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NUCLEAR MAGNETIC RESONANCE  
FLUORINE-FLUORINE COUPLING CONSTANTS

Berkeley, California

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NUCLEAR MAGNETIC RESONANCE  
FLUORINE-FLUORINE COUPLING CONSTANTS

Soon Ng and C. H. Sederholm

November 1963

**Nuclear Magnetic Resonance  
Fluorine-Fluorine Coupling Constants**

**Soon Ng and C. H. Sederholm**

**Inorganic Materials Research Division of the  
Lawrence Radiation Laboratory, and  
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**Abstract**

The pattern of fluorine-fluorine coupling constants is explained on the basis of two spin coupling mechanisms: 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 so that there is 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.

The theory of indirect nuclear spin-spin interactions is based on the complete Hamiltonian for the electron-nuclear interactions as was first outlined by Ramsey and Purcell<sup>1</sup> and later developed in more detail by Ramsey<sup>2</sup>. The portions 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<sup>3</sup>. These three terms represent 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<sup>2,3</sup>. 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.

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<sup>2,4</sup>. It is now generally believed that proton-proton spin coupling proceeds through the electronic structure in the intervening bonds<sup>4</sup>. 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.

Whereas some headway has been made in the theoretical treatment of proton-proton interactions<sup>4</sup>, 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<sup>5</sup>, who applied MO theory to the evaluation of the coupling constants in  $C_2F_4$ . He concluded "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." In view of the additional electronic p orbitals in the vicinity of the nuclei involved, the problem of F-F coupling is certainly more complicated than in the case of coupling between protons. It would not be surprising, therefore, if F-F coupling can proceed via more than one mechanism.

A striking anomaly is observed in F-F coupling constants in fluoro-organic compounds. In 1956, Saika and Gutowsky<sup>6</sup> reported a near-zero coupling constant between the fluorine atoms on adjacent carbon atoms in the molecule  $\text{CF}_3\text{CF}_2\text{N}(\text{CF}_3)_2$ . This was unexpected, particularly since the other two coupling constants are 16 cps and 6 cps for fluorine nuclei separated by four and five bonds, respectively. Since that time a whole host of similar cases have been reported in the literature<sup>7,8</sup>. While the coupling constants between vicinal fluorine atoms are nearly zero in a great number of compounds, the F-F coupling constants in  $\text{HF}_2\text{CCF}_3$ ,  $\text{H}_2\text{FCCF}_3$ <sup>9</sup>,  $\text{BrF}_2\text{CCFBr}_2$ <sup>10</sup>, 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<sup>11</sup>:  $\text{XF}_2\text{CCF}_3$ , 0-5 cps;  $\text{XYFCCF}_3$ , 4-9 cps ( $\text{H}_2\text{FCCF}_3$  gives 15.5 cps<sup>9</sup>);  $\text{XF}_2\text{CCF}_2\text{Y}$ , 1-8 cps; and  $\text{XF}_2\text{CCFXY}$ , 13-24 cps ( $\text{ClF}_2\text{CCFCl}_2$  gives 9.4 cps<sup>12</sup>). The magnitudes of the coupling constants appear to increase as the electronegativity of the substituents decreases in the order  $\text{I} > \text{H} > \text{Br} > \text{Cl} \sim \text{CF}_3 > \text{F}$ .

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 widely been 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<sup>7</sup>. It was further invoked by Harris and Sheppard<sup>11</sup>. This idea, however, was shown to be non-tenable by Petrakis and

Sederholm<sup>8</sup> who advanced another explanation for the vanishing vicinal fluorine coupling constants, that of "through-space" coupling. According to this mechanism, fluorine atoms couple almost completely due to the direct overlap of orbitals on the two fluorine atoms. The orbitals used need not be bonding orbitals. The coupling constant increases monotonically as the amount of overlap increases, i.e., as the F-F distance decreases. They postulated that the coupling constant becomes zero when the distance between the fluorine atoms becomes greater than  $2.72\text{\AA}$  (approximately twice the Van der Waals radius for fluorine atoms). In the perfluoroethyl groups the distance between vicinal fluorine atoms in the favored, staggered configurations, is greater than or equal to  $2.72\text{\AA}$ . Thus, if F-F coupling constants are determined solely by this "through space" mechanism, the near-zero coupling constants are easily explained. Petrakis and Sederholm further explained the non-zero coupling constants observed in compounds such as  $\text{FC}(\text{CF}_3)_3$ <sup>8</sup>,  $\text{Cl}_2\text{FCCF}_3$ <sup>12</sup>, or  $\text{IClFC-CF}_2\text{CF}_3$ <sup>7</sup> in terms of bulky  $\text{CF}_3$ , Cl or I groups forcing the vicinal fluorine atoms together. However, in view of recent data for  $\text{HF}_2\text{CCF}_3$  and  $\text{H}_2\text{FCCF}_3$ <sup>9</sup>, 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  $\text{CF}_2\text{BrCFBr}_2$  is  $16.2\text{ cps}$ <sup>10</sup>, 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 paper we attempt to offer a more complete explanation for fluorine coupling constants. Without abandoning the "through space" mechanism we propose 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. The "through-bond" mechanism ceases to give a contribution when the sum of the electron-withdrawing powers of all atoms attached to the C-C skeleton becomes sufficiently high.

#### "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 has indicated that fluorine geminal coupling constants are dependent on the Pauling electronegativity of the third substituent at the carbon atom<sup>13</sup>. This suggests that highly electronegative substituents withdraw nuclear-spin-information-carrying electrons from the bonds 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  $X_2FC-CFX_2$ , in which each X is any halogen or a H atom, the sum of the Pauling electronegativities of the four X's shows a linear relation with the observed F-F coupling constants. Halogen substituted propanes can be added to this plot if an electronegativity of about 3 is assigned to the groups  $CF_3$ ,  $CF_2Cl$ ,  $CF_2Br$ , and  $CF_2H$  (See Fig. 2). The scatter of the points is somewhat poorer when the propanes are added, no doubt due to the longer carbon skeleton from which excited electrons can be

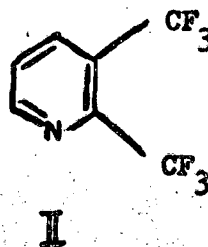
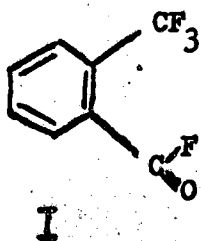
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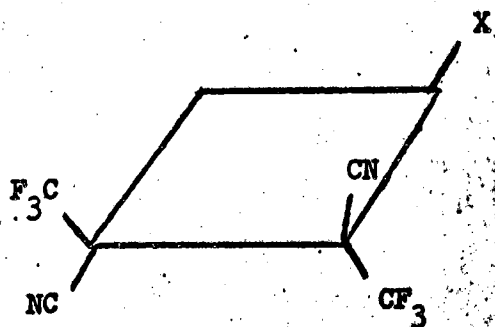
It should be noted that on the basis of such an argument, vicinal fluorine atoms attached to nearly perfluorinated carbon skeletons would be expected to show a zero coupling constant, as is observed. However, this would also predict a zero F-F coupling constant through the bonds between fluorine atoms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

### "Through Space" Coupling

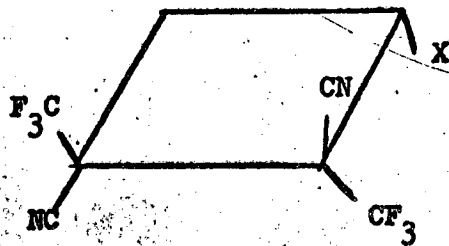
Having shown how electronegativity of substituents affect fluorine coupling through the bonds, it remains to demonstrate that fluorines can also couple through space. This latter mechanism is postulated to come about as a result of overlap of the electronic clouds of the fluorine atoms whenever the geometry 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  $\text{CF}_3\text{CF}_2\text{N}(\text{CF}_3)_2$  and in a large number of other compounds has already been explained in terms of this mechanism<sup>8</sup>.

A crucial test for this "through-space" mechanism would be to study the NMR spectra of molecules whose fluorine nuclei are in close proximity and yet separated by at least five bonds so as to substantially eliminate any coupling through the bonds. We shall discuss the fluorine NMR spectra of several such molecules. These are (I) o-trifluoromethylbenzoyl fluoride, (II) 2,3-bis-(trifluoromethyl)-pyridine, (III a, b, c, d) 1,2-bis-(trifluoromethyl)-1,2-dicyanocyclobutanes.

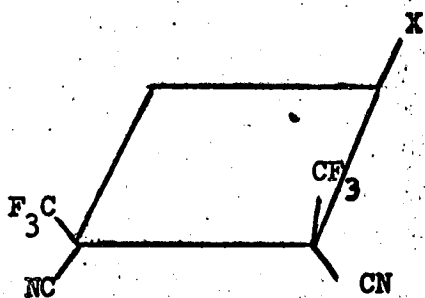




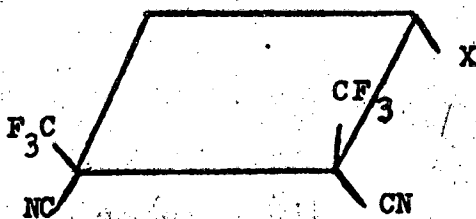
III a



III b



III c



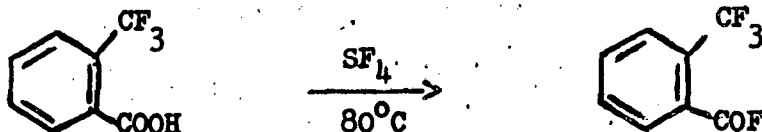
III d

X =  $\text{OCH}_2\text{CH}_3$ ,  $\text{SC}(\text{CH}_3)_3$ ,  $p\text{-CH}_3\text{OC}_6\text{H}_4$

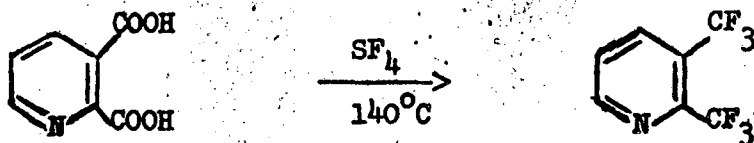
### Experimental

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

The compound o-trifluoromethylbenzoyl fluoride was prepared by reacting o-carboxybenzotrifluoride (Peninsular Chem. Research, Inc.) with SF<sub>4</sub><sup>14</sup> gas in a stainless steel cylinder at 80°C for 10 hours. The product was distilled at 40°C under 2mm pressure.



The compound 2, 3-ditrifluoromethylpyridine was prepared by reacting quinolinic acid with SF<sub>4</sub> gas at 140°C for 14 hours in a stainless steel cylinder. The product was distilled at 35°C under 6mm pressure.



### Discussion

The coupling constants in compounds (I) and (II) can be compared with those in trans-2-chloro-heptafluorobutene-2<sup>15</sup>, the NMR spectrum of which has been reported. The coupling constant between the fluorines in the two-CF<sub>3</sub> groups (trans across the double bond) is 1.3 cps. We consider that this coupling constant is quite normal for fluorine atoms separated by four saturated and one olefinic bonds. As the CF<sub>3</sub> groups are trans across the double bond there can

be no direct overlap between the electronic clouds of the fluorine atoms.

(I) *o*-trifluoromethylbenzoyl fluoride. This compound gives a simple first order fluorine NMR spectrum, consisting of a doublet and a quartet, the latter being at low field. 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<sub>3</sub> group are equidistant from this plane, as shown in Fig. 3, the closest F-F distance is about 2.62<sup>0</sup>Å. Referring to the coupling constant vs. distance curve postulated by Petrakis and Sederholm<sup>8</sup>, 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.

(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. 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<sup>16</sup> have shown the preferred orientation of the two CH<sub>3</sub> groups to be the out of mesh position, the favored orientation of the two CF<sub>3</sub> groups is assumed to be also in the out of mesh position, as shown in Fig. 3. Allowing some angular distortion in the C-C-F bond angles of both groups, the closest F-F distance is approximately 2.5<sup>0</sup>Å. Again referring to the coupling constant vs. distance curve, 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 diastereomers has been reported and their fluorine NMR spectra are described as follows<sup>17</sup>: diastereomer mixture IIIa + IIIb "exhibits a fluorine n.m.r. spectrum consisting of four singlet resonances appearing as two pairs whose components are of equal intensity," and diastereomer mixture IIIc + IIIId "exhibits two pairs of resonances whose components are of equal intensity, . . . , and the resonances appear as quadruplets (due to mutual splitting of the CF<sub>3</sub> groups) rather than singlets." One of the authors, S. Proskow<sup>18</sup>, has provided us with the detailed information about the fluorine NMR spectra of the diastereomer mixtures, together with the fluorine NMR spectra of two sets of the mixtures, Fig. 4. Table I lists the fluorine coupling constants. The components

Table I

cyclobutane diastereomer mixture	X	coupling constant, cps
IIIc + IIIId	OCH <sub>2</sub> CH <sub>3</sub>	12 and 10
IIIc + IIIId	SC(CH <sub>3</sub> ) <sub>3</sub>	11 and 11
IIIc + IIIId	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	12 and 10

of the mixtures IIIa + IIIb have zero coupling constants for all substituents X. In diastereomer mixtures IIIc + IIId it is not 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 first for each set of diastereomers is that for the most abundant product<sup>18</sup>.

Since in cyclobutanes IIIa + IIIb the  $\text{CF}_3$  groups are trans-oriented, 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  $\text{CF}_3$  groups. However, in the case of cyclobutanes IIIc + IIId in which the  $\text{CF}_3$  groups are cis-oriented, the fluorine nuclei are close enough so that there is appreciable overlap of the electronic clouds to effect coupling through space. The 10 to 12 cps coupling constants observed for these cis-oriented  $\text{CF}_3$  groups can be accounted for in no other way. These cyclobutanes with cis- and trans-oriented  $\text{CF}_3$  groups offer, therefore, the most dramatic evidence for the "through-space" mechanism.

#### 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, which would result in very large coupling constants over a wide range, as are observed (150-400 cps). In the case of vicinal fluorines only the "through-bond" mechanism is 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, 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 zig-zag 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 space.

The explanation outlined above for fluorine coupling constants should also be valid for coupling between all magnetic nuclei, particularly those with non-s electrons. Highly electronegative substituents have the same effect on proton coupling constants<sup>19,20</sup>. Roberts<sup>21</sup> 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  $\text{CF}_2\text{BrCF}_2\text{Br}$ <sup>11</sup>,  $J_g=12$  cps,  $J_t=1.5$  cps; and in  $\text{CF}_2\text{BrCFBr}_2$ <sup>10</sup>,  $J_g=18.6$  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.



We wish to thank Professor Stanley M. Williamson of this Department for his assistance in the preparation of compounds I and II. We are grateful to Dr. S. Proskow of du Pont Co. for providing us with the detailed information about the NMR spectra of the cyclobutanes as well as the sample fluorine NMR spectra of these compounds (Fig. 4). We are indebted to Mr. Richard A. Newmark for his assistance. Finally, we wish to thank the United States Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory for support of this work.

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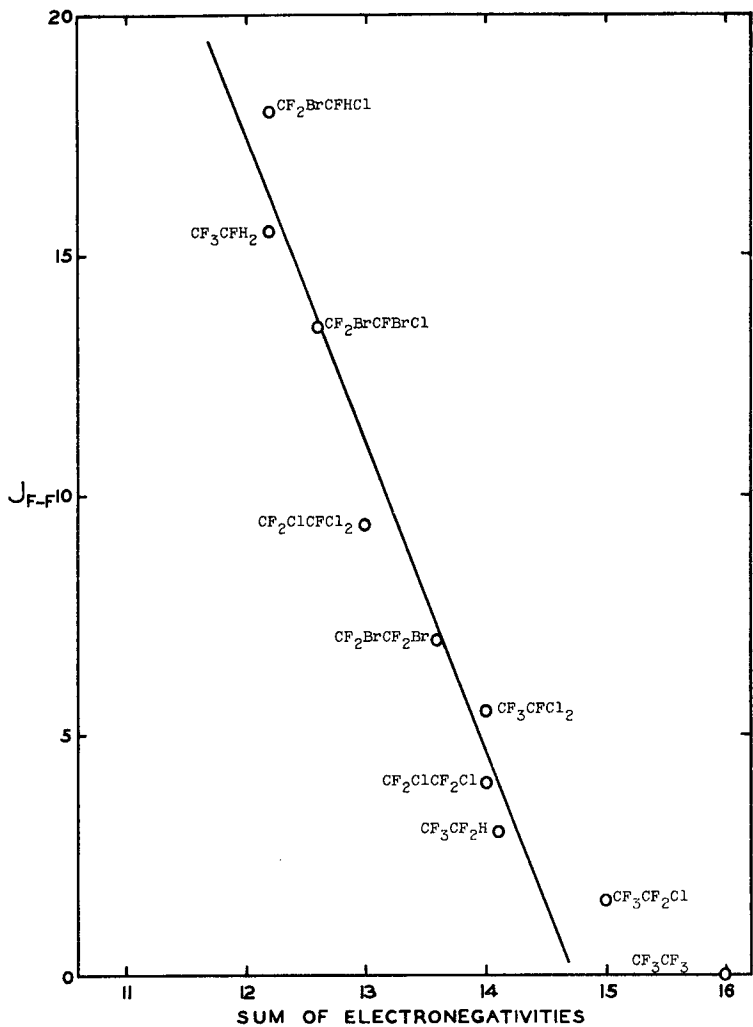
Figure Captions

Figure 1. Plot of  $J_{F-F}$  vs. sum of electronegativities of substituents in ethanes.

Figure 2. Plot of vicinal  $J_{F-F}$  vs. sum of electronegativities of substituents in ethanes and propanes.

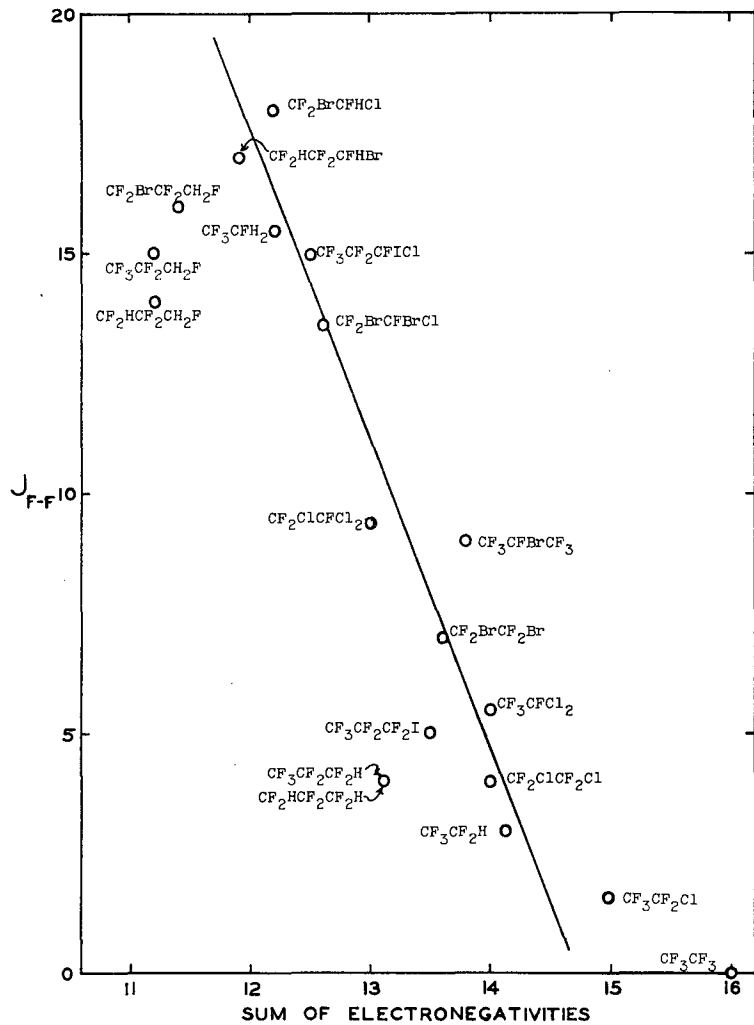
Figure 3. Projections of compounds I, o-trifluoromethylbenzoyl fluoride, and II, 2,3-bis-(trifluoromethyl)-pyridine in the plane perpendicular to the aromatic ring and parallel to the aromatic bond between the groups of F atoms. Dashed lines represent the aromatic ring.

Figure 4.  $F^{19}$  NMR spectra of the cyclobutane diastereomer mixture:  $X = SC(CH_3)_3$ , (a) IIIa + IIIb; (b) IIIc + III d. Spectra determined in  $CCl_4$  at 56.4 Mcps and externally referenced in terms of displacement in p.p.m. relative to "Freon 112," 1,2-difluoro-1,1,2,2,-tetrachloroethane. Relative areas are indicated in parentheses.



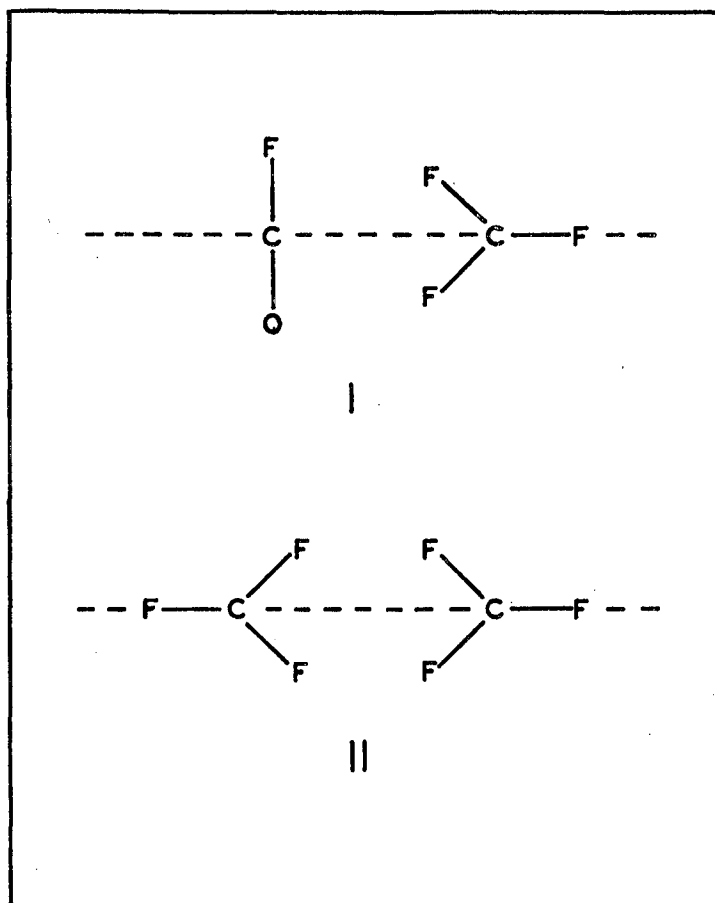
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Fig. 1



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Fig. 2



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Fig. 3

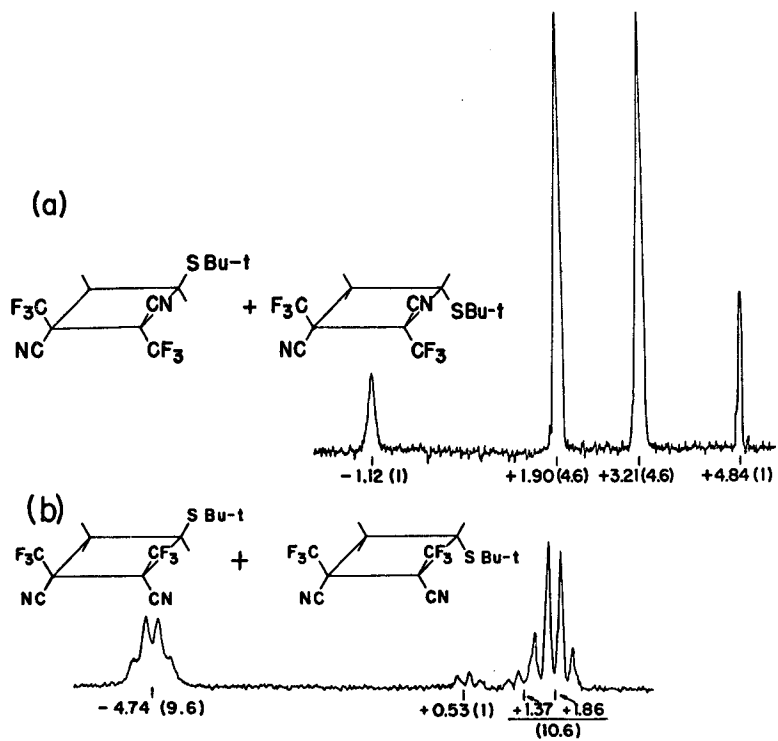


Fig. 4

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