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## NUCLEAR MAGNETIC RESONANCE STUDIES

Part I. $F^{19}$ Spin-Spin Coupling Constants

Part II. The Effect of Solvents on $F^{19}$ Spin-Spin Coupling Constants

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Lawrence Radiation Laboratory
Berkeley, California

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## PART I. $F^{19}$ Spin-Spin Coupling Constants

## PART II. The Effect of Solvents on $F^{19}$ Spin-Spin Coupling Constants

Soon Ng

(Ph.D. Thesis)

May 1964

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# NUCLEAR MAGNETIC RESONANCE STUDIES

## PART I: $F^{19}$ SPIN-SPIN COUPLING CONSTANTS

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# NUCLEAR MAGNETIC RESONANCE STUDIES

## PART I: $F^{19}$ SPIN-SPIN COUPLING CONSTANTS

Soon Ng

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ABSTRACT

The pattern of fluorine-fluorine coupling constants is explained on the basis of two mechanisms for nuclear spin-spin coupling: the "through-bond" and the "through-space" mechanisms. In the former, the interaction proceeds via the electronic structure in the intervening bonds. It is highly dependent on the electron-withdrawing power of the substituents on the carbon skeleton. This contribution to the coupling constant goes to zero when the sum of the electronegativities of the substituents becomes sufficiently high. The latter mechanism is operative when two fluorine atoms are sufficiently close in space for there to be appreciable overlap of their electronic clouds. This "through-space" interaction proceeds via an electronic structure where there is no bond per se. Experimental evidence for the existence of both mechanisms is given.

# PART I: $F^{19}$ SPIN-SPIN COUPLING CONSTANTS

## I. INTRODUCTION

The usual nuclear magnetic resonance (NMR) spectrum exhibits two kinds of fine structure. The first kind is known as the chemical shift.[1,2,3] It arises as a result of small variations in the electronic shielding of the nuclei or groups of magnetically equivalent nuclei in the molecule. The magnetic field at the nucleus of an atom differs by a small amount from the applied magnetic field, due to an interaction between the applied field and the orbital motion of the electrons surrounding the nucleus. The local field created by this interaction is generally opposed to the applied field, and the nucleus, therefore, is said to be shielded from the magnetic field by surrounding electrons. Since this shielding field is found to be proportional to the applied field, a shielding parameter of the nucleus can be defined as the ratio of the shielding field to the applied field. This parameter is then a reflection of the actual electronic (chemical) environment of the nucleus. The second kind of fine structure is attributed to an indirect coupling of the magnetic moments of pairs of nuclei in the same molecule.[4,5] Direct magnetic dipole-dipole interactions average to zero because of the high-frequency molecular motions characteristic of the liquid state. This indirect magnetic interaction between nuclear spins was found to be proportional to the scalar product of the nuclear spin vectors

$$\underline{I}(i) \cdot \underline{I}(j),$$

the proportionality constant is known as the coupling constant, usually expressed in cycles per second.

The theory of indirect nuclear spin-spin interactions is based on the complete Hamiltonian for the electron-nuclear interactions as first outlined by Ramsey and Purcell[6] and later developed in more detail by Ramsey.[7] The portion of the Hamiltonian important for indirect nuclear interactions consists of three principal parts which may be called the electron-orbital, electron-dipole, and the contact terms; and may be written as

$$\mathcal{H} = \mathcal{H}_{(1)} + \mathcal{H}_{(2)} + \mathcal{H}_{(3)} .$$

These three terms represent, respectively, the interaction of the nuclear magnetic moments with the electron orbital motion and with the electron spin density at a distance from, and at the nucleus.[7,8] Essentially, the mechanism is the magnetic interaction of each nucleus with the spin or orbital angular momentum of a "local" electron, together with the coupling of electron spins and/or orbital angular momenta with each other, i.e., the indirect nuclear interaction proceeds via the electronic structure in the molecule.

The first term $\mathcal{H}_{(1)}$ involves the total electronic kinetic energy, the magnetic interactions between electronic orbital motions and nuclear moments, and the various interactions between the electrons. Since the ordinary momentum $\bar{p}$ of a free particle must be replaced by the generalized momentum $\bar{P} = (p + \frac{e}{c} \bar{A})$ for the particle in an electromagnetic field, where $\bar{A}$ is the magnetic vector potential defined as curl $\bar{A} = \bar{H}$ and div. $\bar{A} = 0$, and where $\bar{P}$ is the generalized momentum of the particle, $\mathcal{H}_{(1)}$ can be written as

$$\mathcal{H}_{(1)} = \sum_k \left(\frac{1}{2m}\right) \left[\bar{p}_k + \frac{e}{c} \bar{A}_{kn}\right]^2 + \text{other terms not involving nuclear spin vectors,}$$

where m is the electron mass, $\bar{p}_k$ the linear momentum of the k-th electron, and $A_k$ the vector potential for the same electron due to the nuclear moments. $\mathcal{H}_{(1)}$ can be put in the appropriate quantum mechanical form by making the substitution $\bar{p}_k \rightarrow \frac{\hbar}{i}\bar{\nabla}$. Also a specific choice of vector potential $\bar{A}_k$ is made in terms of the nuclear magnetic moment $\bar{\mu}_n = \gamma_n \hbar \bar{I}_n$ and the distance $\bar{r}_{kn} = \bar{r}_k - \bar{r}_n$ between the k-th and the nucleus by writing $\bar{A}_k = \bar{\mu}_n \times \bar{r}_{kn}/r_{kn}^3$. Thus this first term in the Hamiltonian is written

$$\mathcal{H}_{(1)} = \sum_k \left(\frac{1}{2m}\right)\left[\frac{\hbar}{i}\bar{\nabla} + \frac{e}{c}\sum_n \hbar \gamma_n \bar{I}_n \times \bar{r}_{kn}/r_{kn}^3\right]^2 + \text{other terms}$$

where $\gamma_n$ is the magnetogyric ratio of nucleus n and $\bar{I}_n$ its spin vector operator.

$\mathcal{H}_{(2)}$ represents the dipole-dipole interaction between the nuclear magnetic moments and the spins of electrons in non-S orbitals:

$$\mathcal{H}_{(2)} = -\bar{\mu}_n \cdot \mathcal{H}_{el},$$

where $$\mathcal{H}_{el} = -\frac{\bar{\mu}_e}{r^3} + \frac{3(\bar{\mu}_e \cdot \bar{r})(\bar{r})}{r^5},$$

and $\bar{\mu}_e = -2\beta\bar{S}$ is the magnetic moment due to the electron spin, $\beta$ is the Bohr magneton and $\bar{S}$ is the electron spin. Thus for a system of k electrons and n nuclei, $\mathcal{H}_{(2)}$ may be written

$$\mathcal{H}_{(2)} = 2\beta\hbar\sum_{k,n}\gamma_n\left[\frac{3(\bar{S}_k \cdot \bar{r}_{kn})(\bar{I}_n \cdot \bar{r}_{kn})}{r_{kn}^5} - \frac{\bar{S}_k \cdot \bar{I}_n}{r_{kn}^3}\right].$$

Finally, the third term[9] represents the interaction between electrons in s orbitals and nuclear spins, and is

$$\mathcal{H}(3) = \frac{16\pi\beta h}{3} \sum_{k,n} \gamma_n \delta(\bar{r}_{kn}) \bar{S}_k \cdot \bar{I}_n$$

The Dirac delta function $\delta(\bar{r}_{kn})$ in the term implies that the interaction depends on the probability of the electrons being at the nucleus. Such a contact term was introduced by Fermi to explain the hyperfine structure in atomic spectra, and it is also used in the discussion of electron resonance experiments.[10]

To find the energies of the indirect nuclear moment coupling that proceed via the electronic system, one may treat the parts of the above Hamiltonian depending on $\bar{I}_n$ as a perturbation on the remainder, and carry the calculation to second order. Such a calculation of the coupling energy requires a knowledge of the energies and wave functions of the triplet states. The perturbational calculation involves the summation of an infinite number of terms, but most theoretical interpretations have been based on an approximation of the original general equations, using an average excitation energy. In this approximation, only the ground-state wave function is required, and for this purpose both LCAO-MO and valence bond wave functions have been used.

It has been shown that for protons the Fermi contact term makes the principal contribution to the coupling, and that the electron-dipole and the electron-orbital interactions may be neglected.[7,11] It is now generally believed that proton-proton spin coupling proceeds through the electronic structure in the intervening bonds. This "through-bond" effect is compatible with the common observation that the magnitude of the coupling constants attenuates with increasing number of bonds separating the nuclei. McConnell has suggested an

attenuation factor of 10 for each additional intervening saturated bond.[12]

Whereas some headway has been made in the theoretical treatment of proton-proton interactions,[11] not much progress has been made in the prediction of fluorine-fluorine coupling constants, although a large number of such coupling constants have been determined experimentally. Perhaps the most complete treatment of the problem is due to McConnell,[13] who applied MO theory to the evaluation of the coupling constants in $C_2F_4$. He stated that "nuclear spin coupling between pairs of nuclei other than protons present a much more complex problem from a theoretical point of view. This is true because, in general, both one-electron orbital and two-electron spin and orbital interactions can make significant and sometimes comparable contributions to nuclear spin coupling." The conclusion he made was that "nuclear spin couplings between nuclei that are not directly bonded to one another but which make use of both s and p atomic orbitals for molecular binding will involve significant contributions from both electron spin and electron orbital interactions with the nuclei." Karplus[11] attempted to interpret the observed coupling constants in fluoro-ethylenes by considering only the contact term, although he suggested that fluorine-fluorine couplings are more complicated than the proton-proton coupling because terms other than the contact term may make significant contributions. Recently, Gutowsky and Mochel,[14] found that the coupling constants ($J_{FF}$) for some 2-Fluorobenzotrifluorides depend upon the 6-substituent. They found that the approximate, theoretical expression developed by Pople for the orbital contribution to $J_{FF}$, and which relates the

anisotropy of the chemical shift and the molecular geometry to the orbital contribution, leads to values which depend on the angle between the principal axis of the chemical shift tensor, which lies along the C-F bond, and the F-F vector, and on the F-F internuclear distance. These angular dependent values are too small by at least an order of magnitude to account for the results they observed. They also noted that Karplus' valence-bond estimate of the contact contribution to $J_{FF}$ differs by a twofold factor for cis and trans fluorines in fluoroethylenes,[11] which factor is similar to that they found for the cis and trans rotamers of 2-Fluorobenzotrifluorides, in which the $CF_3$ group has two distinguishable, preferred orientations with respect to the plane of the benzene ring, such that an F from the $CF_3$ group is cis, in one case, and trans, in the other case, to the 6-substituent. They suggest, therefore, that the theoretical explanation of their results should be sought first in the contact term and its dependence upon molecular geometry and substituents.

In view of the additional electronic p orbitals in the vicinity of the nuclei involved, the problem of fluorine-fluorine coupling is certainly more complicated than is the case of coupling between protons. It would not be surprising, therefore, if fluorine-fluorine coupling could proceed via more than one mechanism.

## II. FLUORINE-FLUORINE COUPLING CONSTANTS

A striking anomaly is observed in fluorine coupling constants in fluoro-organic compounds. In 1956 Saika and Gutowsky[15] reported a near-zero coupling constant between the fluorine atoms on adjacent carbon atoms on adjacent carbon atoms in the molecule $CF_3CF_2N(CF_3)_2$. This was unexpected, since fluorine-fluorine coupling constants were known to be large, and particularly since the other two coupling constants are 16 and 6 cps for the fluorine nuclei separated by four and five bonds, respectively. Since that time about 20 similar cases have been reported in the literature.[16, 17] While the coupling constants between vicinal fluorine atoms are nearly zero in a great number of compounds, the F-F coupling constants in $HF_2CCF_3$,[18] $H_2FCCF_3$,[18] $BrF_2CCFBr_2$,[19] and many other substituted ethanes are large. In fact, the range of vicinal fluorine coupling constants for the different halogen substituted ethanes appears as follows:[20]

$XF_2CCF_3$, 0-5 cps;

$XYFCCF_3$, 4-9 cps ($H_2FCCF_3$ gives 15.5 cps[18]);

$XF_2CCF_2Y$, 1-8 cps;

$XF_2CCFXY$, 13-24 cps ($ClF_2CCFCl_2$ gives 9.4 cps[21]).

The magnitudes of the coupling constants appear to increase as the electronegativity of the substituents decrease in the order I > H > Br > Cl > $CF_3$ > F.

Several hypotheses have been advanced to explain the near-zero coupling constants between some vicinal fluorine atoms. In the case of

perfluoroethyl groups it has been widely assumed that the near-zero coupling constants come about as a result of the accidental averaging to zero of the non-zero coupling constants for the three stable configurations with respect to rotation about the connecting carbon-carbon bond. This idea was originally presented in the literature by Crapo and Sederholm.[16] It was further invoked by Harris and Sheppard.[20] But Petrakis and Sederholm[17] found that while the coupling constants between a $CF_3$ group and a vicinal $CF_2$ are nonvanishing in some compounds, this coupling constant is nearly zero in many compounds. They argued that if the explanation offered above is valid, one must assume that the coupling constant does not vary much from compound to compound, but is only a function of the dihedral angle. This would lead one to predict that the coupling constants in all compounds having the $CF_3CF_2$-group would be nearly zero, which is not the case. This idea was thus shown to be untenable by Petrakis and Sederholm.[17] Recently, it has been established that in substituted ethanes the trans and gauche coupling constants have the same sign[19, 21] so that no accidental averaging to zero of the non-zero coupling constants can occur for the three-stable configurations with respect to rotation about the connecting carbon-carbon bond. Petrakis and Sederholm[17] advanced another explanation for the vanishing vicinal fluorine coupling constants, that of "through-space" coupling. According to this explanation, fluorine atoms couple almost completely due to the direct overlap of orbitals on two fluorine atoms. The overlapping orbitals need not be bonding orbitals. The coupling constant is assumed to increase monotonically as the amount of overlap increases, i.e., as the fluorine-fluorine distance decreases. Petrakis and Sederholm postulated

that the coupling constant goes to zero when the distance between the fluorine atoms becomes greater than 2.73Å. This distance is just the sum of the Van der Waal radii of the two interacting fluorine atoms. Assuming normal bond lengths and bond angles, and assuming that the staggered configurations are the favored ones, the closest fluorine-fluorine approach between the two set sets of fluorine atoms in the $CF_3$-$CF_2$ or R-$CF_2$-$CF_2$-R' group is 2.73Å. Thus, if F-F coupling constants are determined solely by this non-bonded interaction, the near-zero coupling constants are easily explained. Petrakis and Sederholm further explain that the non-zero coupling constants observed in compounds such as $FC(CF_3)_3$,[17] $Cl_2FCCF_3$,[22] or $IClFCCF_2CF_3$[16] in terms of bulky $CF_3$, Cl or I groups forcing the vicinal fluorine atoms together. However, in view of recent data for $HF_2CCF_3$ and $H_2FCCF_3$,[18] which have coupling constants of 2.8 and 15.5 cps, respectively, and in which the substituents are smaller than the fluorine atoms they replace, the latter part of this explanation is seriously questioned. This, and the fact that the trans coupling constant in $CF_2BrCFBr_2$ is 16.2 cps,[19] whereas a near-zero value would be expected on the basis of "through-space" interaction only, cast doubt on the validity of the "through-space" mechanism as the complete explanation for the overall pattern of F-F coupling constants.

In the present work an attempt is made to offer a more complete explanation for fluorine coupling constants. Without abandoning the "through-space" mechanism it is proposed here that for vicinal fluorine coupling constants both "through-bond" and "through-space" mechanisms are important. The "through-space" mechanism gives a contribution to the coupling when two fluorine atoms get close to each other in space.

## III. "THROUGH-BOND" COUPLING

As pointed out in the previous section, vicinal fluorine coupling constants depend upon the electronegativity of the substituents present. In a study of some substituted ethanes Dyer[23] has indicated that fluorine geminal coupling constants are dependent on the Pauling electronegativity of the third substituent at the carbon atom. This suggests that highly electronegative substituents withdraw electrons carrying nuclear spin information between the interacting nuclei, thereby reducing the coupling constants. In the case of vicinal coupling constants, it is probably the C-C bond which is being depleted. One need not picture the highly electronegative substituents as substantially reducing the electron density in the carbon-carbon bond, but only reducing the density of electrons in excited triplet or $\pi$ states which are responsible for the transmission of spin information.

If this "vampire effect" of the highly electronegative substituents is part of the explanation for the pattern of vicinal fluorine coupling constants, it should be possible to correlate the observed coupling constants with the sum of the electronegativities of the substituents. Such a correlation is shown in Fig. 1, where, for a series of substituted ethanes $X_2FC\text{-}CFX_2$, in which each X is any halogen or a hydrogen atom, a plot of the sum of the Pauling electronegativities of the four X's vs the observed F-F coupling constants shows an excellent correlation. Halogen substituted propanes can be added to this plot if an electronegativity of about three is assigned to the groups $CF_3$, $CF_2Cl$, $CF_2Br$, and $CF_2H$. This second plot is shown in Fig. 2. The scatter of the points is somewhat poorer when the propanes are added, probably due to

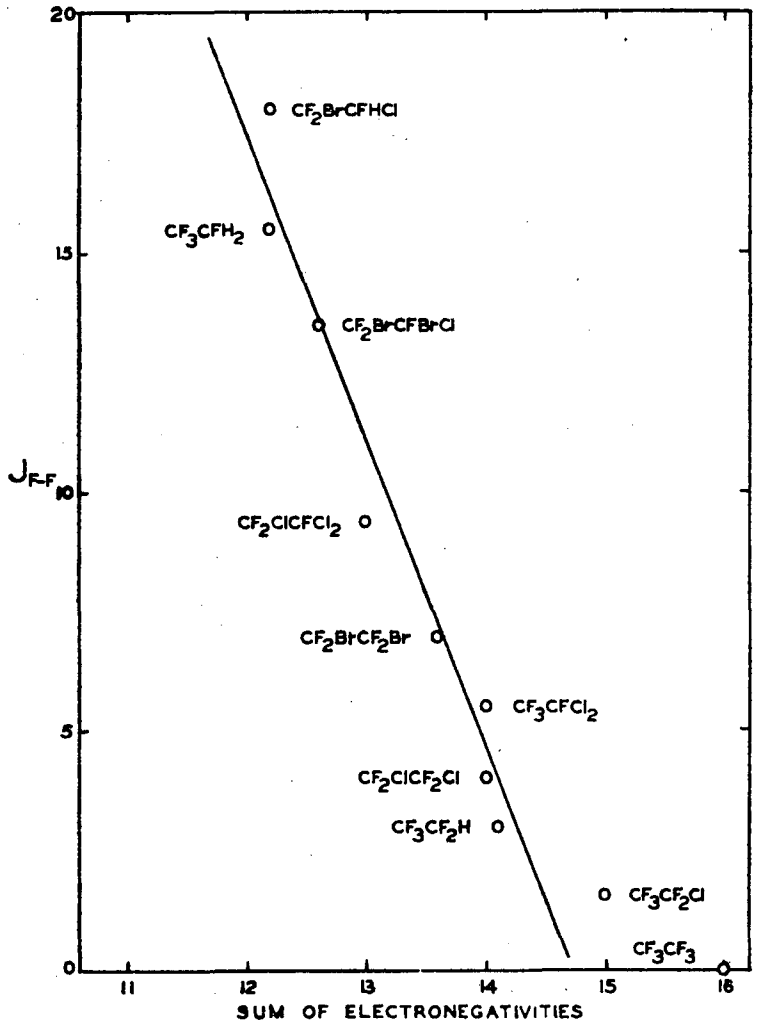

20
15
10
5
0
$J_{F-F}$
$CF_2BrCFHCl$
$CF_3CFH_2$
$CF_2BrCFBrCl$
$CF_2ClCFCl_2$
$CF_2BrCF_2Br$
$CF_3CFCl_2$
$CF_2ClCF_2Cl$
$CF_3CF_2H$
$CF_3CF_2Cl$
$CF_3CF_3$
11
12
13
14
15
18
SUM OF ELECTRONEGATIVITIES
MU-33566

Fig. 1-I

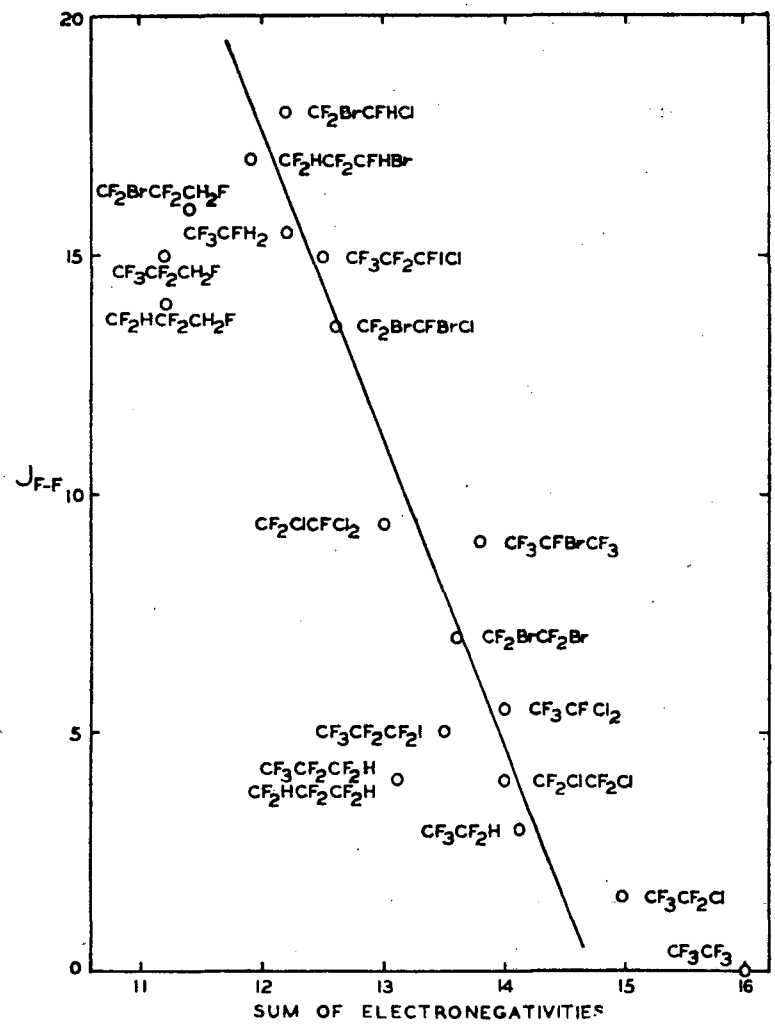

20
15
10
5
0
$J_{F-F}$
$CF_2BrCFHCl$
$CF_2HCF_2CFHBr$
$CF_2BrCF_2CH_2F$
$CF_3CFH_2$
$CF_3CF_2CFICl$
$CF_3CF_2CH_2F$
$CF_2HCF_2CH_2F$
$CF_2BrCFBrCl$
$CF_2ClCFCl_2$
$CF_3CFBrCF_3$
$CF_2BrCF_2Br$
$CF_3CFCl_2$
$CF_3CF_2CF_2I$
$CF_3CF_2CF_2H$
$CF_2HCF_2CF_2H$
$CF_2ClCF_2Cl$
$CF_3CF_2H$
$CF_3CF_2Cl$
$CF_3CF_3$
11
12
13
14
15
16
SUM OF ELECTRONEGATIVITIES
MU-33567

Fig. 2-I

the longer carbon skeleton from which excited electrons can be withdrawn.

It should be noted that on the basis of such an argument, vicinal fluorine atoms attached to nearly perfluorinated carbon skeletons would be expected to show a zero coupling constant, as observed. However, this would also predict a zero F-F coupling constant <u>through the bonds</u> between fluorine atoms separated by more than three bonds in nearly perfluorinated groups.

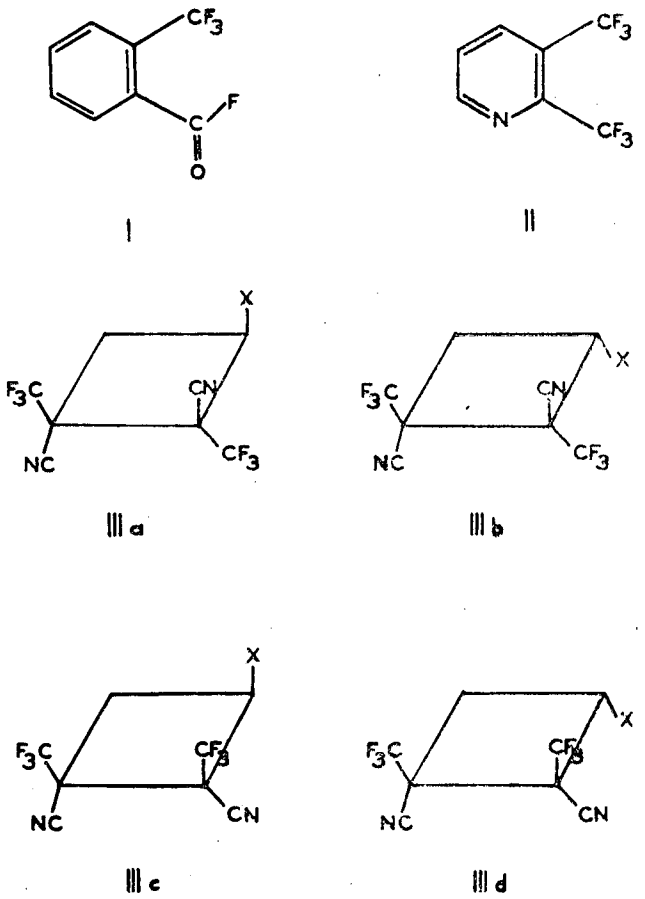
## IV. "THROUGH-SPACE" COUPLING

Having shown how electronegativity of substituents affects fluorine coupling through the bonds, it remains to demonstrate that fluorine can also couple through non-bonded interactions. This latter mechanism is postulated to come about as a result of overlap of the electronic clouds of the fluorine atoms whenever the geometry of the molecules offers such opportunity. This fluorine interaction proceeds via an electronic structure where there is no bond per se. The sizeable coupling constants observed between fluorine nuclei separated by more than three bonds as in $CF_3CF_2N(CF_3)_2$ and in a large number of other compounds have already been explained in terms of this mechanism.[17]

In this work a crucial experimental test for this "through-space" mechanism is attempted. For this purpose a study is made of the NMR spectra of molecules whose fluorine nuclei are in close proximity and yet separated by at least five bonds so as to eliminate substantially any coupling through the bonds. The fluorine NMR spectra of several such molecules will be discussed. These are (I) o-trifluoromethylbenzoyl fluoride, (II) 2,3-bis(trifluoromethyl)-pyridine, (III a, b, c, d) 1,2-bis-(trifluoremthyl)-1,2-dicyanocyclobutanes, as shown in Fig. 3.

### Experimental

The NMR spectra were taken at room temperature with a Varian Associates HR-60 spectrometer operating at 56.4 mc/sec. Audio-frequency modulation of the magnetic field was used to produce sidebands for calibration. The values of the coupling constants are the averages of 10 to 15 determinations.




I II

III a III b

III c III d

X = $OCH_2CH_3$, $SC(CH_3)_3$, *p*-$CH_3OC_6H_4$.

MU-33570

Fig. 3-I

The preparation of Compounds I and II was done in a stainless steel cylinder constructed as follows: a 75-ml Hoke stainless steel cylinder, closed at one end, is connected to a stainless steel T-joint, at whose leg #2 is fitted a Hoke needle valve, and to the other end of this valve is connected a short piece of copper tubing ending with a 10/30 standard tapered copper joint; in addition, leg #3 of the T-joint is fitted with a stainless steel cap. A diagram of the whole assembly is shown in Fig. 4. Such a high pressure cylinder was necessary since the fluorinating agent used was sulfur tetrafluoride, $SF_4$,[24] which has a boiling point of -38 to -37°C and vapor pressures of 150 p.s.i. gauge (approx.) at 26°C and 350 p.s.i. gauge (approx.) at 55°C.

Sulfur tetrafluoride has the special property of converting carbonyl groups into difluorides and carboxylic acid groups first in acyl fluorides and then into trifluorides upon further reaction:[25]

$$SF_4 + >C{=}O \longrightarrow CF_2 + SOF_2$$

$$SF_4 + -COOH \longrightarrow COF \longrightarrow CF_3 + SOF_2$$

The reaction cylinder was prepared for carrying out each reaction in it as follows: the Hoke valve was removed from the T-joint. After the cylinder was flushed with nitrogen, a weighed quantity of the sample to be reacted with $SF_4$ was introduced into it by means of a funnel placed at the T-joint where the value was removed. A tiny drop of water was also introduced since this reacts with $SF_4$ to produce HF, which is a catalyst for the $SF_4$ reaction. The Hoke valve was then secured in position, the threads made gas tight by means of Teflon tape. The cap at leg #3 of the T-joint was also made gas tight by means of a piece of Teflon placed inside it. With the Hoke needle valve closed,

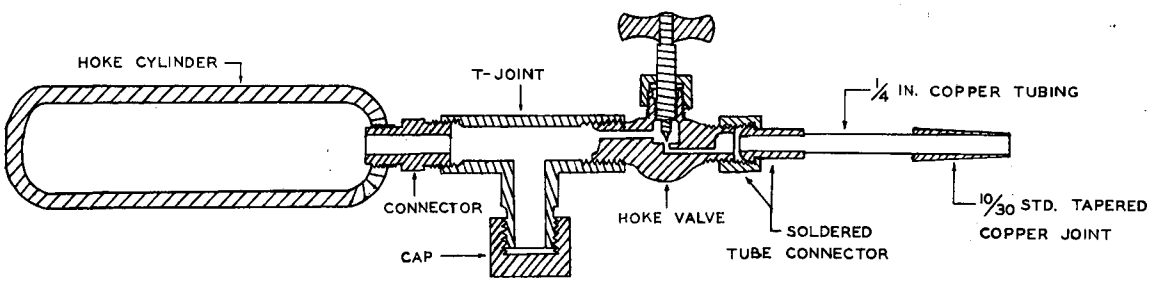
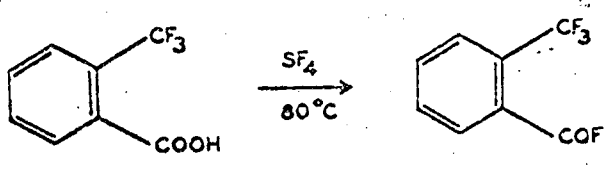

HOKE CYLINDER
T-JOINT
1/4 IN. COPPER TUBING
CONNECTOR
HOKE VALVE
SOLDERED
TUBE CONNECTOR
10/30 STD. TAPERED
COPPER JOINT
CAP
MU-33565

Fig. 4-I

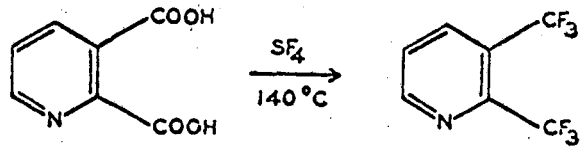
the assembly was then connected to a vacuum line at the tapered copper joint. The cylinder was now cooled with liquid nitrogen and then evacuated. $SF_4$ gas was introduced into a 5-liter round flask connected to the vacuum line, which also had a barometer attached to it. The pressure of the required amount of $SF_4$ gas in the 5-liter flask was calculated. The amount of gas thus measured was transferred into the reaction cylinder via the vacuum line. The assembly, upon warming, was immersed in an oil bath and heated at a temperature and for a period of time, estimated from similar reactions reported in the literature.[25]

After the experiment the cylinder was cooled in an ice-salt bath and the gases in it vented through the needle valve. This step presumed that the reaction products had low vapor pressures. Then a small quantity of solvent was introduced into the cylinder through leg No. 3 of the T-joint so as to recover the reaction products. The product was then purified, usually by distillation.

The compound o-trifluoromethylbenzoyl fluoride was prepared by reacting o-carboxybenzotrifluoride (Peninsula Chemresearch, Inc.) with $SF_4$ gas in the cylinder, as described above, at 80°C for 10 hours. The product was distilled at 40°C under 2 mm Hg pressure.

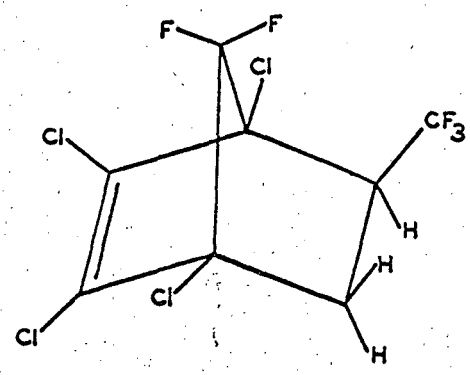


The compound 2,3-bis-(trifluoromethyl)-pyridine was prepared by reacting quinolinic acid with $SF_4$ gas at 140°C for 14 hours. The product was distilled at 35°C under 6 mm Hg. pressure.

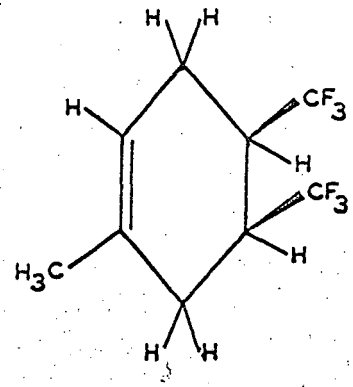



Attempts to Synthesize Other Compounds

Attempts were made to synthesize the following compounds: (IV) 1,4,5,6-tetrachloro-bicyclo (2,2,1)-5-heptene-7,7-difluoro exo-2-trifluoromethyl, and (V) 3-methyl-4-cyclohexene-sic-1,2-bis-(trifluoromethyl).




(IV)

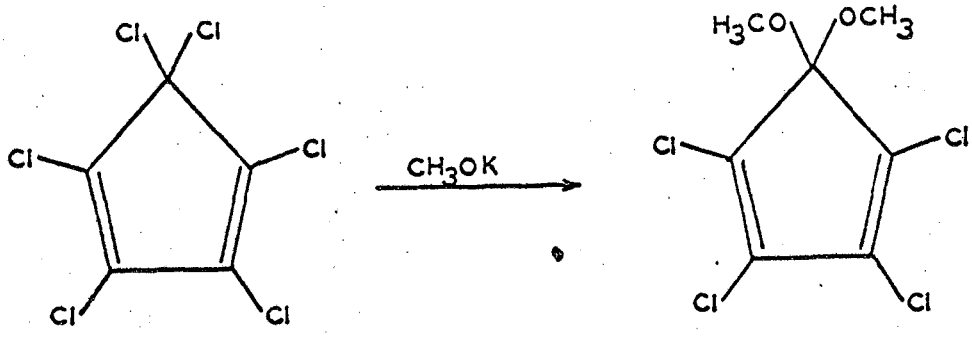



(V)

MU-33832

Compound (IV)

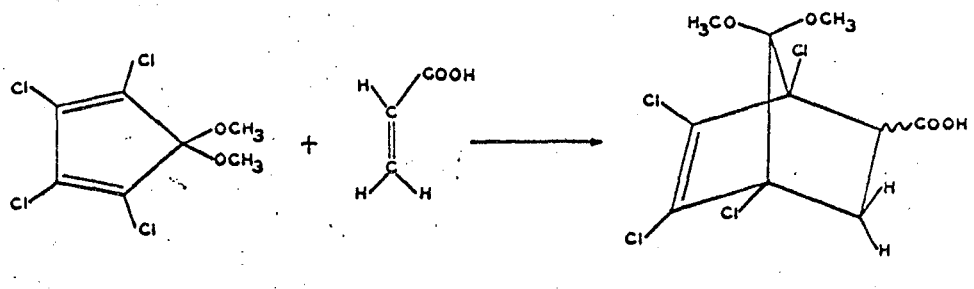
Hexachloropentadiene was converted to 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene in the following reaction:[26]




MU-33831

The product was distilled at 110°C under 12 mm Hg. pressure.

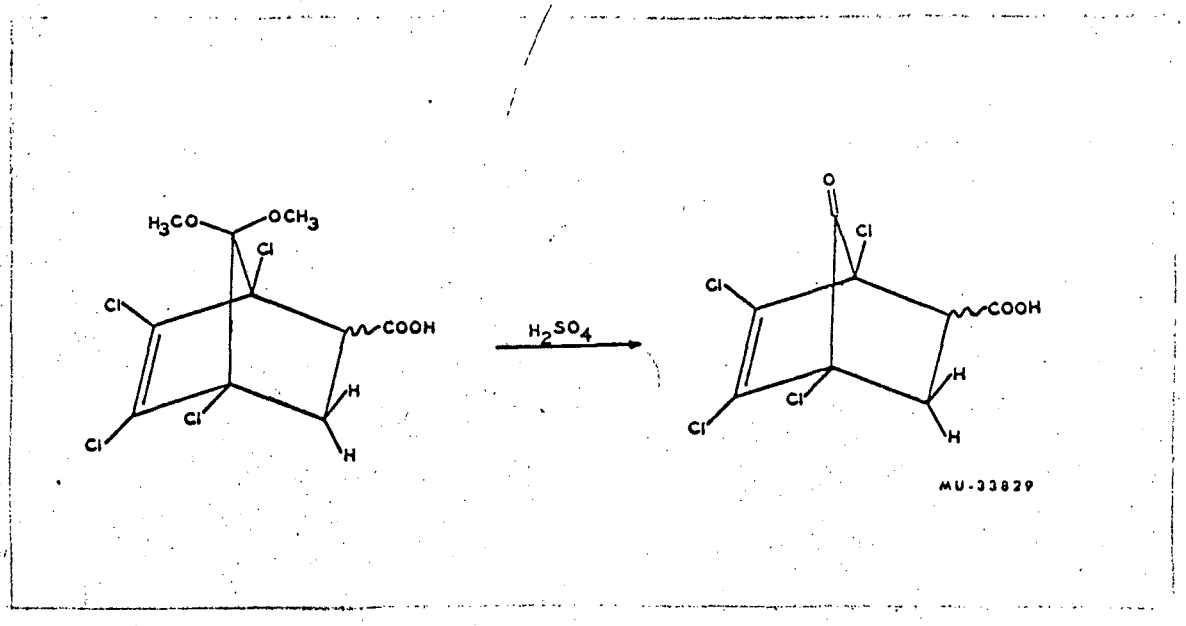
The next step in the synthesis was the Diels-Alder condensation between equimolar amounts of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and acrylic acid, $CH_2$ = CH-COOH.[27]




MU-33830

The product 1,4,5,6-tetrachloro-bicyclo (2,2,1)-5-heptene-7,7 dimethoxy-2-carboxylic acid, was crystallized from benzene. M.P. = 163-164°C. It was not known whether the carboxylic acid group was oriented exo or endo. The sharp melting point indicated that there was only one isomer in the product. In view of the large methoxy group at the 7-position on the same side of the bridge in the molecule as the acid group, steric considerations would favor the endo isomer as the sole product. However, which isomer the product was could not be determined.

The next step was the hydrolysis of the two methoxy groups at the 7-position of the bicyclic compound to the corresponding ketone group.[27] This was done with concentrated sulfuric acid (96%) in 20 times excess for 50 hours in the cold. After the hydrolysis, the concentrated reaction mixture was diluted and allowed to stay overnight with stirring. The product was then extracted with ether.




The product, having a ketone group on the bridge of the molecule, showed a strong absorption at 5.5 microns on the infrared spectrum, indicating a

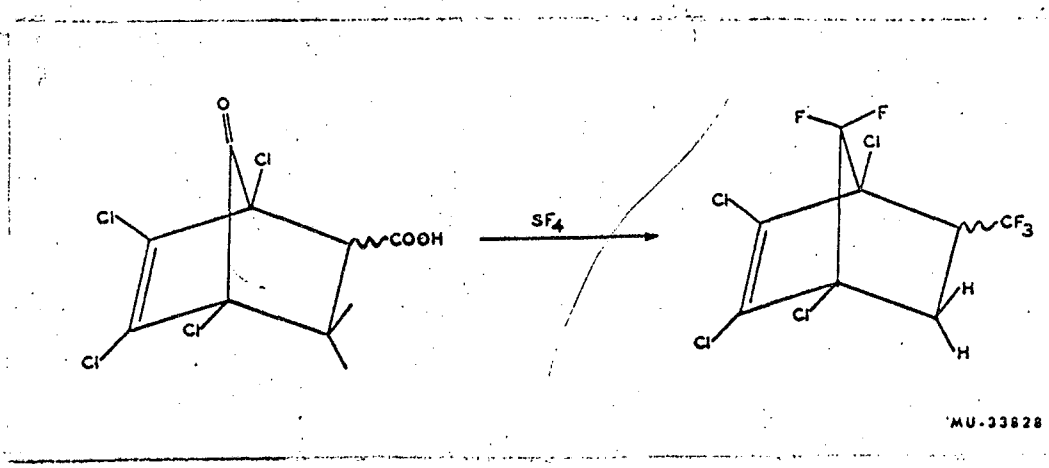
highly strained carbonyl group. M.P. = 90°C. This compound is hereafter referred to as ketone-acid.

With the 7-carbon forming a carbonyl group, steric factors would now permit the carboxylic acid group in the exo orientation. The acid group could, in principle, be oriented by epimerizing with a base.

For the epimerization, the ester was made, and a solution of sodium methoxide, $NaOCH_3$ in methyl alcohol was added to the ester dissolved in methyl alcohol. However, the reaction failed. It resulted in the loss of the carbonyl group, as indicated by the infrared spectrum of the resulting product, which now was chemically and spectroscopically different from the original ester.

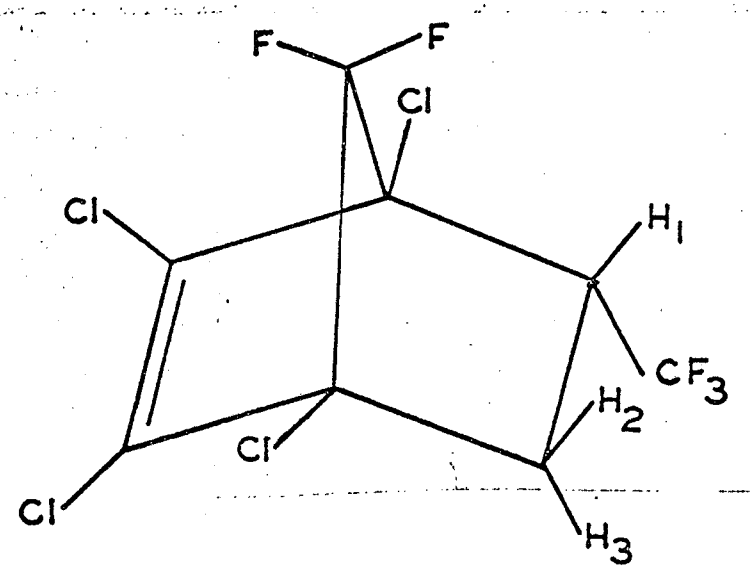
It was felt that the treatment applied for the hydrolysis was sufficient to epimerize the carboxylic acid group. In fact, the proton NMR spectrum of the ketone-acid product was found to be the superposition of two ABC spectra, arising from the 3 protons on the molecule. This NMR spectrum indicated that both isomers were present in the ketone-acid product. It was not possible to separate the two isomers.

Nevertheless, the ketone-acid product was reacted with sulfur tetrafluoride, $SF_4$, to effect the following reaction:



The reaction was carried at 40°C for 3 hours and at 120°C for 20 hours. The reaction products were passed through alumina. Only one fraction gave a reasonable fluorine NMR spectrum of the expected products. The spectrum is described below.

The fluorine NMR spectrum exhibited a doublet and two pairs of resonances, the areas under these two sets of resonances bore the ratio 3:2. The separation in the doublet was 8 cps and that between the components of each of the two pairs was 157 cps. The components were not of equal intensity, but the pairs were identical. One of the pairs further exhibited a doublet structure in each of the components, with a separation of 3 cps. This spectrum could be explained in terms of the following compound:

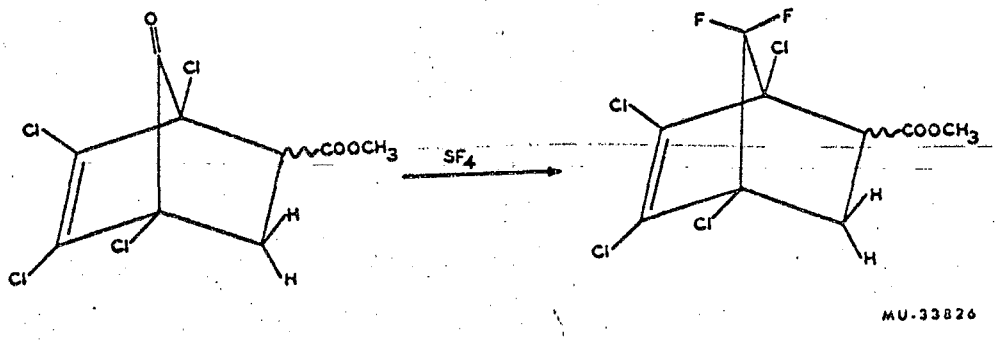



The two pairs of resonances were attributed to the AB spectrum of $F_1$ and $F_2$, and the 157 cps separation was the coupling constant between the two fluorine nuclei. The large doublet was attributed to the $CF_3$ group and the separation of 8 cps was the coupling between $H_1$ and

the $CF_3$ group. The separation of 3 cps in one of the pairs of the resonances must be due to one of the two fluorine nuclei coupling with a proton, presumably $F_1$ coupling with either $H_1$ or $H_2$.

In the above compound, it could not be ascertained whether the $CF_3$ group was oriented endo or exo. The NMR spectrum described above was consistent with the endo isomer. It appeared that the reaction of $SF_4$ with the isomers of the ketone-acid resulted in a one-isomer product. In terms of steric considerations, the isomer with the $CF_3$ group endo would be the favored product. This isomer with the $CF_3$ group endo was not the desired product.

Another approach to the synthesis of the desired compound has been proposed. This involves the following reaction:




Having placed two fluorine atoms on the bridge of the molecule, the ester group could be epimerized with a base such as sodium methoxide. This epimerization reaction could be ascertained from the proton NMR spectrum of the 3 hydrogen atoms on the molecule. If it could be

ascertained that the ester group has the exo orientation, then conversion of this ester group to the $CF_3$ group would result in the desired compound.

Compound (V)

A series of attempts was made to react 3-methyl-4-cyclohexene-cis-1,2-dicarboxylic acid with sulfur tetrafluoride, $SF_4$, to obtain the above-named compound. The reaction was never successful.

## Discussion

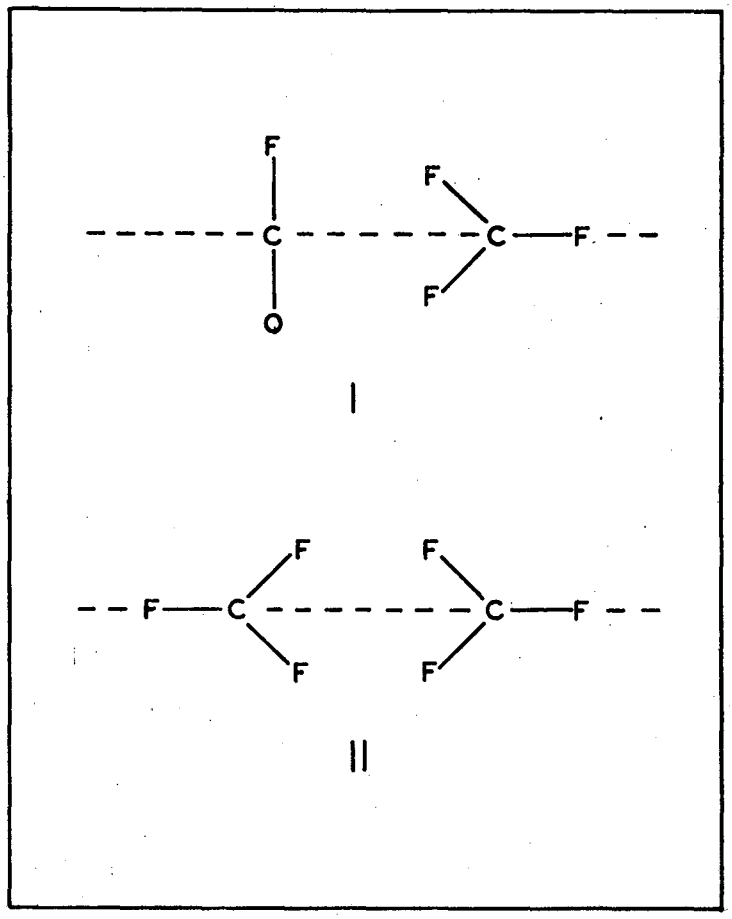
The coupling constants in compounds (I) and (II) can be compared with those in trans-2-chloro-heptafluorobutene-2.[28] The coupling constant between the fluorines in the two $CF_3$ groups (trans across the double bond) is 1.3 cps. This coupling constant is quite normal for fluorine atoms separated by four saturated and one olefinic bonds. As the $CF_3$ groups are trans across the double bond there can be no direct overlap between the electronic clouds of the fluorine atoms.

(I) o-trifluoromethylbenzoyl fluorine. This compound gives a simple first order fluorine NMR spectrum, consisting of a doublet and a quartet, the latter being at low field; see Fig. 5. The coupling constant between the fluorine nuclei is 10.9 cps and the chemical shift is 5438 cps. As the interacting fluorine nuclei are separated by one aromatic and four saturated bonds, the through-bond coupling is assumed to be of the order of 1 cps as in the case of the butene cited above. The 10.9 cps must be due almost entirely to "through-space" coupling as the geometry of the molecule provides excellent opportunity for the direct overlap of the electronic clouds of the fluorine nuclei.

Assuming that the equilibrium configuration is such that the plane of the acyl group is perpendicular to the benzene ring and two atoms of the $CF_3$ group are equidistant from this plane, as shown in Fig. 6, the closest F-F distance is about 2.62Å. Referring to the coupling constant vs distance curve (Fig. 7) postulated by Petrakis and Sederholm,[17] this distance should give a coupling constant of 30-35 cps, which, when weighted by 1/3, agrees with the experimentally observed averaged value of 10.9 cps.

MUB-2453

Fig. 5-I




MU-32498

Fig. 6-I

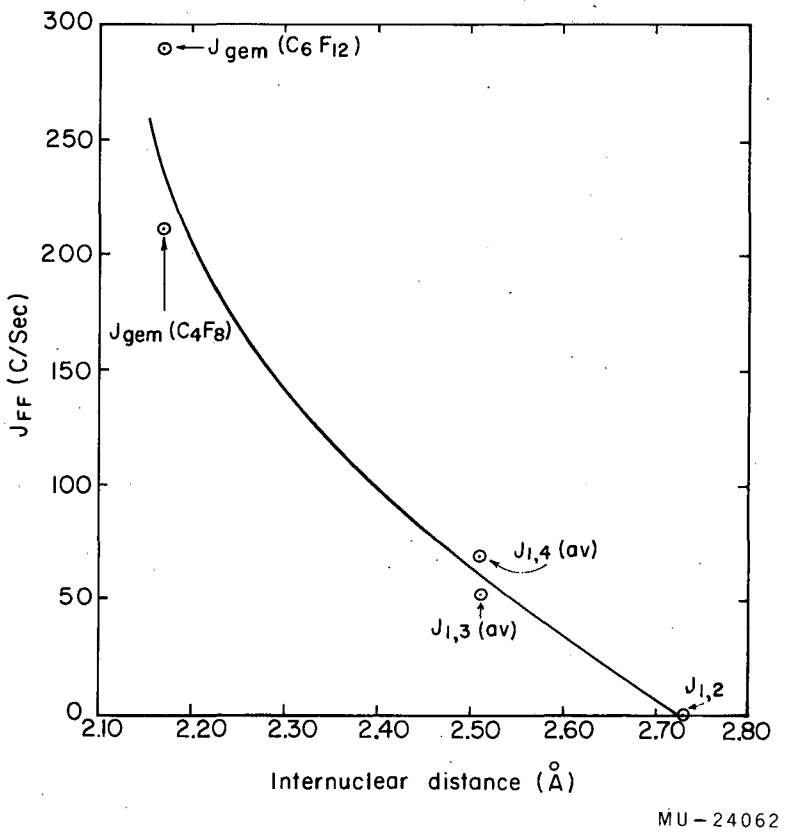
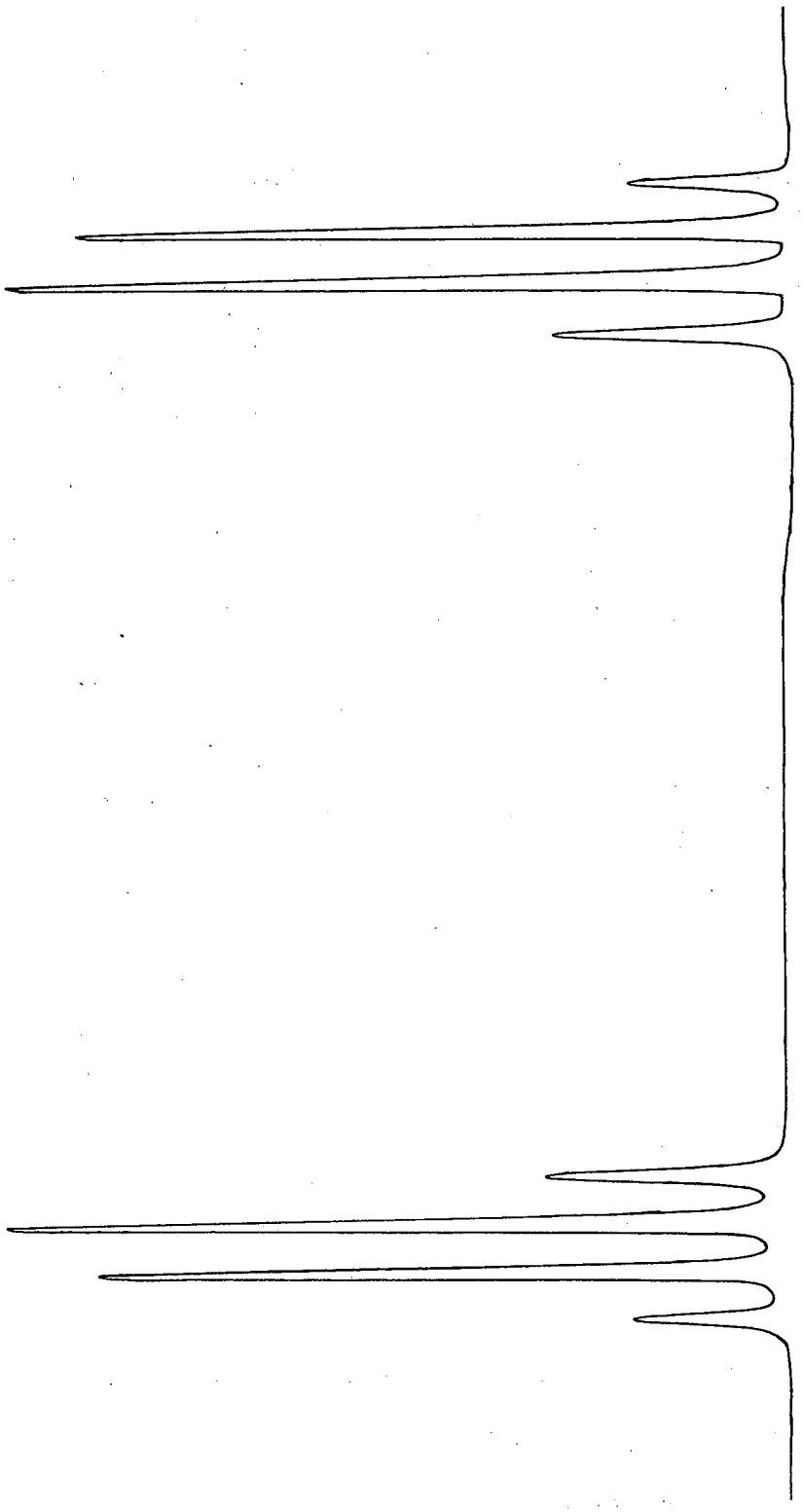

300
250
200
150
100
50
0
$J_{FF}$ (C/Sec)
$J_{gem}$ ($C_6F_{12}$)
$J_{gem}$ ($C_4F_8$)
$J_{1,4}$ (av)
$J_{1,3}$ (av)
$J_{1,2}$
2.10
2.20
2.30
2.40
2.50
2.60
2.70
2.80
Internuclear distance (Å)
MU-24062

Fig. 7-I

(II) 2,3-bis-(trifluoromethyl)-pyridine. The fluorine NMR spectrum of this compound consists of two quartets. Due to the rather small chemical shift (239 cps), the quartets are not of the genuine 1:3:3:1 pattern. See Fig. 8. The coupling constant is 12.8 cps. The fluorine nuclei are separated by one aromatic and four saturated bonds so that any coupling through the bonds should again be no more than one or two cps as in the case of the butene cited above. The close proximity of the fluorine nuclei again provides ample overlap of their electronic clouds so that the large coupling constant observed must be due almost entirely to "through-space" coupling.

By drawing analogy with o-xylene, for which Pitzer and Scott[29] have shown the preferred orientation of the two $CH_3$ groups to be the out-of-mesh position, the favored orientation of the two $CF_3$ groups is assumed to be also in the out-of-mesh position, as shown in Fig. 6. Allowing some angular distortion in the C-C-F bond angles of both groups, the closest F-F distance is approximately 2.5Å. Again referring to the coupling constant vs distance curve[17] (Fig. 7), this distance predicts a coupling constant of about 60 cps, which, when weighted by 2/9, gives approximately the experimentally observed averaged value of 12.8 cps.

(III a, b, c, d) 1,2-bis-(trifluoromethyl)-1,2-dicyanocyclobutanes. Recently, the preparation of a series of 1,2-bis-(trifluoromethyl)1,2-dicyanocyclobutane diastereoisomers has been reported and their fluorine NMR spectra are described as follows:[30] diastereoisomer mixture IIIa + IIIb "exhibits a fluorine NMR spectrum consisting of four singlet resonances appearing as two pairs whose components are of equal intensity," and diastereoisomer mixture IIIc + IIIc "exhibits two pairs of



MUB-2452

Fig. 8-I

resonances whose components are of equal intensity, ... , and the resonances appear as quadruplets (due to mutual-splitting of the $CF_3$- groups) rather than singlets." One of the authors, S. Proskow,[31] has provided the detailed information about the fluorine NMR spectra of the diastereoisomer mixtures, Fig. 9. Table I lists the fluorine coupling

Table I. Coupling Constants for the Cyclobutanes

| cyclobutane diastereoisomer mixture | Substituent X | Coupling Constant, cps |
|---|---|---|
| IIIc + IIId | $OCH_2CH_3$ | 12 and 10 |
| IIIc + IIId | $SC(CH_3)_3$ | 11 and 11 |
| IIIc + IIId | $p\text{-}CH_3OC_6H_4$ | 12 and 10 |

constants. The components of the mixtures IIIa + IIIb have zero coupling constants for all substituents X. In diastereoisomer mixtures IIIc + IIId it is known which value of the pair of coupling constants belongs to which stereoisomer since the configurations of the individual compounds are not established. The value listed forst for each set of diastereoisomers is that for the more abundant product.

Since in cyclobutanes IIIa + IIIb the $CF_3$ groups are transoriented, the closest F-F distance certainly falls outside the range for coupling through space to be effective. As the fluorine nuclei are separated by five saturated bonds, it is not expected that through-bond coupling is operative. Hence, the "singlet resonances" observed for the $CF_3$ groups. However, in the case of cyclobutanes IIIc + IIId in which the $CF_3$ groups are cis-oriented, the fluorine nuclei are close enough so that there is

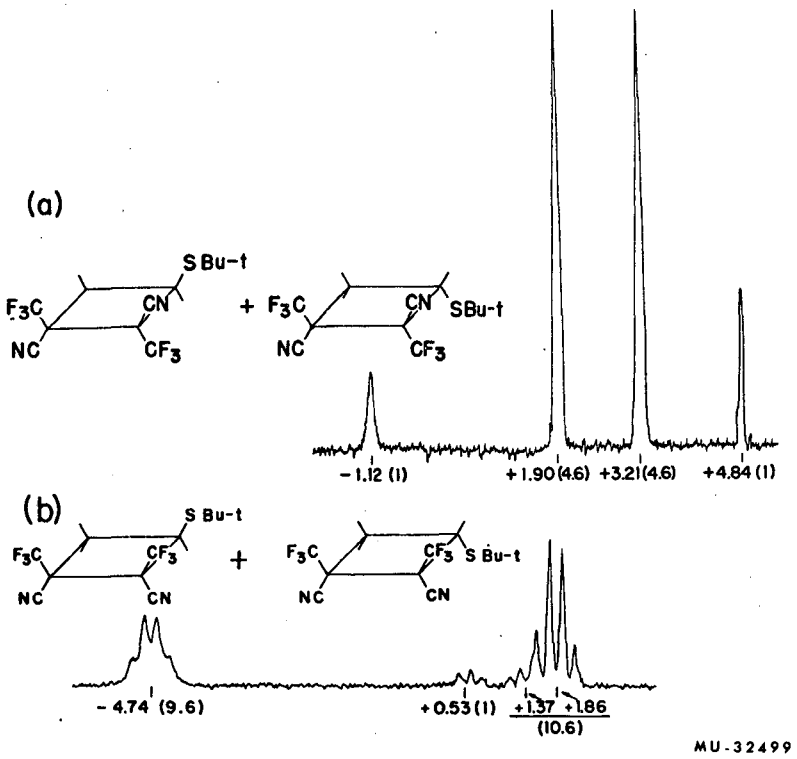

(a)
S Bu-t
F3C
CN
NC
CF3
+
F3C
CN
SBu-t
NC
CF3
-1.12 (1)
+1.90 (4.6)
+3.21 (4.6)
+4.84 (1)
(b)
S Bu-t
F3C
CF3
NC
CN
+
F3C
CF3
S Bu-t
NC
CN
-4.74 (9.6)
+0.53 (1)
+1.37
+1.86
(10.6)
MU-32499

Fig. 9-I

appreciable overlap of the electronic clouds to effect coupling through space. The 10 to 12 cps coupling constants observed for these cis-oriented $CF_3$ groups can be accounted for in no other way. These cyclobutanes with cis- and trans-oriented $CF_3$ groups offer, therefore, the most dramatic evidence for the "through-space" mechanism.

## V. CONCLUDING REMARKS

The above sections show quite explicitly that fluorine nuclei couple via two mechanisms. The "through-bond" mechanism proceeds through the electronic structure in the intervening bonds, as is the case with proton coupling, whereas the "through-space" mechanism becomes operative only when there is direct overlap of the electronic clouds of the fluorine atoms, proceeding through an electronic structure where there is no bond per se. For fluorine nuclei separated by two bonds, i.e., geminal fluorines, the two mechanisms may operate simultaneously, and indeed are not distinguishable. The two contributions would result in very large coupling constants ranging, as observed, from 150 to 400 cps. In the case of vicinal fluorines only the "through-bond" mechanism is normally important. The magnitude of the "through-bond" coupling is governed by the electron-withdrawing power of the other substituents attached to the carbon skeleton which can cause the coupling to vanish. When the fluorine nuclei are separated by more than three bonds, the coupling between them, though diminishingly small from the "through-bond" mechanism, may be enhanced if the geometry of the molecule allows the nuclei to get into close proximity so that the "through-space" mechanism becomes operative. The zigzag pattern of the carbon skeleton and the angular bonds formed by atoms such as N, O, etc., give rise to situations which can cause fluorine nuclei to couple through non-bonded interactions. Qualitatively then, one can readily account for all F-F coupling constants in saturated compounds so far investigated in terms of these two mechanisms.

It is expected that in the case of F-F coupling the contributions from the magnetic dipolar and electron-orbital terms, in addition to

the Fermi contact term, may be significant, although this is not yet established. This is because for non-s electrons the Fermi contact term vanishes and, as a result, the other spin-coupling terms which depend on the presence of angle-dependent atomic orbitals may become important. The Fermi interaction, proportional to $|\psi(r=0)|^2$, makes the principal contribution to the coupling constant between protons, because electrons on a hydrogen atom are well represented by 1-s atomic orbitals. However, since the s and p characters of the bonding are not known, it is difficult to assess the relative importance of the different parts of the Hamiltonian discussed in the introduction. But it is known that atomic p orbitals centered on F atoms contribute greatly to the bonding, while the p character of atomic orbitals centered on protons is generally considered small.

The large excursion of the p electrons centered on fluorine atoms makes it reasonable to assume that direct through-space coupling could be significant in F-F coupling constants, and less significant in H-H coupling constants. Direct through-space coupling of two nuclei A and B, separated by two or more bonds, may take place either through one-electron or two-electron interactions. Physically, the one-electron part arises because nucleus A interacts magnetically with an electron, which in turn interacts with nucleus B (nuclear moment A: electron: nuclear moment B); the two-electron part arises because nucleus A induces a perturbation on a local electron, which in turn interacts directly with an electron on nucleus B which then interacts magnetically with nucleus B (nuclear moment A: electron 1: electron 2: nuclear moment B).

The explanation outlined above for fluorine coupling constants should also be valid for coupling between all nuclei, particularly those with non-s electrons. Highly electronegative substituents have the same effect on proton coupling constants.[32,33] Roberts[34] et al have reported several examples of long-range H-H and H-F spin-spin couplings and have asserted that these couplings are exerted through space instead of through the bonds. In all these examples the favored conformation of the molecules is appropriate for the "through-space" mechanism to be effective. Hence fluorine-fluorine coupling constants no longer seem to need special explanations.

It is interesting to note that geminal and vicinal fluorine coupling constants can reveal the nature of the other substituents at the carbon atoms, owing to the "vampire effect" of the substituents. "Through-space" coupling can help decide the relative orientations of the interacting nuclei, as in the case of the cyclobutanes in the previous section. While a dihedral angular dependence of fluorine coupling constants has not been established, indications are that in substituted ethanes, the trans value is less than the gauche value, drawing from a few examples: in $CF_2BrCF_2Br$, $J_g$ = 12 cps, $J_t$ = 1.5 cps; and in $CF_2BrCFBr_2$, $J_g$ = 18.6 cps, $J_t$ = 16.2 cps. (This is just the reverse of what is known for proton coupling.) Future studies of fluorine coupling constants in molecules promise to be important in the elucidation of their structures.

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FIGURE CAPTIONS

Fig. 1, Part I. Plot of vicinal $J_{F-F}$ vs. sum of electronegativities of substituents in ethanes.

Fig. 2, Part I. Plot of vicinal $J_{F-F}$ vs. sum of electronegativities of substituents in ethanes and propanes.

Fig. 3, Part I. Compounds (I) o-trifluoromethylbenzoyl fluoride, (II) 2,3-bis-(trifluoromethyl)-pyridine, and (III) a,b,c,d) 1,2-bis-(trifluoromethyl)-1,2-dicyanocyclobutanes.

Fig. 4, Part I. Cross-section diagram of stainless steel reaction cylinder.

Fig. 5, Part I. $F^{19}$ NMR spectrum of Compound (I) o-trifluoromethyl-benzoyl fluoride.

Fig. 6, Part I. Projections of Compounds (I), o-trifluoromethyl-benzoyl fluoride, and (II), 2,3-bis-(trifluoromethyl)-pyridine in the plane perpendicular to the aromatic ring and parallel to the aromatic bond between the groups of F atoms. Dashed lines represent the aromatic ring.

Fig. 7, Part I. Plot of $F^{19}$ spin coupling constants as a function of internuclear distance between interacting nuclei.

Fig. 8, Part I. $F^{19}$ NMR spectrum of Compound (II) 2,3,-bis-(trifluoromethyl)-pyridine.

Fig. 9, Part I. $F^{19}$ NMR spectra of the cyclobutane diastereoisomer mixture: X = $SC(CH_3)_3$, (a) IIIa + IIIb; (b) IIIc + IIId. Spectra determined in $CCl_4$ at 56.4 Mc/sec and externally referenced in terms of displacement in parts per million relative to "Freon 112," 1,2-difluoro-1,1,2,2-tetrachloroethane. Relative areas are indicated in parentheses.

# NUCLEAR MAGNETIC RESONANCE STUDIES

## PART II: THE EFFECT OF SOLVENTS ON $F^{19}$ SPIN-SPIN COUPLING CONSTANTS


### ABSTRACT

The effect of solvents on the coupling constants of the compounds, bromotrifluoroethylene, 1,1-dichlorotetrafluoroethane, and the rotamers of 1,1,2-trifluoro-1,2-dibromo-2-chloroethane has been studied. The coupling constants are found to vary with the solvents. This implies that intermolecular interactions affect coupling constants to a degree that is not negligible. This effect of molecular interactions on fluorine coupling constants may be due to the dipolar character and polarizability of the interacting molecules. The interactions appear to be essentially of the same kind, and detailed differences arise from the nature and dipolar character of the solvent molecules.

The temperature dependence of fluorine coupling constants that has been reported previously may be due to this temperature dependent molecular interaction as well as population of excited vibrational states.

# PART II: THE EFFECT OF SOLVENTS ON $F^{19}$ SPIN-SPIN COUPLING CONSTANTS

## I. INTRODUCTION

Studies of nuclear magnetic resonance (NMR) coupling constants are significant as the details of the coupling phenomenon are yet to be unravelled. It has been shown that indirect fluorine-fluorine interactions are exerted through one or both of two mechanisms for nuclear spin-spin coupling: the though-bond and through-space mechanisms.[1] Factors that have been regarded as influencing NMR coupling constants are molecular vibrations and temperature dependent intermolecular interactions. Schug, McMahon and Gutowsky[2] have investigated the first phenomenon for vicinal proton coupling constants. The second phenomenon is the subject of this study. Investigation of these subtle effects on coupling constants between atoms other than hydrogen is important not only for a better understanding of the coupling phenomenon in some of its due complexity but also for the application of NMR techniques in the study of molecular geometry and of conformational isomerism.

In compounds, substituted ethanes in particular, in which rotational averaging occurs, it has been assumed that the chemical shifts and coupling constants of each rotamer can be obtained by a least squares fitting of the experimentally observed temperature dependent chemical shifts and coupling constants, which are time-weighted averages.[3] The averaged chemical shift can be written in the form[3]

$$\langle \nu_i \rangle = Q_{\phi}^{-1}[\nu_1^i \exp\left(-\frac{\Delta E_1}{RT}\right) + \nu_2^i \exp\left(-\frac{\Delta E_2}{RT}\right) + \nu_3^i], \qquad (1)$$

where $Q_\phi$ is the internal rotation partition function for three rotamers in thermal equilibrium,

$$Q_\phi = \exp\left(-\frac{\Delta E_1}{RT}\right) + \exp\left(-\frac{\Delta E_2}{RT}\right) + 1$$

The relative energies of the rotamers are defined by setting $\Delta E_1 = E_1 - E_3$ and $\Delta E_2 = E_2 - E_3$. The averaged coupling constant can likewise be written in the form[3]

$$\langle J_{ij} \rangle = Q_\phi^{-1} \left[ J_1^{ij} \exp\left(-\frac{\Delta E_1}{RT}\right) + J_2^{ij} \exp\left(-\frac{\Delta E_2}{RT}\right) + J_3^{ij} \right] \qquad (2)$$

It is obvious from Eq. (1) and (2) that the least squares fitting procedure assumes that the temperature dependence of $\langle \nu_i \rangle$ and $\langle J_{ij} \rangle$ results only from changes in the equilibrium populations of the rotamers and that the chemical shift and coupling constant have no intrinsic temperature dependence. However, recently Brey and Ramey[4] have observed the temperature dependence of the fluorine coupling constants of some fluoro-organic compounds, which exist only as one isomer. They attributed this temperature dependence of the coupling constants to populations of higher torsional and other vibrational states, giving larger weight to angles and atomic positions not corresponding to the equilibrium configuration. They subsequently reported that molecular interactions have negligible effect on the coupling constants.[5]

Newmark and Sederholm[6] have studied the time-weighted-average approximation in the NMR spectrum of $CF_2BrCFBrCl$ and found that there is a discrepancy of the order of 10% between the calculated high temperature and the observed averaged coupling constants. They

attributed this discrepancy to either population of excited torsional states or temperature dependent molecular interactions.

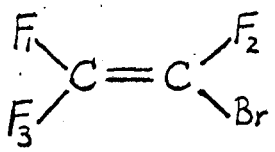
In this investigation the effect of solvents, and therefore molecular interactions, on F-F coupling constants in some halogen substituted ethylene and ethanes has been studied. Hitherto, it was believed that changes in medium affect coupling constants through changes in (a) the relative energies of two or more rapidly equilibrating isomers whose time-average coupling constant is being observed, or (b) the bond order of the bond connecting the coupled nuclei.[7] The first effect cannot be true in molecules with relatively rigid geometry as in ethylenic compounds or in molecules like $CF_3CFCl_2$ in which the $CF_3$ unit has threefold symmetry. The second effect has been called upon to explain the proton magnetic resonance measurements on solutions of formamide ($HCONH_2$) in acetone and in water, in which there was pronounced medium dependence of the proton coupling constants.[8] This coupling constant dependence on solvent probably arises as a result of changes in the molecular geometry and/or the molecular charge distribution, induced by intermolecular interactions, which in this case must be primarily hydrogen-bonding. In molecules in which hydrogen-bonding is not possible, the effect of molecular interactions on the NMR spectral parameters may be due to the dipolar character and polarizability of the interacting molecules. With different solvents the nature and/or extent of the intermolecular interactions would vary.

## II. EXPERIMENTAL

The compound $CF_2BrCFBrCl$ was prepared by bromination of $CF_2 = CFCl$ in a sealed tube. The ethylene was used in excess and allowed to boil off from the product, which was then used without further purification. The compounds $CF_2 = CFCl$, $CF_2 = CFBr$, and $CF_3CFCl_2$ were obtained from Peninsula Chemresearch, Inc.

The spectra were recorded on a Varian HR-60 spectrometer operating at 56.4 mc/sec. The variable temperature insert has been described previously.[9] The coupling constants were determined by the usual audio-frequency sideband technique and are the averages taken over 10-15 spectra.

# III. DISCUSSION AND RESULTS




Bromotrifluoroethylene

The coupling constants of this compound have been previously reported.[10] The NMR spectrum is shown in Fig. 1. Since the relatively rigid geometry of the molecule precludes the existence of any rotational isomerism, the effect of solvents on the coupling constants in this molecule at constant temperature is then attributable solely to molecular interactions.

Table I shows the coupling constants of this compound determined in different solvents (50% by volume) and the percentage deviation of the coupling constants from that in the neat sample. As shown in Fig. 2 and 3, the percentage deviation in $J_{13}$ and $J_{12}$ is plotted against the dipole moments[11] of the solvents. There appears to be some correlation, though somewhat poor. However, it is noted that in some solvents the geminal ($J_{13}$) and the cis ($J_{12}$) couplings are noticeably different from the corresponding ones in the neat sample. The trans coupling

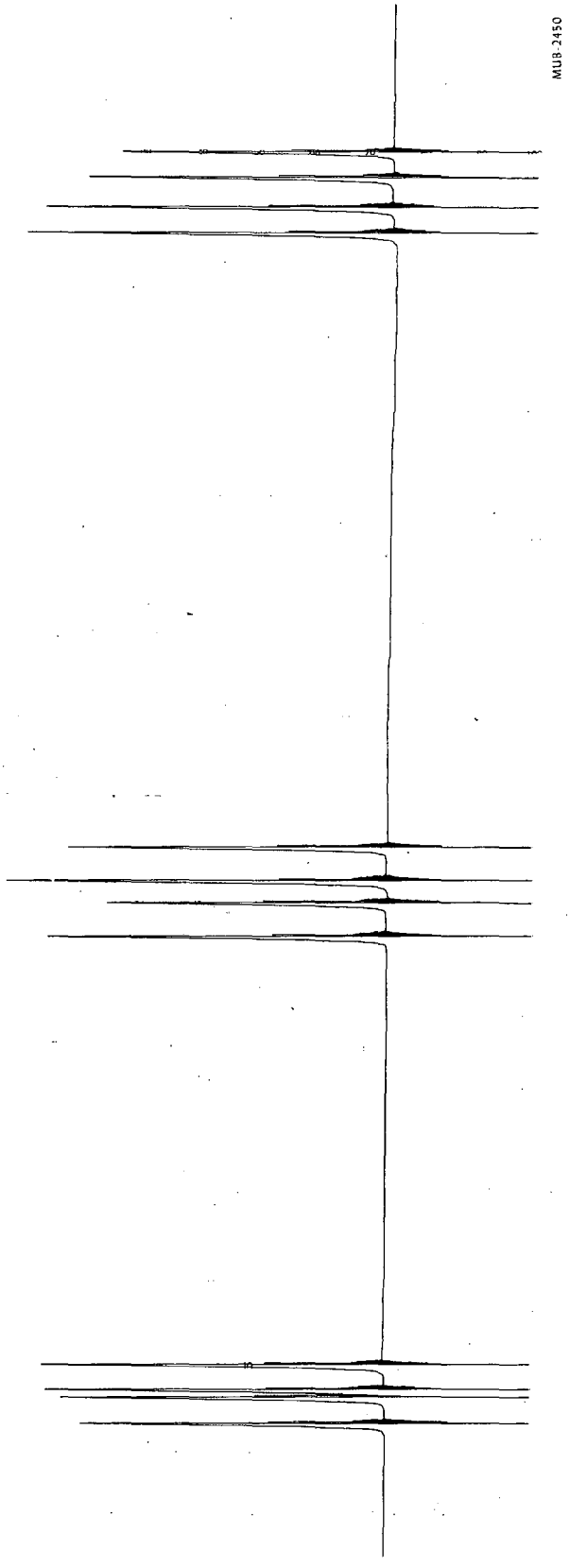



Fig. 1-II

Table I Coupling constants of Bromotrifluoroethylene, cps.[1] (The values within brackets were determined at -105°C.)

| Solvent | Dipole Moment - Debye | $J_{13}$ | % Deviation from neat sample[2] | $J_{12}$ | % Deviation from neat sample[2] | $J_{23}$ | % Deviation from neat sample[2] |
|---|---|---|---|---|---|---|---|
| $CF_2$=CFBr | | 73.74 | 0 | 56.58 | 0 | 122.83 | 0 |
| | | (72.76) | 0 | (55.48) | 0 | (123.40) | 0 |
| S=C=S | 0 | 71.70 | -2.77 | 56.42 | -0.28 | 123.11 | +0.23 |
| | | (71.77) | (-1.36) | (55.37) | (-0.20) | (123.44) | ( 0.00) |
| $CF_2BrCF_2Br$ | ~0.2 | 73.30 | -0.60 | 56.50 | -0.14 | 123.17 | +0.28 |
| $CF_2ClCFCl_2$ | ~0.3 | 73.64 | -0.14 | 56.69 | +0.19 | 123.18 | +0.28 |
| $CFCl_3$ | 0.45 | 73.26 | -0.65 | 56.84 | +0.46 | 123.38 | -0.37 |
| | | (72.09) | (-0.92) | (55.32) | (-0.29) | (123.22) | (-0.15) |
| dioxane | 0.45 | 73.78 | +0.05 | 55.08 | -2.65 | 122.61 | -0.18 |
| $CH_3CSCH_3$ | | 74.26 | +0.71 | 53.69 | -5.11 | 122.46 | -0.29 |
| $CH_3COOH$ | 0.8 | 74.31 | +0.77 | 55.98 | -1.06 | 122.73 | -0.08 |
| $(CH_3CH_2)_2O$ | 1.20 | 73.84 | +0.14 | 55.99 | -1.04 | 123.10 | +0.22 |
| | | (73.84) | (+1.48) | (53.04) | (-4.40) | (123.09) | (-0.25) |
| $OSCl_2$ | 1.38 | 72.05 | -2.29 | 55.82 | -1.34 | 122.42 | -0.33 |
| $CH_3OH$ | 1.61 | 74.47 | +0.99 | 55.74 | -1.48 | 122.86 | +0.02 |
| $CH_3CH_2OH$ | 1.63 | 73.90 | +0.22 | 55.86 | -1.27 | 122.89 | +0.05 |
| | | (73.86) | (+1.51) | (53.85) | (-2.94) | (123.12) | (-0.23) |
| $CH_2$=$CHCH_2Cl$ | 2.0 | 73.08 | -0.90 | 56.10 | -0.85 | 122.99 | +0.13 |
| $CH_3CHO$ | 2.49 | 74.23 | +0.66 | 55.10 | -2.62 | 122.55 | -0.23 |

Table I (continued)

| Solvent | Dipole Moment Debye | $J_{13}$ | % Deviation from neat sample[2] | $J_{12}$ | % Deviation from neat sample[2] | $J_{23}$ | % Deviation from neat sample[2] |
|---|---|---|---|---|---|---|---|
| | | (74.11) | (+1.86) | (53.54) | (-3.50) | (123.18) | (-0.18) |
| $CH_3COCH_3$ | 2.70 | 74.88 | +1.55 | 54.85 | -3.06 | 122.47 | -0.29 |
| $(CH_3CO)_2O$ | 2.70 | 74.39 | +0.88 | 55.40 | -2.09 | -122.60 | -0.18 |
| $CH_3CN$ | 4.0 | 74.61 | +1.18 | 54.86 | -3.04 | -121.93 | -0.73 |

1. Most probable errors are less than ±0.10 cps.
2. The most probable errors are ±0.14% in $J_{13}$, ±0.18% in $J_{12}$, and ±0.08% in $J_{23}$.

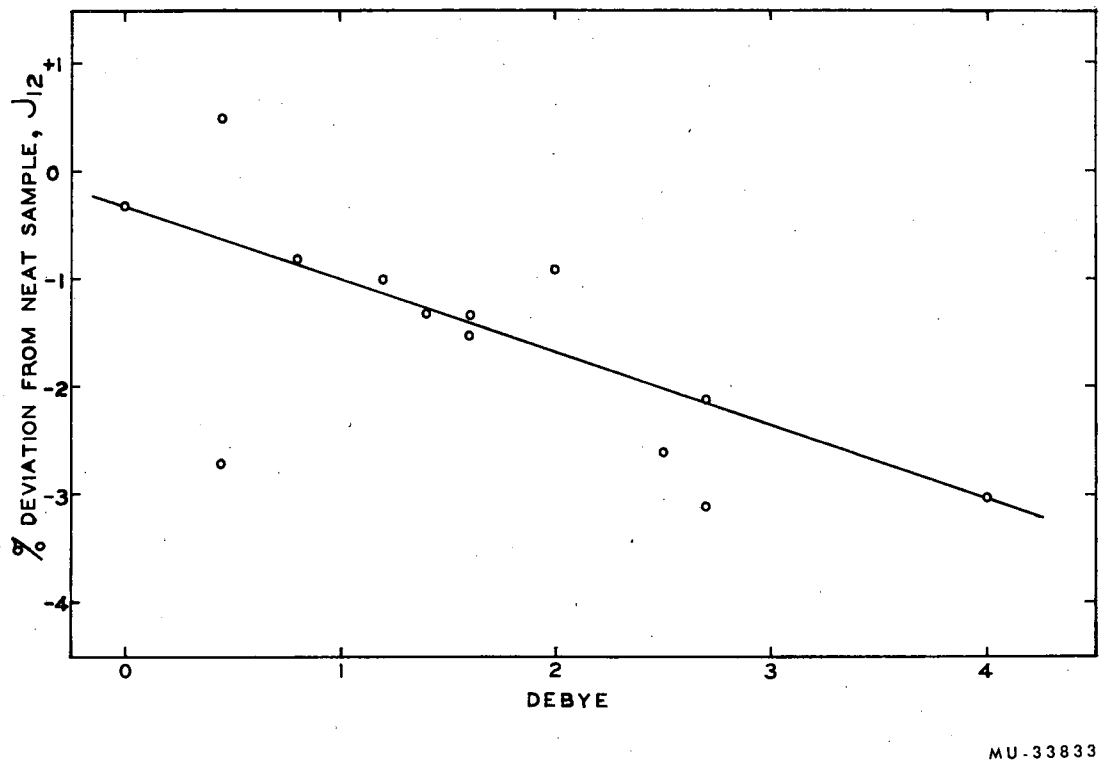



Fig. 2-II

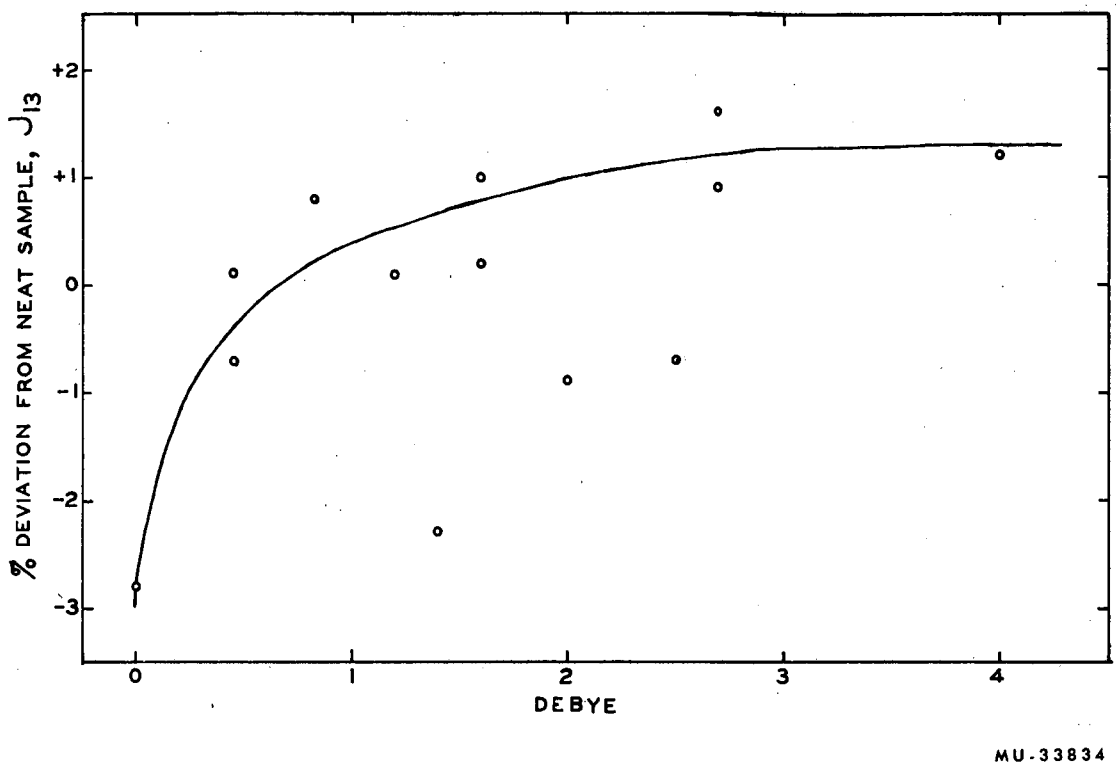



Fig. 3-II

constant ($J_{23}$), however, remains essentially unaffected. The following trends are observable: the value of $J_{12}$ in various solvents is never substantially larger than in the neat sample, whereas $J_{13}$ is shifted in both directions by solvents; solvent molecules with highly polar or polarizable centers tend to cause more pronounced changes in the coupling constants; and finally, smaller solvent molecules tend to cause larger changes in the coupling constants. The solvents which are similar in nature to this olefin, namely, the halogenated ethanes and "Freon 11" ($CFCl_3$), do not cause large changes in the coupling constants.

At -105°C the coupling constants in the neat sample are noticeably different from those at room temperature (20°C). At this low temperature, as shown in Table I, the coupling constants of this compound also vary from solvent to solvent, and the differences in the coupling constants follow the same trends as at room temperature. However, the differences in the coupling constants between those determined in the solvents and those in the neat sample are enhanced at this lower temperature. It is interesting to note that in those solvents which cause large changes from the neat sample, the geminal coupling constant does not seem to be temperature dependent whereas the vicinal one is strongly temperature dependent. It must be emphasized that as the differences in the coupling constants are large, amounting to as much as 3 cps, they are well outside of experimental errors.

$CF_3CFCl_2$

1,1-dichlorotetrafluoroethane

Since this compound has the $CF_3$ unit with threefold symmetry, rotation about the C-C bond will not affect the observed coupling constant. Brey and Ramey[4] have reported the temperature dependence of the coupling constant of this compound. In this work the coupling constant has been determined in a number of solvents (50% by volume) at two temperatures. The NMR spectrum is shown in Fig. 4.

Table II shows the coupling constants determined in different solvents. The percentage deviation of the coupling constants from that in the neat sample is listed in this table. The coupling constants determined in the solvents are invariably larger than that in the neat sample at both the temperatures. The coupling constants determined at the lower temperature (-60°C) are invariably larger than those determined at the higher temperature (20°C).

In the solvent $CF_2ClCFCl_2$, which is similar to the solute, the coupling constant is 5.76 cps. This value is identical with that in the neat sample.

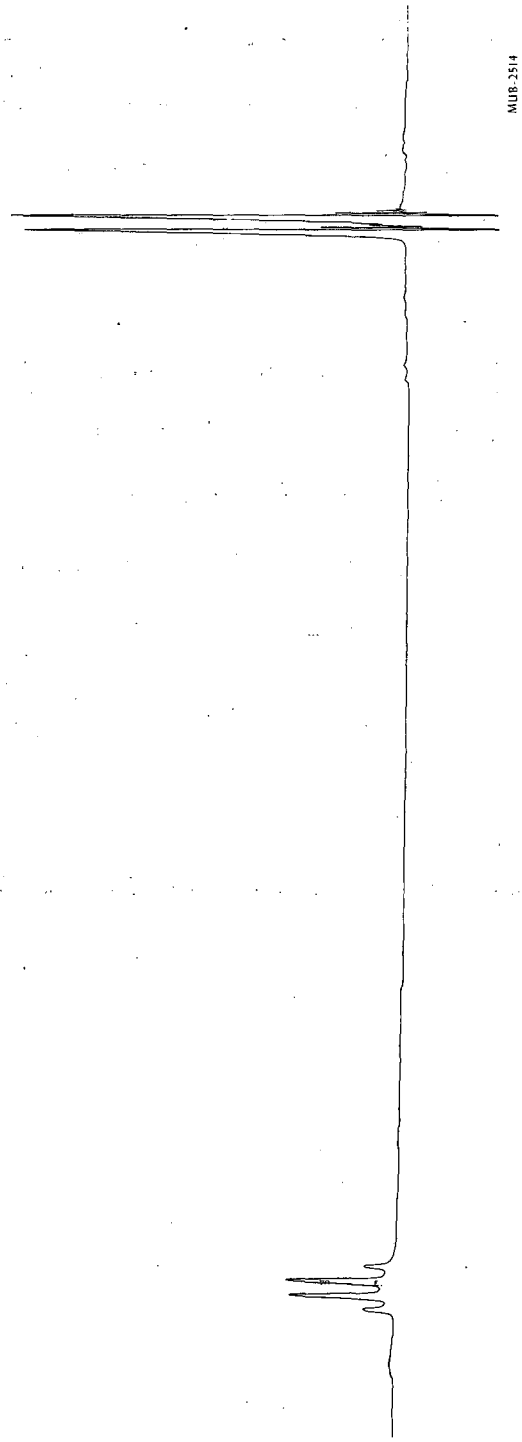



Fig. 4-II

Table II. Coupling Constants of $CF_3CFCl_2$, in cps[1]

| Solvent | $J_{(20°C)}$ | % Deviation from neat sample[2] | $J_{(-60°C)}$ | % Deviation from neat sample[2] |
|---|---|---|---|---|
| $CF_3CFl_2$ (neat) | 5.73 | 0 | 5.97 | 0 |
| $CH_3COCH_3$ | 5.92 | + 3.32 | 6.24 | + 4.52 |
| $CH_3OH$ | 5.91 | + 3.14 | 6.21 | + 4.02 |
| $CH_3CH_2CH_2CH_3$ | 5.84 | + 1.92 | 6.18 | + 3.52 |
| $CH_3CHO$ | 5.85 | + 2.09 | 6.15 | + 3.02 |
| $CH_3OCH_3$ | 5.89 | + 2.79 | 6.24 | + 4.52 |
| $CF_2ClCFCl_2$ | 5.76 | + 0.52 | | |
| $CFCl_3$ | 5.81 | + 1.40 | 6.20 | + 3.85 |

[1]All values are accurate to better than ± 0.10 cps.

[2]The deviation due to errors is less than ±1.74% for $J_{(20°C)}$ and ±1.68% for $J_{(-60°C)}$.

$CF_2BrCFBrCl$

1,1,2-trifluoro-1,2-dibromo-2-chloroethane

This compound gives rise to three rotamers as shown in Fig. 5. The low temperature NMR spectrum of this compound is a superposition of the ABX spectrum of each of the three rotamers. Such a low temperature spectrum is shown in Fig. 6. The spectrum at -123°C has been assigned.[6] The coupling constants of the two more abundant rotamers have been determined in four solvents at -123°C, and the results are shown in Table III. Dipole moment and steric considerations lead to the assignment of the most stable rotamer to correspond to drawing A, and the next stable rotamer to correspond to drawing B.[6]

Examination of Table III shows that the coupling constants of the two rotamers do vary with the solvents at temperatures at which the rotamers were "frozen out." Rotamer I shows for $J_{AB}$ a high value in $CH_3CH_2Cl$ as the solvent and a low value in the non-polar solvent butane, $CH_3CH_2CH_2CH_3$. The difference between these two values is 1.5 cps, a magnitude which is well beyond experimental error. For the same rotamer, $J_{AX} + J_{BX}$, determined in cis-2-butene, is noticeably different from the other three values. Rotamer II shows slightly different values of the coupling constant in the different solvents. The differences between these values may be small but not negligible.

Table III. Coupling Constants of the Rotamers of $CF_2BrCFBrCl$ at - 123°C[1]

| Solvent | Rotamer I $J_{AB}$ | Rotamer I $J_{AX}+J_{BX}$ | Rotamer II $1/2(J_{AX}+J_{BX})$ |
|---|---|---|---|
| $CH_3CH_2CH_2CH_3$ | 169.15 | -26.32 | -13-36 |
| $CH_3CH_2Cl$ | 170.61 | -26.58 | -13.58 |
| $CFCl_3$ | 170.0 | -26.60 | -13.97 |
| cis-2-butene | 170.23 | -25.53 | -13.26 |

[1] $J_{AB}$ is accurate to better than ± 0.4 cps, and the two sums $(J_{AX}+J_{BX})$ are accurate to better than ± 0.25 cps. The most probable errors in all cases are better than ± 0.1 cps.

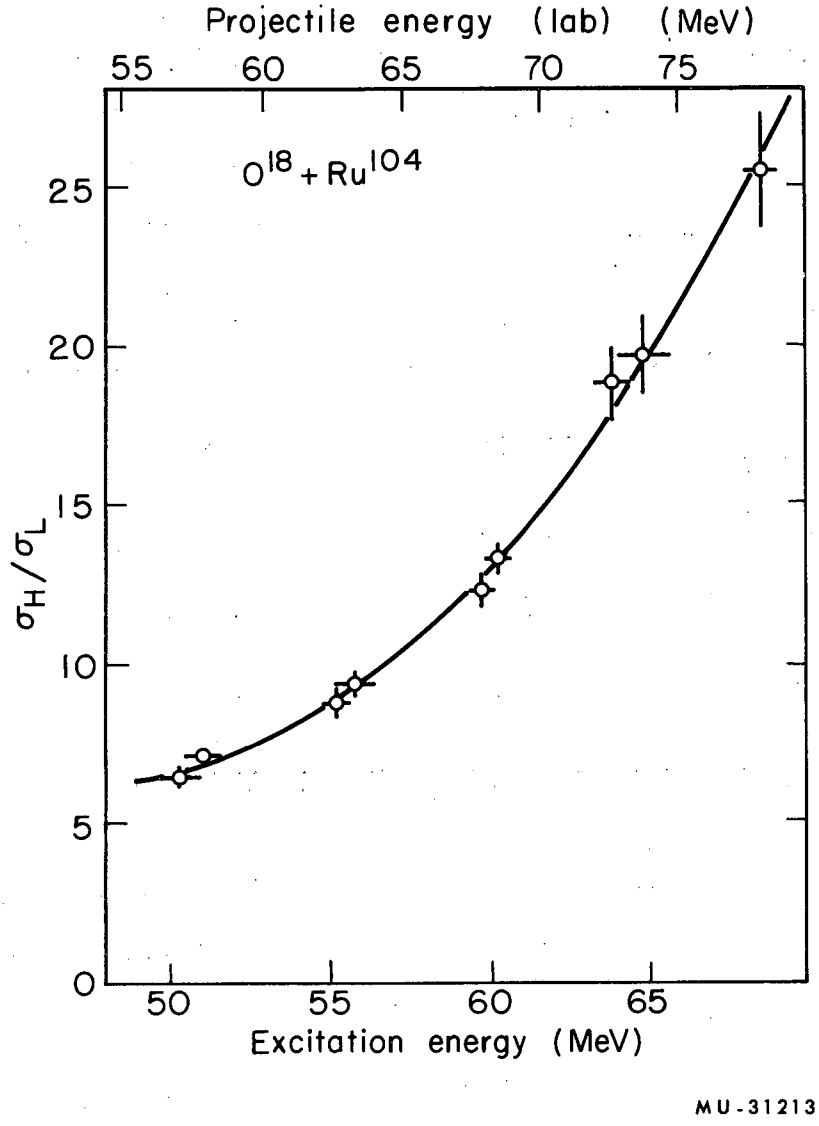

Projectile energy (lab) (MeV)
55
60
65
70
75
$O^{18} + Ru^{104}$
25
20
15
10
5
0
$\sigma_H/\sigma_L$
50
55
60
65
Excitation energy (MeV)
MU-31213

Fig. 5-II

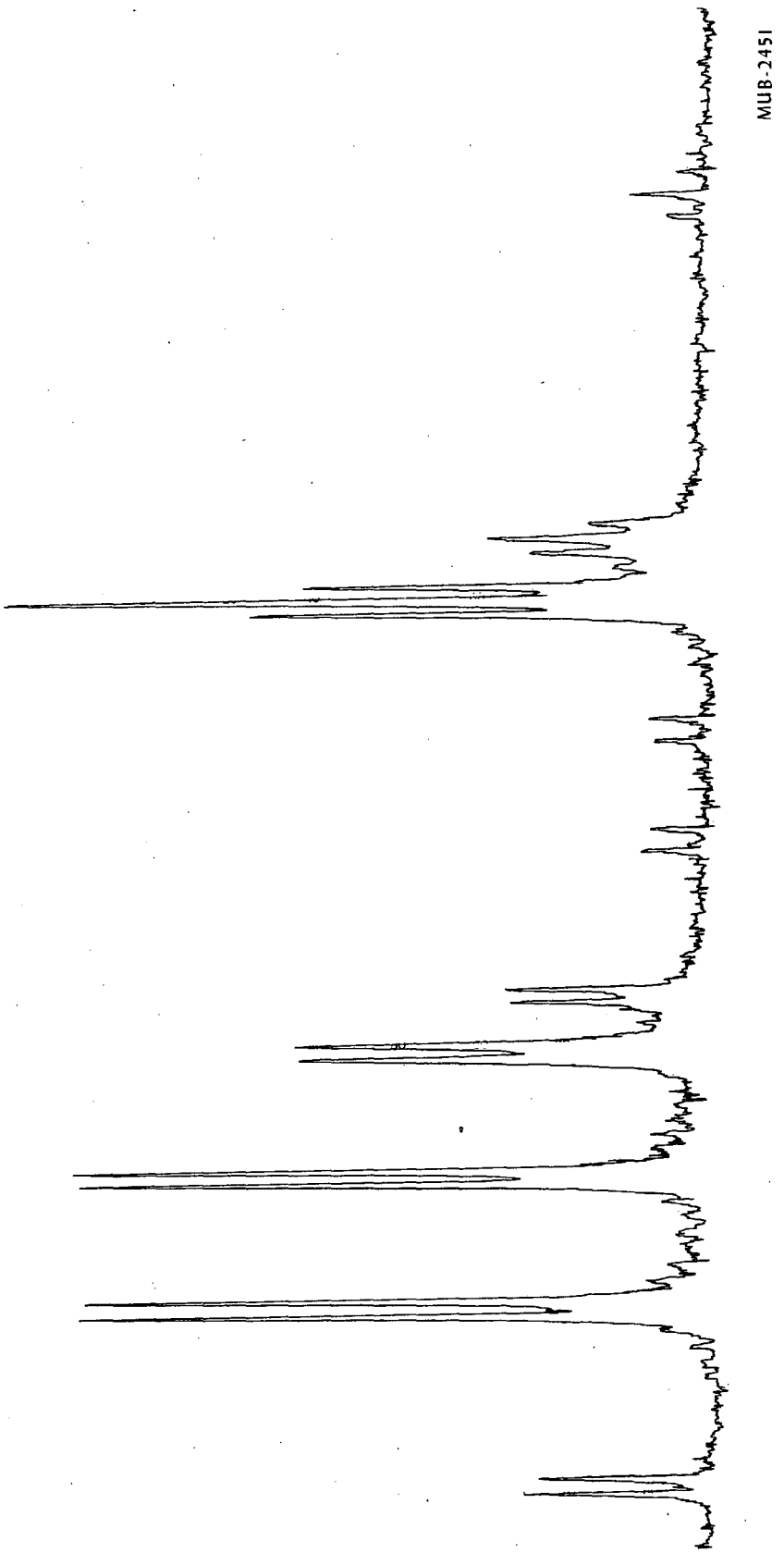



Fig. 6-II

Discussion

The results on the three compounds studied indicate that fluorine coupling constants are solvent dependent. The effect of solvents on coupling constants can be quite pronounced if the solute and solvent molecules differ substantially in structure and have highly polar or polarizable centers. This solvent dependence is the effect which would be expected from molecular associations, which might induce changes in the electron distribution in the molecules. Therefore, it is expected that the contribution to the coupling constant by non-bonded nuclear spin-spin interaction ("through-space" coupling) can be affected strongly by intermolecular interactions. It is noted that the solvent dependence of the coupling constants is of the same order of magnitude as the observed temperature dependence of coupling constants.

In the compound Bromotrifluoroethylene the fact the trans $J_{23}$ remains about the same in different solvents seems to indicate that the electronic structure in the intervening bonds is not affected to any appreciable extent, if at all. This implies that the contribution to the coupling constants $J_{13}$ and $J_{12}$ by the through-bond mechanism for nuclear spin-spin coupling is probably not affected. Therefore the observed changes in $J_{13}$ and $J_{12}$ in different solvents probably comes about as a result of changes in the contribution to the coupling constant by non-bonded interaction ("through-space" coupling). It might be postulated that the polar centers of the solvent molecules interact with the non-bonding electron densities directly between the atoms $F_1$ and $F_2$ and between the atoms $F_1$ and $F_3$, either aiding in relaying nuclear spin information across or hindering the transmission of same. The size and geometry of the solvent molecule

certainly determine how close it can approach the solute molecule, thereby determining the extent of the interaction. It is to be noted that with some solvents, particularly those solvent molecules which are similar to the solute molecules, the molecular interactions may be similar to that inherent in the next sample. In this case no significant changes in the coupling constants would be observable. At lower temperatures weak molecular interactions would be enhanced, whereas strong molecular interactions would be present regardless of temperature. The enhancement of weak molecular interactions would be accompanied by changes in the coupling constants. The observations made earlier bear out these statements. These observations bring out the point that interactions are all of essentially the same kind, and detailed differences arise from the nature and dipolar character of the solvent molecules.

In Bromotrifluoroethylene the geminal $J_{13}$ shows no temperature dependence in solvents which would be expected to associate strongly with the solute. It is probable that almost every solute molecule is strongly associated with the solvent molecules at any reasonable temperature; therefore, there would be very little temperature dependence of the molecular association and hence the temperature dependence of coupling parameters is entirely due to vibrational excitation. Since $J_{13}$ shows little or no temperature dependence in these solvents, it can be stated that this geminal coupling constant is not strongly affected by excitation of vibrational modes. Having shown, thus, that $J_{13}$ is not affected by excitation of vibrational modes, the large temperature dependence of $J_{13}$ in two cases - in the neat sample and in the solvent $CFCl_3$ - must have come about as a result of temperature dependent molecular associations. In the case of the vicinal $J_{12}$, there is obviously a contribution

from both factors - vibrational excitation and molecular association.

It might be expected that the geminal $J_{13}$ and the trans $J_{23}$ have little dependence on excitation of vibrational modes. In the case of $J_{13}$, the $CF_2$ end of the molecule should not vary much with excitation of the low-lying vibrational modes. Likewise, if $J_{23}$ comes about through the Π-bonding, this might not be affected much by populations of the torsional mode. On the other hand, a good deal of the vicinal $J_{12}$ must come about through space and this would depend strongly upon the excitation of the torsional mode, as observed.

## IV. CONCLUSION

This study of the effect of solvents on the coupling constants of three compounds, bromotrifluoroethylene, 1,1-dichlorotetrafluoroethane, and 1,1,2-trifluoro-1,2-dibromo-2-chloroethane, shows that the coupling constants vary with the solvents. This implies that intermolecular interactions affect fluorine coupling constants to a degree that is not negligible. This effect of molecular interactions on coupling constants may be due to the dipolar character and polarizability of the interacting molecules. The interactions appear to be essentially of the same kind, and detailed differences arise from the nature and dipolar character of the solvent molecules.

The results of this study, in conjunction with the results of Brey and Ramey[4] show the magnitude of the error which can be made when one makes the assumption that the observed temperature dependence of coupling constants of compounds, substituted ethanes in particular, arises solely from changes in the equilibrium populations of the rotamers. This study demonstrates that the temperature dependence of coupling constants for a given isomer may in large part come about as the result of temperature dependent molecular association as well as population of excited vibrational states.

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FIGURE CAPTIONS

Fig. 1, Part II — The spectrum of $CF_2 = CFBr$

Fig. 2, Part II — Plot of the percentage deviation of cis $J_{12}$ determined in solvents from that in the neat sample vs the dipole moments of the solvents. The most probable error in each point is ±0.18%.

Fig. 3, Part II — Plot of the percentage deviation of geminal $J_{13}$ determined in solvents from that in the neat sample vs the dipole moments of the solvents. The most probable error in each point is ±0.14%.

Fig. 4, Part II — The spectrum of $CF_3CFCl_2$.

Fig. 5, Part II — The three rotamers of $CF_2BrCFBrCl$.

Fig. 6, Part II — The spectrum of $CF_2BrCFBrCl$ in $CH_3CH_2Cl$ (50% solution by volume) at -123°C.

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