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Substituent effect on c-f stretching frequency in substituted aryl fluorides

Vinod Shah

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SUBSTITUENT EFFECT ON C-F STRETCHING FREQUENCY IN SUBSTITUTED ARYL FLUORIDES

A THESIS
SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE

BY
VINOD SHAH

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA
MAY 1975
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INTRODUCTION

The changes that occur in the physical and chemical properties of an organic molecule as a result of the substitution of a hydrogen atom by an electroactive group are known as substituent effects. It is generally agreed that the transmission of this substituent effect to a distant reaction center may be caused by at least five distinct processes: the effect may be transmitted by:

1. The electric dipole field of the polar substituent-substrate bond (field effect).

2. The successive polarization of the intervening $\sigma$-bonds ($\sigma$-inductive effect).

3. The polarization of the corresponding $\Pi$-electrons by the electrostatic charge set up at a conjugated atom adjacent to the substituent ($\Pi$-inductive effect).

4. The polarization of the $\Pi$-electron system by resonance interactions with the substituent (resonance effect).

5. The mutual conjugation between the substituent and reaction center through an intervening conjugated system (electromeric effect).
The first three of the above processes are polar effects and are initiated by the polarity of the bond linking the substituent to the substrate. The last two are of the resonance or electromeric type and are initiated by resonance interactions between the substituent and substrate. All the above effects are qualitative in nature.

One of the earliest methods for studying the substituent effect was based on the measurements of substituted and unsubstituted acid strengths. In recent years, many other physical properties of the organic molecule, such as changes in bond length, dipole moment, infrared frequency shift, and chemical shift in nmr spectroscopy, have been employed to study the substituent effects. Recently $^{19}\text{F}$ nuclear magnetic resonance spectroscopy has been used to study substituent induced chemical shifts to determine how remote substituents transmit their influence across a molecule. Taft and co-workers studied $^{19}\text{F}$ chemical shifts for meta and para substituted fluorobenzenes. They showed that a correlation exists between $^{19}\text{F}$ chemical shift and $\sigma_I$ for meta substituted fluorobenzenes and $\sigma_I$ and $\sigma_R$ for para substituted fluorobenzenes; $\sigma_I$ and $\sigma_R$ are inductive and resonance parameters respectively. This approach works well for substituted fluorobenzenes, but is too simplified for other systems.

Dewar and co-workers approached the problem of influence of substituents on $^{19}\text{F}$ chemical shifts and transmission mechanisms for such effects differently. They evaluated substituent
effects in terms of resonance, independent field (F), and \(\pi\)-polarization (M) effect contributions, assuming that the \(\sigma\)-inductive contribution is negligible. This approach called the FM method, works reasonable well for some substituted fluoronaphthalenes and fluorobiphenyls. However, the FM method does not provide direct evidence of the relative magnitude of the field and \(\pi\)-polarization effects.

Anderson provided experimental evidence that the polar substituent effect contribution to the chemical shift is small. Also, a comparative study of the \(^{19}\text{F SCS}\) (substituent chemical shift) of conjugated and unconjugated systems provided additional evidence that \(\pi\)-electrons are essential for large chemical shifts, and the \(\pi\)-inductive effect contribution is at least as large as the resonance effect. Moreover, it has been shown that substituent effects should include contributions from polar, \(\pi\)-inductive, and resonance effects.

Infrared (IR) spectroscopy\(^3\) has been used for different types of structural investigations, as well as substituent effect studies, because of the ideal wavelength (wave numbers of 10,000-100 cm\(^{-1}\)) region it covers in the electromagnetic spectrum.

In a simple diatomic molecule XY, the only vibration which can occur is the periodic stretching along the X-Y bond. The stretching vibration may be visualized as an oscillation of two bodies, X and Y, of mass \(M_x\) and \(M_y\) connected by a spring of stiffness \(K\). Application of Hooke's law gives the expression for the vibrational frequency:
\[ V = \frac{1}{2\pi C} \sqrt{\frac{K}{\mu}} \]

Where: \( V \) = vibrational frequency in cm\(^{-1}\)

\( C \) = velocity of light cm/sec

\( K \) = force constant of bond

\( \mu \) = reduced mass of the molecule

\( \mu \) = the reduced mass is defined as:

\[ \mu = \frac{M_x M_y}{M_x + M_y} \]

Where \( M_x \) and \( M_y \) are the atomic masses of \( X \) and \( Y \).

From the equation (1), it is noted that the frequency depends only on the force constant \( K \) and the reduced mass \( \mu \); hence, the factors that effect reduced mass \( \mu \) and force constant \( K \) also influence stretching frequency. The reduced mass is affected by mass distribution in the molecule. The force constant is affected by a variety of the intermolecular and intramolecular interactions. The dielectric constant of solvent, hydrogen bonding, and the electric field in a crystal are examples of intermolecular interactions. The important intramolecular factors are electrical effects (inductive and resonance effects), hydrogen bonding, symmetry, conjugation, bond angle strain, field effects, and vibrational coupling effects. Hydrogen bonding can be of intermolecular or intramolecular type. Only the electrical effects affecting force constant are of interest for this study and are discussed in detail.

Various inductive, resonance, and dipolar field effects which operate in the local environment of a vibrating group are
included in the term electrical effects. These effects basically alter the state of hybridization of the atoms to which they are bonded. Hybridization affects bond angles, bond polarities, and bond lengths. Since bond strength is associated with bond length, bond strength also is affected by hybridization. This relationship is incorporated in Badger's Rule which states that bond force constants increase with decrease in bond lengths. Also, bond lengths decrease with an increase in s content of bond. Therefore, an increase in s content of bond as reflected by the change from sp$^3$ to sp character, increases the force constant and stretching frequency.

It is of interest to determine the effect of electronegativity of groups on stretching frequency. Electronegative groups affect atom hybridization. This, in turn, should affect such molecular properties as bond angles, bond lengths, and proton-$^{13}$C coupling constants. Indeed, the effect of atom hybridization and electronegative substituents on bond angles, bond lengths, and proton-$^{13}$C coupling constants can be explained as follows: A replacement in the structure X-C-H of X by an atom or group more electronegative than X, causes the carbon atom to rehybridize in such a manner as to increase the s character of the carbon-hydrogen bond. An analogous conclusion regarding the effect of electronegative groups on bond lengths is that the replacement in structure X-C-Y of X by a group more electronegative than X, causes the carbon atom to rehybridize in such a manner as to increase the s character in C-Y bond. This increase in s character should increase the force constant, the
stretching frequency, and decrease bond length.

Various types of correlations of electrical effects of substituents in a related series of organic molecules have been reported in literature. The most successful and useful correlations of infrared group frequencies and band intensity are those with the substituent constants of the groups. Essentially, the correlations are of the linear type, and of the following form:

\[ V = V_0 + \rho \sigma \]

Where: 
- \( V \) = group frequency in substituted compound
- \( V_0 \) = group frequency in unsubstituted compound
- \( \rho \) = reaction constant
- \( \sigma \) = substituent constant

Rao has shown correlations of stretching frequencies of C=O, NO₂, C≡N, and OH groups in aliphatic and aromatic series of compounds. Mohanty and Sarin studied the ¹³C-F spin-spin coupling constants from ¹³C satellites in ¹⁹F nmr spectra and C-F stretching vibrational frequencies. The IR vibrational frequency data were mostly collected from the literature and partly measured by them. They observed that generally, C-F stretching vibrational frequencies increase with an increase of electronegativity (expressed through Hammet \( \sigma \)-parameters) of the substituents.

The purpose of this study was to determine the effect of the substituent on C-F stretching frequencies of substituted aryl fluorides. Mohanty and Sarin had either collected or measured the C-F stretching frequencies of CH₃, NH₂, OH, OCH₃, F, Cl, Br, NO₂, I, and CHO substituents in para-substituted
fluorobenzenes. In this study, in addition to the above mentioned substituents (except I and CHO), five more substituents, namely, NHAc, CN, COOH, COOC$_2$H$_5$, and OAc were considered. C-F stretching frequencies are measured for all the compounds under uniform experimental conditions to make the results meaningful.
RESULTS AND DISCUSSION

The synthesis of compounds used in this study and significant results are discussed in this section.

p-Fluorophenyl acetate was prepared by acetylation\(^{11}\) of p-fluorophenol in aqueous NaOH solution.

\[
\text{F} \quad (\text{CH}_3\text{CO})_2\text{O} \quad \text{aq. NaOH} \quad \text{F} \quad \text{O}\text{COCH}_3
\]

The first step in preparing 4-substituted-1-fluoronaphthalenes is to obtain 4-bromo-1-fluoronaphthalene and 4-nitro-1-fluoronaphthalene. These were obtained by bromination and nitration, respectively, of 1-fluoronaphthalene. The method for preparing these compounds has been described by Schiemann.\(^{12}\)

The method described by Dewar\(^{7}\) was used to obtain 4-cyano-1-fluoronaphthalene, 4-fluoro-naphthoic acid, and methyl-4-fluoro-1-naphthoate from 4-bromo-1-fluoronaphthalene. This is shown in Scheme 1. The preparation of 4-nitro-1-fluoronaphthalene is shown in Scheme 2.
SCHEME 1

\[
\begin{align*}
\text{F} & \quad \text{Br}_2 \\
& \quad \text{CCl}_4 \\
& \quad \text{Br} \\
& \quad \text{CuCN} \\
& \quad \text{DMP, Pyridine}
\end{align*}
\]

SCHEME 2

\[
\begin{align*}
\text{F} & \quad \text{COOH} \\
& \quad \text{Conc. H}_2\text{SO}_4, \text{CH}_3\text{COOH} \\
& \quad \text{Conc. H}_2\text{SO}_4, \text{CH}_3\text{OH} \\
& \quad \text{COOCH}_3
\end{align*}
\]

(5)
4-Amino-1-fluoronaphthalene and 4-acetamido-1-fluoronaphthalene were obtained from 4-nitro-1-fluoronaphthalene. 4-Amino-1-fluoronaphthalene was prepared by reduction of 4-nitro-1-fluoronaphthalene. The method described by Bassilios, et al., was used to reduce 1-fluoro-4-nitronaphthalene to the corresponding amine with Fe and HCl. This, in turn, was converted to 1-acetamido-4-fluoronaphthalene by the method described by Dewar.

\[
\text{Scheme 3}
\]

![Diagram of chemical reactions]

Only 10-nitro-9-fluoroanthracene and 10-acetylamino-9-fluoroanthracene were synthesized in the laboratory for this study. The method described by Braun was used to obtain 9-nitroanthracene from anthracene.

\[
\text{(7)}
\]
9-Nitroanthracene-10-pyridinium bromide was obtained from 9-nitroanthracene by using the method of Barnett, et al.\textsuperscript{15}

\[
\begin{array}{c}
\text{NO}_2 \quad \text{Br}_2 \\
\stackrel{\text{Pyridine}}{\longrightarrow} \\
\text{NO}_2 \quad \text{Br}^{-} \\
\end{array}
\]

A method described by Anderson\textsuperscript{8} was used to prepare 10-nitro-9-fluoroanthracene and 10-acetylamino-9-fluoroanthracene from 9-nitroanthracene-10-pyridinium bromide.

\[
\begin{array}{c}
\text{NO}_2 \\
\stackrel{\text{Zn}}{\text{CH}_3\text{COOH},} \\
\text{NO}_2 \\
\end{array}
\]

\[
\begin{array}{c}
\text{F} \\
\text{NH-C-CH}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{F} \\
\text{NO}_2 \\
\end{array}
\]

\[
\begin{array}{c}
\text{NaF, TMS} \\
\end{array}
\]
As stated earlier, IR C-F stretching frequencies of substituted aryl fluorides were measured under uniform experimental conditions to obtain valid conclusions.

Table 1 shows the comparison of measured and reported C-F stretching frequencies for selected p-substituted fluorobenzenes. The differences in measured and reported values of C-F stretching frequencies in Table 1 for CH₂, NH₂, F, Cl, Br, and NO₂ groups may be due to the fact that Mohanty and Sarin¹⁰ did not measure all the C-F stretching frequencies. The C-F stretching frequencies for p-chlorofluorobenzene, p-bromofluorobenzene, p-nitrofluorobenzene, p-difluorobenzene, p-fluoroaniline, and p-fluorotoluen were collected from the literature and different experimental conditions may account for the difference.

It is observed from the data in Table 1 that the substituent has a tendency to shift the C-F stretching frequency. This shift in C-F stretching frequency, due to substituent, will be called Substituent Frequency Shift (SFS). The Substituent Frequency Shift (SFS) is defined as follows:

\[ \text{SFS}_x = \text{SF}_x - \text{SF}_H \]

Where: "x" represents the substituent and SF_H and SF_x represent the C-F stretching frequency for unsubstituted and corresponding substituted compound. SFS_x is the C-F stretching frequency shift due to substituent. Values of SFS_x are positive for SF_x > SF_H, and negative for SF_x < SF_H.
In order to observe the trend, if any, between the SFS (Substituent Frequency Shift) and the electrical properties of the substituent, the substituents were classified in two groups according to their electrical effects: (1) electron attracting (electron withdrawing); and (2) electron donating. The groups which are better electron attractors than the hydrogen atom are said to exhibit negative (-I) polar effects, whereas those which are poorer electron attractors than hydrogen display positive (+I) polar effects. Using the same analogy, a group is of +R character, if it supplies by resonance effect, electron density to a conjugated system, and a group is of -R character that withdraws electron density from such systems.

Table 2 shows SFS for (-I, -R) substituents in p-substituted fluorobenzenes. It is observed from the data in Table 2 that the substituents CN, COOH, COOCH$_2$H$_5$, and NO$_2$ cause a shift in C-F stretching frequency. Also, these substituents cause a shift in C-F SFS to a higher wavenumber. This shift to a higher wavenumber can be explained in terms of change in electron density of carbon atom attached to fluorine atom. The substituents of (-I, -R) electrical properties decrease the electron density of carbon atom attached to fluorine atom by (-I) polar and (-R) resonance effect. This decrease in electron density affects the hybridization of the carbon atom and which may, in turn, increase the s character in C-F bonding orbital. As discussed previously, this increase in s character causes an increase in force constant and, therefore, an increase in C-F stretching frequency. It should be noted that both the negative (-I) polar and nega-
TABLE 1
C-F STRETCHING FREQUENCIES FOR SELECTED p-SUBSTITUTED FLUOROBENZENES

<table>
<thead>
<tr>
<th>Substituent</th>
<th>C-F Frequency cm⁻¹</th>
<th>Measuredᵃ</th>
<th>Reportedᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1224</td>
<td>1220</td>
<td></td>
</tr>
<tr>
<td>NHCOCH₃</td>
<td>1223</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>1226</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>OCH₃</td>
<td>1223</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>1228</td>
<td>1220</td>
<td></td>
</tr>
<tr>
<td>NH₂</td>
<td>1227</td>
<td>1220</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1216</td>
<td>1220</td>
<td></td>
</tr>
<tr>
<td>OCOCH₃</td>
<td>1222</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>1234</td>
<td>1233</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>1235</td>
<td>1231</td>
<td></td>
</tr>
<tr>
<td>CN</td>
<td>1241</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>COOH</td>
<td>1242</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>COOC₂H₅</td>
<td>1244</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>1248</td>
<td>1236</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Infrared spectra recorded in 10% (w/w) carbon tetrachloride solution except (c) as potassium bromide pellets.


NR Not Reported
tive (-R) resonance effects influence the C-F stretching frequency in the same way, that is, both increase the C-F stretching frequency.

### TABLE 2

**C-F SFS IN **<sup>p</sup>-**SUBSTITUTED FLUOROBENZENES**  
**FOR -I, -R SUBSTITUENTS**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>SFS cm&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>+17</td>
</tr>
<tr>
<td>COOH</td>
<td>+18</td>
</tr>
<tr>
<td>COOC&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>+20</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>+24</td>
</tr>
</tbody>
</table>

It is seen that the effect of (-I, +R) substituents in <sup>p</sup>-substituted fluorobenzenes, in contrast to (-I, -R) substituents, is not uniform.

Table 3 shows the effect of (-I, +R) substituents on SFS for <sup>p</sup>-substituted fluorobenzenes. OAc, NHAc, and OCH<sub>3</sub> group decrease the C-F stretching frequency, whereas, NH<sub>2</sub> and OH group increase the C-F stretching frequency. This behavior is due to the nature of the substituents. Of these groups, negative (-I) polar and (+R) resonance effects have a counteracting influence on C-F stretching frequency. The negative (-I) polar effects tend to increase the C-F stretching frequency and positive (+R) resonance effects tend to decrease the C-F stretching frequency. Hence, the decrease in C-F stretching frequency for OAc, NHAc,
and OCH₃ groups may be due to predominance of resonance effect over the polar effect. The predominance of the polar effect over resonance effect may account for shift to a higher wavenumber in C-F stretching frequency for NH₂ and OH group. As is to be expected, the magnitude of this increase is not as large as the increase observed for (-I, -R) substituents where both negative (-I) polar and negative (-R) resonance act in unison.

TABLE 3

<table>
<thead>
<tr>
<th>Substituent</th>
<th>SFS -cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>OAc</td>
<td>-2</td>
</tr>
<tr>
<td>NHAc</td>
<td>-1</td>
</tr>
<tr>
<td>OCH₃</td>
<td>-1</td>
</tr>
<tr>
<td>NH₂</td>
<td>+3</td>
</tr>
<tr>
<td>OH</td>
<td>+4</td>
</tr>
</tbody>
</table>

The SFS due to halogen group in fluorobenzenes is shown in Table 4. The halogens as a group are electron attracting by a negative (-I) polar effect and electron donating by a positive (+R) resonance effect. As discussed previously, the shift to higher wavenumber for Cl and Br may be due to a stronger polar effect. Whereas, for F, predominance of resonance effect over polar may account for decrease in C-F stretching frequency.
In the discussion of data in Table 2, through Table 4, all the substituents except \( \text{CH}_3 \), considered in Table 1, have been accounted for. \( \text{CH}_3 \) group can donate electrons by polar and hyperconjugation effect and this should lower the C-F stretching frequency. It is seen from Table 1, \( \text{CH}_3 \) group shifts the C-F stretching frequency to a higher wavenumber.

The C-F stretching frequencies and SFS for 4-substituted-1-fluoronaphthalenes are shown in Table 5.

As was done in the case of \( p \)-substituted fluorobenzenes, the data of Table 5 is reorganized according to electrical characteristics of the substituents. Table 6 shows the C-F substituent frequency shift for (-I, -R) substituents.

A comparison of data of Table 6 with Table 2 shows that the substituents \( \text{CN} \), \( \text{NO}_2 \), and \( \text{COOH} \) shift the C-F stretching frequency in 4-substituted-1-naphthalenes as well as in \( p \)-substituted fluorobenzenes to a higher wavenumber. This is expected as negative (-I) polar and negative (-R) resonance effects decrease the electron density at a carbon atom attached to the fluorine.

### Table 4

<table>
<thead>
<tr>
<th>Substituent</th>
<th>SFS cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-8</td>
</tr>
<tr>
<td>Cl</td>
<td>+10</td>
</tr>
<tr>
<td>Br</td>
<td>+11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substituent</th>
<th>SFS cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-8</td>
</tr>
<tr>
<td>Cl</td>
<td>+10</td>
</tr>
<tr>
<td>Br</td>
<td>+11</td>
</tr>
</tbody>
</table>
atom in both fluoronaphthalenes, and fluorobenzenes.

TABLE 5

C-F STRETCHING FREQUENCIES AND SFS FOR 4-SUBSTITUTED-1-FLUORONAPHTHALENES

<table>
<thead>
<tr>
<th>Substituent</th>
<th>C-F Frequency cm$^{-1}$</th>
<th>SFS cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1234$^a$</td>
<td>----</td>
</tr>
<tr>
<td>NHCOCH$_3$</td>
<td>1232$^b$</td>
<td>- 2</td>
</tr>
<tr>
<td>Br</td>
<td>1233</td>
<td>- 1</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>1239</td>
<td>+ 5</td>
</tr>
<tr>
<td>CN</td>
<td>1239</td>
<td>+ 5</td>
</tr>
<tr>
<td>COOCH$_3$</td>
<td>1240</td>
<td>+ 6</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>1241</td>
<td>+ 7</td>
</tr>
<tr>
<td>COOH</td>
<td>1246$^b$</td>
<td>+12</td>
</tr>
</tbody>
</table>


$^b$ C-F Stretching frequencies measured as KBr pellets. All other frequencies measured in 10% carbon tetrachloride solution.

Also, it is noted that SFS for 4-substituted naphthalenes is smaller than for p-substituted fluorobenzenes. In case of bulky groups, such as COOH, NO$_2$, and COOCH$_3$, the steric effect of one peri hydrogen forces the substituent out of plane of the ring. So, the influence of the resonance effect on SFS is small for these groups. The cyano group is cylindrically symmetrical and the steric effects are negligible. Therefore, SFS (or C-F stretching frequency) for C=N group in p-fluorobenzonitrile
should be the same or slightly smaller than SFS for 1-fluoro-4-cyanonaphthalene. It is seen from data of Table 1 and Table 5 that SFS for \( p \)-fluorobenzonitrile is +17, whereas SFS for 1-fluoro-4-cyanonaphthalene is +5. This behavior of the C\( =N \) group is contrary to expectation because according to molecular orbital theory resonance interaction increases from benzene to naphthalene.

The substituents NHCOCH\(_3\), NH\(_2\), and Br are of \((-I, +R)\) type. From data in Table 5, it is seen that NH\(_2\) group increases, whereas, NHCOCH\(_3\) and Br groups decrease the C-F stretching frequency. The same behavior for NH\(_2\) and NHCOCH\(_3\) groups in fluorobenzenes was observed. In case of \( p \)-substituted fluorobenzenes, the Br group increases the stretching frequency. A predominance of the resonance effect over the polar effect by Br group in fluoronaphthalenes may account for decrease in C-F stretching frequency.

**TABLE 6**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>SFS cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>+5</td>
</tr>
<tr>
<td>COOCH(_3)</td>
<td>+6</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>+7</td>
</tr>
<tr>
<td>COOH</td>
<td>+12</td>
</tr>
</tbody>
</table>
The effect of various substituents on C-F stretching frequency and SFS in the fluoroanthracenes series is shown on Table 7.

**TABLE 7**

**C-F STRETCHING FREQUENCIES AND SFS FOR 10-SUBSTITUTED-9-FLUOROANTHRACENES**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>C-F Frequency cm⁻¹</th>
<th>SFS cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1072</td>
<td>-</td>
</tr>
<tr>
<td>OAc</td>
<td>1052</td>
<td>-20</td>
</tr>
<tr>
<td>NHAc</td>
<td>1057&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-15</td>
</tr>
<tr>
<td>Br</td>
<td>1067</td>
<td>-5</td>
</tr>
<tr>
<td>Cl</td>
<td>1075</td>
<td>+3</td>
</tr>
<tr>
<td>COOH</td>
<td>1077&lt;sup&gt;a&lt;/sup&gt;</td>
<td>+5</td>
</tr>
<tr>
<td>NO₂</td>
<td>1082&lt;sup&gt;b&lt;/sup&gt;</td>
<td>+10</td>
</tr>
<tr>
<td>CN</td>
<td>1096</td>
<td>+24</td>
</tr>
</tbody>
</table>

<sup>a</sup> C-F stretching frequency measured as KBr pellets. All other measurements in 10% carbon tetrachloride solution.


Data of Table 8 shows the substituent frequency shifts for (-I,-R) substituents in fluoroanthracene series. Table 8 shows the effect of (-I,-R) substituents in the 10-substituted-9-fluoroanthracenes. Of all the substituents listed in Table 7, substituents COOH, NO₂, and CN are of (-I,-R) type. The groups COOH, NO₂, and CN increase the C-F stretching frequency. This behavior is the same as observed for fluorobenzene and fluoronaphthalene series. The substituents NHCOCH₃, OCOCH₃, and Br
are of (-I,+R) type. Groups NHCOOCH$_3$, OCOCH$_3$, and Br lower the frequency, whereas a Cl group increases the frequency. This behavior of chlorine in fluoroanthracenes is similar to that observed in the fluorobenzene series. However, a Cl group causes a large SFS in fluorobenzenes unlike anthracenes. In contrast to the inconsistent behavior observed for NHCOOCH$_3$, OCOCH$_3$, and Br groups in fluorobenzenes and fluoronaphthalenes, these groups consistently lower the frequency in fluoroanthracenes.

TABLE 8

C-F SFS IN 10-SUBSTITUTED-9-FLUOROANTHRACENES
FOR -I, -R SUBSTITUENTS

<table>
<thead>
<tr>
<th>Substituent</th>
<th>SFS cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH</td>
<td>+5</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>+10</td>
</tr>
<tr>
<td>CN</td>
<td>+24</td>
</tr>
</tbody>
</table>

Table 9 shows the comparison of measured C-F substituent frequency shifts (SFS) for substituents in p-substituted fluorobenzene, 4-substituted-1-fluoronaphthalene and 10-substituted-9-fluoroanthracene. The following observations are made from data in Table 9:

1. SFS for all substituents in fluoronaphthalene series and all substituents, except CN group, in fluoroanthracene series is less than corresponding SFS in p-substituted fluorobenzenes.
2. NHAc group causes shift in C-F stretching frequency in all the three series towards lower wavenumber. Measurements of SFS for OAc group in fluoronaphthalene series are not available; however, it probably also causes a shift towards lower wavenumbers in C-F stretching frequency.

3. The SFS for NO$_2$ and COOH groups is smaller in fluoronaphthalene and fluoroanthracene than for corresponding p-substituted fluorobenzenes. This is so because steric effect of peri hydrogens in naphthalene and anthracene decreases the resonance contribution to SFS. Trotter$^{16}$ has determined that the nitro group in 9-nitroanthracene is 85 degrees out of the plane of the aromatic ring. It can be inferred that because of the bulkiness of COOH group, the steric effect decreases the resonance contribution. The SFS for the Br group decreases from fluorobenzene to anthracene. If the SFS for cyano group in naphthalene is disregarded, then SFS for cyano group is larger in anthracene than SFS in fluorobenzene. This behavior of Br and CN group can be explained on the basis of molecular orbital theory. According to this theory, resonance interaction increases from benzene to naphthalene to anthracene. The effect of the increasing resonance effect is to decrease SFS for Br group and to increase SFS for CN group. The same observation has been made by Norman and Ralph$^{17}$ regarding nitrile stretching frequency in p-substituted
benzonitrile and 10-substituted-9-cyanoanthracene.

**TABLE 9**

COMPARISON OF SFS FOR \( p \)-SUBSTITUTED FLUOROBENZENES, 4-SUBSTITUTED-1-FLUORONAPHTHALENES, AND 10-SUBSTITUTED-9-FLUOROANTHRACENES

<table>
<thead>
<tr>
<th>Substituent</th>
<th>SFS cm(^{-1})</th>
<th>4-Sub-1-Fluoronaphthalene</th>
<th>10-Sub-9-Fluoroanthracene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4-Sub-Fluorobenzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OAc</td>
<td>- 2</td>
<td>---</td>
<td>-20</td>
</tr>
<tr>
<td>NHCOCH(_3)</td>
<td>- 1</td>
<td>- 2</td>
<td>-15</td>
</tr>
<tr>
<td>Br</td>
<td>+11</td>
<td>- 1</td>
<td>- 5</td>
</tr>
<tr>
<td>CN</td>
<td>+17</td>
<td>+ 5</td>
<td>+24</td>
</tr>
<tr>
<td>COOH</td>
<td>+18</td>
<td>+12</td>
<td>+ 5</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>+24</td>
<td>+ 7</td>
<td>+10</td>
</tr>
</tbody>
</table>
CONCLUSIONS

This study has shown that:

1. All three substituents of (-I, -R) characteristics increase the C-F stretching frequency. This increase in frequency is attributed to an increase in s character in the C-F orbital.

2. The substituent frequency shift for bulky groups such as COOH and NO₂ is smaller in fluoronaphthalenes and fluoroanthracenes than for corresponding substituents in fluorobenzenes.

3. There is no definite trend for (-I, +R) substituents. It may increase or decrease the C-F stretching frequency.
EXPERIMENTAL

The C-F stretching frequencies of substituted aryl fluorides were recorded on a Perkin-Elmer 567 grating spectrophotometer having a range of 200-4000 cm\(^{-1}\). With the exceptions shown below, a 10% (by weight) carbon tetrachloride solution in sealed sodium chloride cells (0.025 mm thickness) was used for recording IR spectra. \(p\)-Fluorobenzoic acid, 1-fluoro-4-naphthoic acid, 10-carboxy-9-fluoroanthracene, and 10-acetylamino-0-fluoroanthracene are not soluble in carbon tetrachloride, so potassium bromide pellets were used for recording IR spectra. A polystyrene peak at 3060 cm\(^{-1}\) was used to calibrate all infrared spectra. The regions between 1200-1250 and 1000-1100 cm\(^{-1}\) were expanded 50 and 20 times, respectively, for substituted fluorobenzene. The abscissa accuracy of the IR spectrophotometer is better than ±2 cm\(^{-1}\) in 200-2000 cm\(^{-1}\) range. The frequencies reported are the average values of two scans recorded on two different days.

Para-substituted fluorobenzenes, 4-substituted-1-fluoronaphthalenes, and 10-substituted-9-fluoroanthracenes were selected to study the substituent effect on the infrared C-F stretching frequencies. In the case of fluorobenzenes, all compounds, except \(p\)-fluorophenyl acetate, were obtained from Aldrich Chemical Company, Inc. (USA), and were of the highest purity available commercially. These commercially obtained compounds were distilled thrice under vacuum to further purify them. \(p\)-Fluoro-
phenyl acetate was synthesized in the laboratory. Also, 4-substituted-1-fluoronaphthalenes and 10-substituted-9-fluoroanthracenes used in this study were synthesized in the laboratory. In the case of 10-substituted-9-fluoroanthracenes, of all the required compounds, only 10-nitro-9-fluoroanthracene, and 10-acetylamino-9-fluoroanthracene needed to be synthesized. The remainder of the required compounds were prepared previously by Dr. Anderson and were kindly provided. The purity of commercially available p-substituted fluorobenzenes was checked by using Varian 2700 vapor-phase gas chromatography.

Hence, only the synthesis of p-fluorophenyl acetate, 4-substituted-9-fluoronaphthalenes, 10-nitro-9-fluoroanthracene, and 10-acetylamino-9-fluoroanthracene are described.

**p-Fluorophenylacetate.** — p-Fluorophenol (11.2g, 0.1 m) was dissolved in a sodium hydroxide solution (50 cc, 10%). Ice (50 g) was added to the sodium hydroxide solution. Acetic anhydride (14.0g, 0.12 m) was added quickly and the mixture was shaken vigorously for a few seconds. p-Fluorophenyl acetate separated at once as a colorless liquid. The product was washed with dilute sodium hydroxide then with water, dried over calcium chloride, and distilled (75°/19 mm, 917g, 62.9%).

Lit. bp 86°/126 mm; ir, λ (neat) = 3.42, 5.68, 8.26, 8.47 ; nmr, δ (CCl₄) = 6.85 (-4H doublet benzene hydrogens) and 2.1 (3H-O=CH-CH₃)

Anal: Calcd. for C₈H₇O₂F, C, 66.6; H, 4.57;

Found: C, 66.82; H, 4.59.

Calcd: Mol. Wt. 154.36, found mol. wt. (mass spectroscopy) 154.0
1-Fluoro-4-Bromonaphthalene. -- 1-Fluoronaphthalene was brominated according to the procedure of G. Schiemann.\textsuperscript{12} 1-Fluoronaphthalene (10.0 g, 0.07 m) was dissolved in carbon tetrachloride (20 cc). Bromine (11.0 g, 0.14 m) was added dropwise to the stirred solution. After the addition of bromine was over, the reaction mixture was heated in a water bath (75-85\textdegree) for three hours. The reaction mixture was washed with water and dried over magnesium sulfate. The solvent was removed in vacuo. The oily residue formed white needle-like crystals after two days (8.6 g, 54.81\%). The product was recrystallized from petroleum ether (7.9 g, 50.3\%) mp. 35-36\degree.

Lit.\textsuperscript{12} 37\degree; ir, \(\lambda (\text{CCl}_4)=3.24, 7.28, 7.87, 8.06\); nmr, \(\delta (\text{CCl}_4)=7.01\) (6H multiplet naphthalene hydrogens).

Anal: Calcd. for C_{10}H_{6}FBr: C, 53.33; H, 2.33;

Found: C, 53.61; H, 2.78.

Calcd: Mol. Wt. 225.05.

Found: mol. wt. (mass spectroscopy) 225.

1-Fluoro-4-Nitronaphthalene. -- 1-Fluoronaphthalene was nitrated according to the procedure of G. Schiemann.\textsuperscript{12} Fuming nitric acid (40.0 g, 0.63 m) was added dropwise to a stirred solution of 1-fluoronaphthalene (20.0 g, 0.13 m) dissolved in glacial acetic acid (40 cc). After one-third of the fuming nitric acid had been added, the temperature had risen to 80\degree. The reaction mixture was heated for five hours (60-70\degree). The product was collected from the cooled reaction mixture and washed with water (16.1 g, 55.9\%). The product was recrystallized from ethanol to
give (14.9g, 52.9%), product forming lachrymatory yellow needles. mp. 75-76°. Lit.12 75-77°; ir, λ (CCl₄) = 3.24, 6.58, 7.41, 7.88, 8.06, nmr, δ (CCl₄) = 7.03 (6H multiplet naphthalene hydrogens).
Found: C, 63.32; H, 3.21.
Calcd: Mol. Wt. 191.06.
Found: mol. wt. (mass spectroscopy) 191.

1-Fluoro-4-Cyanonaphthalene.-- A solution of 1-fluoro-4-bromonaphthalene (5.5g, 0.024 m), cuprous cyanide (2.28g, 0.02 m), dimethylformamide (25.0 ml) and two drops of pyridine was heated under reflux for five hours. The hot solution was poured into ammonium hydroxide solution (25 ml, 28%) containing crushed ice (25.0g). The resulting suspension was extracted twice with chloroform (100 ml), washed with dilute hydrochloric acid (10%) and water and dried over magnesium sulfate. Evaporation gave crude 1-fluoro-4-cyanonaphthalene which was purified by chromatography (alumina, petroleum ether). The product was recrystallized from petroleum ether (3.3g, 82.5%) mp. 90-91°.
Lit.7 89.5-90.5°; ir, λ (CCl₄) = 3.24, 4.48, 6.25, 6.79, 7.03, nmr, δ (CCl₄) = 7.03 (6H multiplet, naphthalene hydrogens).
Anal: Calcd. for C₁₁H₆NF; C, 77.18; H, 3.53.
Found: C, 77.36; H, 3.82.
Calcd: Mol. Wt. 171.15.
Found: mol. wt. (mass spectroscopy) 171.0.

1-Fluoro-4-naphthoic Acid. -- A mixture of 1-fluoro-4-cyanonaphthalene (2.0g, 0.01 m), glacial acetic acid (30 ml), con-
centrated sulfuric acid (15 ml) and water was heated under reflux for 14 hours. The reaction mixture was treated with sodium carbonate solution (25 ml, 10%). The filtrate was acidified with dilute hydrochloric acid yielding crude l-fluoro-4-naphthoic acid (1.7g, 89.5%). The acid was crystallized from aqueous ethanol to give white needles, mp. 224-225°. Lit.7 224-225°, ir, λ (KBr Pellet): 3.22, 5.95, 6.25, 7.69, 6.94, nmr, δ (DMF) = 7.1 (6H naphthalene hydrogens) 10.8 (1H acid proton).
Anal: Calcd. for C₁₁H₇O₂F: C, 69.47; H, 3.68;
Found: C, 69.63; H, 3.66.
Calcd: Mol. Wt. 190.16.
Found: mol. wt. (mass spectroscopy) 190.0.

1-Fluoro-4-Naphthylamine. — A refluxed solution of 1-fluoro-4-nitronaphthalene (5g, 0.02 m) in ethanol (80 ml) and concentrated hydrochloric acid (5 ml) was treated with five one-gram portions of iron powder allowing five minutes to pass between each two additions. Vigorous refluxing was maintained for two hours, after which the mixture was neutralized with alcoholic sodium hydroxide, filtered hot, and the residue was extracted with hot ethanol. The combined alcoholic solution was concentrated, whereby, crystals of 1-fluoro-4-naphthylamine separated on cooling yielded (3.7g, 79%) mp. 44-46°. Lit.7 43-45°; ir, λ (CCl₄) = 2.87, 2.19, 6.25, 6.62, nmr, δ (CCl₄) = 7.05 (6H multiplet naphthalene hydrogens) 5.5 (2NH₂).
Anal: Calcd. for C₁₀H₉NF: C, 74.52; H, 5.00.
Found: C, 74.75; H, 5.12.
Calcd: Mol. Wt. 161.
Found: mol. wt. (mass spectroscopy) 161.

1-Acetaamido-4-Fluoronaphthalene. -- A solution of 1-amino-4-fluoronaphthalene (2.0g, 0.01 m) in glacial acetic acid (20 ml) and acetic anhydride (0.6g) was warmed on a steam bath for thirty minutes and then evaporated in vacuo. The acetyl derivative was recrystallized from aqueous ethanol in white needles (1.3g, 65%) mp. 182-183°. Lit. 7 182-183°; ir, λ (KBr Pellet): 2.90, 3.35, 5.96, 6.14, nmr, δ (DMF): 7.1 (6H naphthalene hydrogens), 8.2 (1H NH), 2.3 (3H CO-CH₃).

Anal: Calcd. for C₁₂H₁₀ONF: C, 70.92; H, 4.96.
Found: C, 71.19; H, 5.08.

Calcd: Mol. Wt. 203.
Found: mol. wt. (mass spectroscopy) 203.

Methyl-4-Fluoro-1-Naphthoate. -- A solution of 1-fluoro-4-naphthoic acid (5g, 0.02 m), methanol (30 ml) and concentrated sulfuric acid (2 ml) was refluxed for 4 hours. The reaction mixture was allowed to cool and extracted with chloroform (75 ml). The chloroform layer was washed with 10% NaHCO₃ solution (25 ml) and saturated NaCl solution (25 ml). The organic layer was dried over Na₂SO₄. Evaporation gave crude methyl-4-fluoro-1-naphthoate (2.6g, 72.21%). The ester was recrystallized from petroleum ether (2.0g, 55.51%) mp. 52.53°. Lit. 7 52-53°, ir, λ (CCl₄) = 2.92, 5.78, 8.03, nmr, δ(CCl₄), 7.1 (6H naphthalene hydrogens), 3.5 (0-CH₃ proton).

Anal: Calcd. for C₁₂H₉O₂F: C, 70.58; H, 4.44.
Found: C, 70.74; H, 4.62.
9-Nitroanthracene. -- 9-Nitroanthracene was prepared according to the procedure of Brown.\textsuperscript{14} Nitric acid (60 ml) was added dropwise to a suspension of anthracene (100 g, 0.56 m) in glacial acetic acid (400 ml) maintained below 30° by means of ice water bath. The reaction mixture was stirred below 30° temperature for two hours and filtered. A solution of concentrated hydrochloric acid (250 ml) in acetic acid (250 ml) was added to the filtrate. The product was isolated, and washed with several portions of water to remove the base. The crude product was air dried and recrystallized from glacial acetic acid to yield 9-nitroanthracene (75.6 g, 60.4\%). mp. 144-145°. Lit.\textsuperscript{14} 145-146°, ir, $\lambda$ (CCl$_4$) = 3.24, 6.58, 7.93, nmr, $\delta$ (CCl$_4$) = 7.5 (9H multiplet anthracene hydrogens).

9-Nitroanthracene-10-Pyridinium Bromide. -- 9-Nitroanthracene pyridinium bromide was prepared according to the procedure of Barnett, et al.\textsuperscript{15} Bromine (3.68 g, 0.23 m) was added dropwise to a stirred suspension of 9-nitroanthracene (25.0 g, 0.11 m) in pyridine cooled by means of an ice water bath. Stirring was continued for two hours and the reaction mixture was allowed to stand for three days at room temperature. The crude product was crushed, washed with pyridine and ether, and crystallized from water to give a salt (27.8 g, 64.8%).
9-Nitroanthracene-10-Pyridinium Tetrafluoroborate. -- A suspension of 9-nitroanthracene-10-pyridinium bromide (25.0g, 0.066 m) in fluoroboric acid (150 ml, 48%) was stirred for five hours. The crude product was collected, washed with water, ethanol, and ether, and recrystallized from water to give 9-nitroanthracene-10-pyridinium tetrafluoroborate (12.6g, 48.8%), mp. 258-259°. Lit. 8 259-260°.

10-Nitro-9-Fluoroanthracene.— A mixture of 9-nitroanthracene-10-pyridinium tetrafluoroborate (16.0g, 0.42 m), anhydrous sodium fluoride (15.4g, 0.042 m) and tetramethylene sulfone (100 ml) was heated for five hours (175-185° under nitrogen atmosphere). The reaction mixture was poured, while still hot, into cold water and allowed to stand. The crude product was collected, washed thoroughly with hot water, dissolved in benzene, and dried over calcium sulfate. The benzene solution was concentrated and chromatographed on alumina (benzene). The benzene solution was concentrated and the crude product was recrystallized from benzene cyclohexane (1:4) to yield 10-nitro-9-fluoroanthracene (1.6g) mp. 199-200°. Lit. 8 200-201°, ir, \( \lambda (\text{CCl}_4) = 3.24, 5.95, 6.41, 7.41, 7.81 \), nmr, \( \delta (\text{CCl}_4) = 7.3 \) (8\( \text{H} \) multiplet, anthracene hydrogens).

**10-Acetylamino-9-Fluoroanthracene.** -- 10-Acetylamino-9-fluoroanthracene was prepared according to the procedure of Anderson, et al. Zinc dust (6.67 g, 94%) was added gradually to a stirred solution of 9-nitro-10-fluoroanthracene (1.0 g, 0.0041 m) sodium acetate (67 ml). The reaction mixture was stirred for one hour and filtered. Water was added to the filtrate and the crude product was extracted with methylene chloride. The combined methylene chloride extracts were washed with water and ammonium hydroxide and dried over calcium sulfate. The methylene chloride was removed in vacuo and the residue was crystallized from ethanol to give 10-acetylamino-9-fluoroanthracene (0.4 g, 39.7%). mp. 289-291°. Lit. 289-291°, ir, λ (KBr Pellets): 3.03, 3.22, 6.02, 6.66, 7.14, 7.58, nmr, δ (DMF): 7.3 (8H multiplet, anthracene hydrogens) 7.9 (1H NH), 2.1 (3H COCH₃).

Anal. Calcd. for C₁₆H₁₂FNO: C, 75.88; H, 4.77.

Found: C, 76.20; H, 4.98.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Observed bp or mp</th>
<th>Reported^a bp or mp</th>
<th>Observed nd^25</th>
<th>Reported^a nd^25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorobenzene</td>
<td>84-84.5°</td>
<td>84.8°</td>
<td>1.4646</td>
<td>1.4610</td>
</tr>
<tr>
<td>p-Fluoroanisole</td>
<td>35° (4mm)</td>
<td>157°</td>
<td>1.4851</td>
<td>1.4862</td>
</tr>
<tr>
<td>p-Fluoroaniline</td>
<td>52° (5mm)</td>
<td>188°</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>p-Fluorotoluene</td>
<td>116°</td>
<td>116°</td>
<td>0.9918</td>
<td>0.9920</td>
</tr>
<tr>
<td>p-Bromofluorobenzene</td>
<td>95° (20mm)</td>
<td>151-152°</td>
<td>1.5315</td>
<td>1.5310</td>
</tr>
<tr>
<td>p-Chlorofluorobenzene</td>
<td>130-131°</td>
<td>129-131°</td>
<td>1.4963</td>
<td>1.4963</td>
</tr>
<tr>
<td>p-Nitrofluorobenzene</td>
<td>78° (3mm)</td>
<td>86.6° (14mm)</td>
<td>1.5316</td>
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</tr>
<tr>
<td>p-Difluorobenzene</td>
<td>86.5°</td>
<td>88.4°</td>
<td>1.4388</td>
<td>1.4425</td>
</tr>
<tr>
<td>Ethyl-p-Fluorobenzoate</td>
<td>93.5° (3mm)</td>
<td>210°</td>
<td>1.4842</td>
<td>1.4707</td>
</tr>
<tr>
<td>p-Fluorobenzoic Acid</td>
<td>182-183°</td>
<td>182-184°</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>

### TABLE 11

**PHYSICAL DATA OF 10-SUBSTITUTED-9-FLUOROANTHRACENES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Observed mp</th>
<th>Reported&lt;sup&gt;a&lt;/sup&gt; mp</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-Fluoroanthracene</td>
<td>102-103°</td>
<td>102-103°</td>
</tr>
<tr>
<td>10-Chloro-9-Fluoroanthracene</td>
<td>184-185°</td>
<td>184-185.5°</td>
</tr>
<tr>
<td>10-Nitro-9-Fluoroanthracene</td>
<td>199-201°</td>
<td>200-201°</td>
</tr>
<tr>
<td>10-Cyano-9-Fluoroanthracene</td>
<td>218-220°</td>
<td>218-220°</td>
</tr>
<tr>
<td>10-Acetoxy-9-Fluoroanthracene</td>
<td>125-127°</td>
<td>125-128°</td>
</tr>
</tbody>
</table>

REFERENCES


