Soc. 84, 4100 (1962).

15. G. P. van der Kelen and Z. Eeckhaut, J. Mol. Spectry. 10, 141 (1963).

16. J. L. Hencher and G. W. King, J. Mol. Spectry. 16, 158 (1965).

17. J. L. Hencher and G. W. King, J. Mol. Spectry. 16, 168 (1965).

18. A. F. Wells, Structural Inorganic Chemistry, 3rd ed. Oxford University Press, London, 1962.

19. R. G. Snyder and I. C. Hisatune, J. Mol. Spectry. 1, 139 (1957).

20. I. C. Hisatune, J. P. Devlin and Y. Wada, J. Chem. Phys. 33, 714 (1960).

21. G. M. Begun and W. H. Fletcher, Spectrochim. Acta 13, 1343 (1960).

22. J. N. Gayles and J. Self, J. Chem. Phys. 40, 3530 (1964).

23. A. Finch, I. Hyams and D. Steele, Spectrochim. Acta 21, 1423 (1965).

24. D. E. Mann and L. Fano, J. Chem. Phys. 26, 1665 (1957).

25. K. Hedberg and R. Ryan, J. Chem. Phys. 41, 2214 (1964).

26. E. B. Moore and W. N. Lipscomb, Acta Cryst. 9, 668 (1956).

27. L. Pierce and L. C. Krisher, J. Chem. Phys. 31, 875 (1959).

28. C. C. Lin and J. D. Swalen, Rev. Mod. Phys. 31, 841 (1959).

29. S. S. Butcher and E. B. Wilson, Jr., J. Chem. Phys. 40, 1671 (1964).

30. G. J. Karabatsoo and N. Hei, J. Am. Chem. Soc. 87, 2864 (1965).

31. J. A. Pople and T. Schaeffer, Mol. Phys. 3, 547 (1960).

32. P. Diehl and J. A. Pople, Mol. Phys. 3, 557 (1960).

33. P. Diehl, R. G. Jones and H. J. Bernstein, Can. J. Chem. 43, 81 (1965).

34. W. R. Hasek, W. C. Smith and V. A. Engelhardt, J. Am. Chem. Soc. 82, 543 (1960).

35. D. D. Elleman, L. C. Brown and D. Williams, J. Mol. Spectry. 7, 307 (1961).

36. D. D. Elleman, L. C. Brown and D. Williams, J. Mol. Spectry. 7, 322 (1961).

37. N. Sheppard and J. J. Turner, Proc. Roy. Soc. 252A, 506 (1959).

38. R. J. Abraham and K. G. R. Pachler, Mol. Phys. 7, 165 (1963).

39. A. A. Bothner-By, in J. S. Waugh, ed., Advances in Magnetic Resonance, v. 1. Academic Press, New York, 1965.

40. D. M. Grant, R. C. Hirst and H. S. Gutowsky, J. Chem. Phys. 38, 470 (1963).

41. R. C. Hirst and D. M. Grant, J. Chem. Phys. 40, 1909 (1964).

42. M. Barfield and D. M. Grant, J. Am. Chem. Soc. 85, 1899 (1963).

43. J. A. Pople and A. A. Bothner-By, J. Chem. Phys. 42, 1339 (1965).

44. R. M. Lynden-Bell, Trans. Farad. Soc. 57, 888 (1961).

45. R. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc. A, 269, 385 (1962).

46. R. M. Lynden-Bell, Mol. Phys. 6, 601 (1963).

47. P. Diehl, Helv. Chim. Acta 48, 567 (1965).

48. R. G. Jones and S. M. Walker, Mol. Phys. 10, 363 (1966).

49. C. W. Tullock and D. D. Coffman, J. Org. Chem. 25, 2016 (1960).

50. C. A. Coulson, Chemical Society Symposia, Bristol, 1958. Special Publication No. 12, The Chemical Society, 1958, p. 85.

51. R. D. W. Kemitt and D. W. A. Sharp, Adv. in Fluorine Chem. 4, 142 (1965).

52. K. B. Wiberg, Physical Organic Chemistry. John Wiley & Sons, New York, 1964.

53. N. Muller, J. Chem. Phys. 36, 359 (1962).

54. A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists. John Wiley & Sons, New York, 1961.

55. H. M. McConnell, J. Mol. Spectry. 1, 11 (1957).

56. M. Karplus, J. Chem. Phys. 33, 1842 (1960).

57. J. R. Holmes and D. Kivelson, J. Am. Chem. Soc. 83, 2959 (1961).

58. T. Cole, H. O. Pritchard, N. R. Davidson and H. M. McConnell, Mol. Phys. 1, 406 (1958).

59. H. L. Strauss and G. K. Fraenkel, J. Chem. Phys. 35, 1312 (1961).

60. G. V. D. Tiers, J. Am. Chem. Soc. 84, 3972 (1962).

61. G. V. D. Tiers, J. Phys. Chem. 67, 928 (1963).

62. M. Karplus and G. K. Fraenkel, J. Chem. Phys. 35, 1312 (1961)

63. M. Barfield and D. M. Grant, J. Am. Chem. Soc. 85, 1899 (1963).

64. M. R. Das and B. Venkataraman, J. Chem. Phys. 35, 2262 (1961).

65. P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. 37, 2795 (1962).

66. P. V. Schastnev and G. M. Zhidomirov, J. Struct. Chem. 5, 778 (1964).

67. T. Reuben and A. Demiel, J. Chem. Phys. 44, 2216 (1966).

68. G. V. D. Tiers, J. Phys. Soc. Japan 15, 354 (1960).