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The Electronic Nature of Fluorine-containing Substituents

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The available literature data up to 1973 on the electronic effects of fluorine-containing substituents are considered and discussed in the review.
The bibliography includes 143 references.

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I. INTRODUCTION

The chemistry of organofluorine compounds is developing very vigorously. Novel methods of synthesis are being devised, new reactions and new types of organofluorine compounds are being discovered, and relations are being established between their structures and properties[1,2]. The quantitative characteristics of the electronic effects of 80 fluorine-containing substituents were determined in recent years and the results of a gradual substitution of hydrogen atoms by fluorine in alkyl groups demonstrated, the positions of new fluorine-containing groups in the series of thoroughly investigated substituents were established, and substituents with unique properties (the most pronounced electron-accepting properties among all known compounds) were discovered. The results are of great interest for theoretical organic chemistry. Substituents such as the fluorine atom and the CF_3 group are introduced into organic molecules as frequently as other substituents which do not contain fluorine. Since convenient preparative methods have been developed recently for the synthesis of compounds containing various perfluoroalkyl [CF_3O, CF_3S, CF_3SO_2, and $N(CF_3)_2$] and other similar groups, there is no doubt that these substituents too will soon become commonplace.

Since organic compounds with fluorine-containing substituents are finding increasing application as medicinal preparations, pesticides, dyes, and monomers for thermostable polymers, a review of the available data on the electronic effects of fluorine-containing groups may be useful for the specific synthesis of substances with valuable properties.

The electronic nature of substituents was characterised quantitatively for the first time by Hammett[3,4] in terms of σ_m and σ_p constants. Subsequently the latter were resolved by Taft and Lewis[5-9] into components reflecting the inductive (σ_I) and resonance (σ_R) effects. In the presence of direct polar conjugation between the substituents and the reaction centre, anomalously high σ constants are observed. Therefore one distinguishes σ_p^0 and σ_R^0 constants without taking into account direct polar conjugation from σ constants when such conjugation is taken into account (σ_p^- and σ_R^- for electron-accepting substituents and σ_p^+ and σ_R^+ for electron-donating substituents).[10]

In order to determine the σ constants of fluorine-containing substituents, the following methods are most widely used: ^{19}F NMR on the basis of the chemical shifts δ^F of the fluorine atoms in *meta*- and *para*-substituted fluorobenzenes relative to fluorobenzene[11]; the determination of σ constants from the dissociation constants of *meta*- and *para*-substituted benzoic acids[3,6,12]; the measurement of pK_a for anilinium[6,13] or dimethylanilinium ions[14]; the determination of the dissociation constants of phenols[6,15].

Dewar and Grisdale[16,17] and Swain and Lupton[18] developed new methods for the resolution of σ constants into inductive and resonance components—F and M, and F and R respectively. The electronic nature of fluorine-containing substituents has been investigated also by other correlations between σ constants and absorption band shifts of azo-dyes or passing from a neutral to an acid medium[19], the pK_a of cyanine dyes[20,21], and the absorption intensity in the infrared spectra of monosubstituted benzenes[22,23]. Methods based on the measurement of molecular dipole moments are also used[24]. The determination of interaction dipole moments (μ_{int}), which reflect the direct polar conjugation between the substituent and the reaction centre and are correlated with the σ^- and σ^+ constants[10,24,25], is particularly valuable.

The electronic effects of fluorine-containing substituents can be estimated from their directing influence in electrophilic or nucleophilic substitution reactions involving the aromatic ring. Correlations have been discovered between the reaction rate constants and the σ^+ or σ^- constants[26,27].

The most detailed data on the applications of various σ constants are quoted in a series of monographs and reviews[3,4,10,28-30]. This review deals with published data on the electronic effects of fluorine-containing substituents and a comparison is made with the electronic influence of the analogous substituents without fluorine.

II. FLUORINE AND OTHER HALOGENS

Fluorine is the most electronegative element. The C–F bond is the most polar among bonds between carbon and halogens[31,32]. In aliphatic compounds the fluorine atom exhibits a powerful electron-accepting inductive effect. This can be inferred, for example, from the pK_a values for halogenoacetic acids[33] and the molecular diagram for methyl fluoride[34]:

$$\begin{matrix} 0.00 + 0.187 - 0.187. \\ H_3C - F \end{matrix}$$

Halogen atoms linked to an unsaturated carbon atom or an aromatic ring exhibit an electron-accepting inductive effect ($\sigma_I > 0$) and an electron-donating conjugation† effect ($\sigma_R < 0$), decreasing in the sequence F > Cl > Br > I (Table 1). Among the halogens, the fluorine atom has the smallest covalent radius[32], close to that of the carbon atom, which results in conditions for maximum overlapping of the *p* orbitals. Therefore despite its high electronegativity, the fluorine atom exhibits the most pronounced electron-donating conjugation effect among all the halogens.

Table 1. σ constants of the halogens*.

Substituent	σ_m^{12} B	σ_p^{12} B	$\sigma_p^{0\,35}$	$\sigma_p^{+\,36}$	σ_I B[11]	σ_I A[35]	σ_I F[10]	$\sigma_R^{0\,11}$ B	$\sigma_R^{0\,11}$ F	σ_R^{10} B
F	0.34	0.06	0.17	−0.07	0.52	0.55	0.52	−0.35	−0.32	−0.46
Cl	0.37	0.23	0.27	0.11	0.47	0.43	0.40	−0.20	−0.18	−0.24
Br	0.39	0.23	0.26	0.15	0.45	0.42	0.44	−0.19	−0.16	−0.22
I	0.35	0.28[4]	0.27	0.13	0.39	0.34	0.44	−0.12	−0.14	−0.13

*In this and subsequent tables the methods of determination of σ constants are indicated by letters: B—from the pK_a for benzoic acids; A—from the pK_a for anilinium ions; DA—from the pK_a for dimethylanilinium ions; F—from the δ^F chemical shifts (^{19}F NMR); P—from the pK_a of phenols; i.r.—from infrared spectra; Dy—from $\Delta\lambda$ for azo-dyes; C—from the pK_a for cyanine dyes.

The overall electronic effect of fluorine, characterised by the σ_p constant, is the smallest among all the halogens, since its large conjugation effect to a considerable extent neutralises the inductive effect. The σ_R^0 constant for fluorine in *p*-difluorobenzene, determined by ^{19}F NMR, is smaller than σ_R found from pK_a for *p*-fluorobenzoic acid in which the fluorine atom is involved in direct polar conjugation with the COOH group (−0.32 and −0.46 respectively). As a result the σ_p constant for fluorine is smaller than σ_p^0.

Since the σ_p constant for fluorine is close to zero, the acid-base properties of benzoic acid, phenol, and aniline hardly change when the fluorine atom is introduced into the *para*-position relative to the functional group. The remaining halogens increase the acid properties and reduce the basic properties to a much greater extent than fluorine[37].

† Usually referred to as the resonance effect in English (Ed. of Translation).

The σ_p^+ constants for halogen atoms are much smaller than σ_m, which is usually observed for *ortho*, *para*-directing substituents. Indeed in electrophilic substitution reactions the halogens behave as substituents of the first kind with predominantly *para*-directing properties, particularly in the case of fluorine. In nitration reactions fluorine deactivates the benzene ring but to a much smaller extent than chlorine and bromine[38].

The electrophilic constant σ_p^+ of the fluorine atom is negative, in contrast to the other halogens. Accordingly, fluorobenzene is chlorinated much faster than benzene. The relative rates of chlorination of halogenobenzenes and benzene increase in the sequence F > H > Cl > Br (6.3, 1.0, 0.4, and 0.25 respectively).[38]

The distribution of electrons in vinyl fluoride and fluorobenzene, calculated by the quantum-chemical method taking into account σ and π electrons, confirmed that the inductive effect of the fluorine atoms makes it a powerful electron acceptor and the conjugation effect makes it a powerful electron donor. The overall charge of the fluorine atom in fluorobenzene is negative[39]. Fluoro-, chloro-, bromo-, and iodo-benzenes have dipole moments of 1.47, 1.59, 1.57, and 1.40 D respectively with the negative pole at the halogen atom[24,40].

Many instances where the fluorine atom exhibits not only an inductive effect but also a conjugation effect have been observed in studies on the reactivities of fluoro-olefins and described in reviews[41–43]. An interesting case of the electron-donating effect of fluorine was observed in cyanine dyes with fluorine atoms in the polymethine chain[44]. It was found that, as a powerful electron-donating substituent, fluorine affects the colour of the dyes in a manner similar to that, for example, of the methoxy-group.

Thus, in considering the influence of fluorine atoms on the properties of organic compounds, one must take into account the unusual behaviour of fluorine, related to its dual electronic nature involving a powerful electron-accepting inductive effect and an electron-donating conjugation effect.

III. FLUOROALKYL GROUPS (R_F)

Among the fluoroalkyl groups, the CF_3 group is most frequently introduced as a substituent. The σ constants of this group have been determined by various methods. Their values together with the σ constants of other fluoroalkyl groups are listed in Table 2.

The trifluoromethyl group is a fairly powerful electron-accepting substituent both as regards the inductive and conjugation effects. A number of studies have been made on its unusual properties[14,45,55,56]. The inductive effect plays the main role in its electronic influence. It is somewhat smaller for the CF_3 group than for the fluorine atom. Thus the dissociation constant of trifluoromethylacetic acid is smaller by a factor of 2.2 than that of fluoroacetic acid[57].

The conjugation effects of the CF_3 group and the fluorine atom act in the opposite directions. The electrophilic constant $\sigma_m^+ = 0.52$ of the CF_3 group is smaller than $\sigma_p^+ = 0.61$.[36] In conformity with these data, trifluoromethylbenzene enters into electrophilic substitution reactions with greater difficulty than benzene and its *meta*-position is involved preferentially. Thus the nitration of trifluoromethylbenzene results in the formation of 100% of the *m*-nitro-isomer[58], while chlorination gives 80.2% of the *m*-isomer, 15.7% of the *o*-isomer, and 4.1% of the *p*-isomer[59].

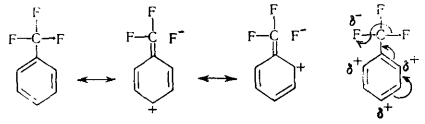
Table 2. σ constants for fluoroalkyl groups.

Substituent	σ_m			σ_p			σ_I			σ_R		
	B	A	F	B	A	F	B	A	F	B	A	F
CH_2F			0.12			0.11			0.13[47,48,a]			−0.02[47–49,b]
CHF_2			0.29			0.32			0.26[47,48,c]			0.06[47–50]
CF_3 *	0.43[12,d]	0.49[14,c]	0.44[14]	0.54[12,f]	0.62[14]	0.49[14]	0.41[11,g]	0.44[14]	0.39[14,3]	0.13[46,i]	0.18[14]	0.10[14]
CH_2CF_3 [2]		0.16	0.12		0.14	0.09			0.14			−0.05
CF_2CF_3 [14]		0.52[j]	0.47		0.69[j]	0.52			0.41			0.11
$(CF_2)_3CF_3$ [14]		0.55[j]	0.47		0.73[j]	0.52			0.39			0.11
$CF(CF_3)_2$ [14]	0.37	0.52	0.50	0.53	0.68	0.52	0.25	0.48	0.48	0.26	0.17	0.04
$C(CF_3)_3$ [51]	0.35	0.39	0.55	0.52	0.71	0.55	0.27		0.55	0.26		0.00
$C(CF_3)_2OH$ [14]		0.35	0.29		0.48	0.30		0.31	0.28		0.15	0.02
$\overline{CF(CF_2)_2CF_2}$ [2]			0.48			0.53			0.45			0.08
$\overline{C(OH)CF_2CF_2CF_2}$ [2]			0.36			0.37			0.35			0.02
m, p-CF_2OCF_2 [52]				0.81								
$CF_2CF_2C_6H_4F$-p [53,54]			0.34			0.39			0.29			0.10

Other data: [a] 0.12;[49,50] [b] −0.01;[50] [c] 0.29;[49,50] [d] 0.41 [45] and 0.42;[14] [e] 0.41;[45] [f] 0.53 [12,14] and 0.55;[4] [g] 0.33;[14] [h] 0.41;[11] [i] 0.18 [14] and 0.11 (i.r.)[23]; [j] (DA).
* $\sigma_p^+ = 0.61$.[36]

The following postulates have been used to account for the electronic nature of the trifluoromethyl group and in particular its electron-accepting conjugation effect.

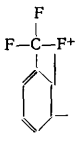
1. The CF_3 group is conjugated with the aromatic ring—a negative hyperconjugation effect[45] (in contrast to the positive hyperconjugation effect of the methyl group, which acts in the opposite direction[60]). This effect can be represented by a series of limiting structures with an unbound fluoride anion or by curving arrows:



2. The trifluoromethyl group exhibits a π-inductive effect (I_π)—it withdraws electrons from the adjacent ring carbon atom at which a partial positive charge arises and withdraws electrons from the *ortho*- and *para*-positions via a resonance mechanism[14,60]:



3. The *p* electrons of the fluorine atoms of the CF_3 group interact with the π electrons of the benzene ring in such a way that the electron density in the *meta*-position is enhanced—*p*-π interaction[14]. Many experimental facts and also quantum-mechanical calculations[55,56], carried out taking into account all the valence electrons in the atom, have shown that not only σ electrons but also ring π electrons are transferred to the CF_3 group in the trifluoromethylbenzene molecule. This confirms the hypothesis of a significant role of the hyperconjugation of the CF_3 group with the aromatic ring.



$+0.0508\,\sigma - 0.0508\,\delta$
$+0.0134\,\pi - 0.0134\,\pi$
$C_6H_5 - CF_3$

Negative hyperconjugation is a consequence of the overlapping of the *p* orbital of the adjacent carbon atom of the aromatic ring and the CF_3 group orbital comprising the orbitals of the fluorine atoms forming σ bonds. As a result of the high electronegativity of the fluorine atom, the hyperconjugation effect leads to a decrease of the π electron density in the aromatic ring and its increase at the fluorine atoms of the CF_3 group. When electron-donating substituents are introduced in the *para*-position of trifluoromethylbenzene, the electron shift to the CF_3 group increases owing to direct polar conjugation. This is confirmed, for example, by calculated data[56] for the distribution of π electrons in *p*-fluoro(trifluoromethyl)benzene in relation to the analogous values for fluorobenzene and trifluoromethylbenzene:

$$\underset{F-\ C_6H_5}{+0.0489\,\pi - 0.0489\,\pi} + \underset{p\text{-}F-\!-\!C_6H_4-\!-\!CF_3}{0.0522\pi - 0.0368\,\pi} - \underset{C_6H_5-CF_3}{0.0154\,\pi + 0.0134\,\pi - 0.0134\,\pi}\ .$$

In the *p*-fluoro(trifluoromethyl)benzene molecule the π electron density at the CF_3 group is higher than in the trifluoromethylbenzene molecule, while at the fluorine atom it is lower than in fluorobenzene, i.e. direct polar conjugation results in a transfer of electrons from the fluorine atom to the trifluoromethyl group.

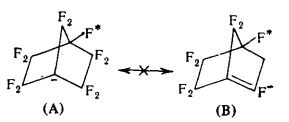
Direct polar conjugation of the CF_3 group with powerful electron-donating substituents (NH_2, NMe_2, O^-) was observed in a study of the dipole moments and chemical properties of *para*-substituted trifluoromethylbenzene. For example, *p*-amino(trifluoromethyl)benzene has μ_{int} = 0.49 D.[61] As a result of direct polar conjugation, *o*- and *p*-hydroxy- and *o*- and *p*-amino-(trifluoromethyl)benzenes readily undergo alkaline hydrolysis, in contrast to the *meta*-isomers[62,63]. For example, this has been used to synthesise 4-trifluoromethylanthranilic acid (a valuable intermediate) from 2,5-di(trifluoromethyl)aniline. In the alkaline hydrolysis of the latter the CF_3 group in the *ortho*-position relative to the amino-group is converted into a carboxy-group, while the substituents in the *meta*-position remain unchanged[64,65].

The high σ constants determined from the pK_a of substituted anilines (σ_D^-), compared with the values found by other methods, have been explained by direct polar conjugation (Table 2).

Andreades[66] investigated the base-catalysed exchange of hydrogen for deuterium in monohydrofluorocarbons: $R_FH + CH_3OD \rightleftharpoons R_FD + CH_3OH$. This reaction proceeds via a stage involving the formation of a carbanion and the

rate of exchange depends on its stability. Comparison of the deuteration rate constants showed that the relative reactivity increases in the series $R_F = CF_3 < CF_3(CF_2)_5CF_2 < (CF_3)_2CF < (CF_3)_3C$, the corresponding values being $1, 6, 2 \times 10^5$, and 10^9. The delocalisation of the charge in the corresponding anions can be described by 0, 2, 6, and 9 resonance structures, the stability of the carbanions and the rate of deuterium exchange increasing in the same sequence. This parallel variation is evidence in support of the hyperconjugation effect.

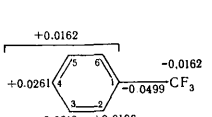
According to Streitwieser and Holtz [67,68] the following observation constitutes evidence against a significant role of negative hyperconjugation in the electronic effect of the CF_3 group. The rate of exchange of protons for the corresponding tritium species in 1*H*-undecafluorobicyclo[2,2,1]heptane is higher by a factor of five than for $(CF_3)_3CH$. Moreover the carbanion of the latter compound is stabilised by nine resonance structures, while the carbanion (A) is not stabilised by resonance in the authors' view, since, according to Bredt's rule, a double bond cannot be located at the bridgehead, i.e. structure (B) is impossible.



(A) (B)

However, these arguments are insufficient for the complete rejection of a contribution by hyperconjugation, since the involvement of the CF_3 group in conjugation does not require a change in the hybridisation of its carbon atom from sp^3 to sp^2 and its hyperconjugation effect is not described exactly by the resonance theory in terms of limiting structures with an unbound fluorine atom and a C=C double bond. As mentioned above, the hyperconjugation of the CF_3 group is due to the overlapping of the *p* orbitals of the adjacent carbon atom with the orbitals of the fluorine atoms of this group without a change in its steric configuration. Thus hyperconjugation in the carbanion (A) can be achieved also without the involvement of (B) type structures. Apart from this, the field effect of the fluorine atom (F*) at the bridgehead can have an influence on the stabilisation of the carbanion (A). [50]

The trifluoromethyl group exerts a powerful electron-accepting inductive effect on the aromatic ring, which is transmitted both via the nearest σ bonds and through space in the form of the field effect. This effect leads to the polarisation not only of σ electrons but also of π electrons, i.e. results in a I_π effect. The influence of the latter is indicated by the calculated π electron distribution in the trifluoromethylbenzene molecule [50]:



According to these data, a negative charge (−0.0499) is concentrated on carbon atom 1, exceeding the charge of the CF_3 group (−0.0162). Thus polarisation of the ring π electrons under the influence of the inductive effect of the CF_3 group is evidence for the presence of an I_π effect.

However, there are also objections to a significant role of the I_π effect [49,71]. They are based on the observation that groups such as $C(CN)_3$ and ICl_2, which have very high inductive effects ($\sigma_I = 0.98$ [49] and 1.3 [71]) do not exhibit a conjugation effect ($\sigma_R = 0.01$ [49] and 0.0 [71] respectively). The $C(CF_3)_3$ group behaves similarly (Table 2). The I_π effect should increase with the inductive effect of the substituents on the ring π electrons and should lead to an increase of the σ_R. However, this is not observed. The I_π effect probably does not play a significant role in the electronic influence of perfluoroalkyl groups.

In the study of the hyperconjugation effect of fluoroalkyl groups, it is interesting to compare the σ constants of the substituents CF_3, CF_2CF_3, $CF(CF_3)_2$, and $C(CF_3)_3$ in which the number of fluorine atoms capable of being involved in conjugation decreases steadily. All these groups are fairly powerful electron-accepting substituents with positive σ_m and σ_p constants.

Comparison of the σ_I and σ_R constants of the above perfluoroalkyl substituents obtained from ^{19}F NMR data (Table 2) shows that the replacement of fluorine atoms in the CF_3 group by trifluoromethyl substituents leads to a gradual increase of the σ_I constant and a decrease of the conjugation constant σ_R. The conjugation constant for the $C(CF_3)_3$ group is zero [51]. These findings confirm the hypothesis of an effect of the hyperconjugation of the fluorine atoms in the trifluoromethyl group with the aromatic ring, which decreases as CF_3 groups accumulate at a single carbon atom.

Despite the fact that the inductive effect of the fluorine atom is greater than that of the trifluoromethyl group, the σ_I constants increase on replacement of the fluorine atoms in the CF_3 group by trifluoromethyl substituents. This can probably be explained by the fact that the inductive effect is transmitted not only via σ bonds but also through space—the field effect *F*. The latter depends on the distance *r*, the dipole moments μ of the bonds in the substituent, the angles θ between the directions of the moments and the lines joining the centres of the dipoles to the reaction centre, and the dielectric constant *D* of the solvent [69,70]: $F = \mu \cos\theta / Dr^2$.

Sheppard explained a similar increase of the σ constant on passing from CN($\sigma_I = 0.47$) to the $C(CN)_3$ group ($\sigma_I = 0.98$) also by an increase of the field effect [49,71].

Since the inductive effect plays a dominant role in the electronic behaviour of perfluoroalkyl substituents, its increase according to ^{19}F NMR data in the series $CF_3 < CF_2CF_3 < CF(CF_3)_2 < C(CF_3)_3$ leads to an increase of the constants σ_m and σ_p in the same sequence despite the decrease of the σ_R. The constants σ_p obtained from the ^{19}F NMR data and the pK_a for the acids are virtually identical.

The σ_m and σ_I constants for the $CF(CF_3)_2$ and $C(CF_3)_3$ groups obtained from the same data differ markedly. The field effect of the $CF(CF_3)_2$ and $C(CF_3)_3$ substituents is greater than that of the CF_3 group and therefore their electronic influence depends to a greater extent on the possible operation of the field effect. In the *para*-position it is transmitted through space in the ring with its low dielectric constant and in the *meta*-position the effect is transmitted via the solvent and greatly depends on its polarity. It decreases with increase of the polarity. The acid dissociation constants were determined in a highly polar solvent—aqueous alcohol. This probably explains why the $CF(CF_3)_2$ and $C(CF_3)_3$ groups in the *meta*-position have a weaker electron-accepting influence than the CF_3 group.

In a series of *para*-substituted derivatives, the decrease of the field effect of the substituents under the influence of the solvent does not occur and therefore the strengths of the *p*-CF_3-, *p*-$CF(CF_3)_2$-, and *p*-$C(CF_3)_3$-benzoic acids are approximately the same [14,51]. The fact that *m*-(perfluoro-t-butyl)aniline is a stronger base and its *para*-isomer a

weaker base than the corresponding trifluoromethylanilines can be explained by a similar field effect[51]. For the same reason, the σ_p constants determined from the pK_a for the anilinium ions (σ_p^-) increase on gradual substitution of the fluorine atoms in the CF_3 group by trifluoromethyl groups.

Examination of the constants $\sigma_R^- = \sigma_p^- - \sigma_I$ shows that, when CF_3 groups accumulate at the same carbon atom, there is a tendency towards a decrease of direct polar conjugation. A similar phenomenon was observed in the study of the dipole moments of aromatic compounds with polyfluoroalkyl substituents. The dipole moments of the compounds C_6H_5X, where $X = CF_3$, C_2F_5, $CF(CF_3)_2$, and $C(CF_3)_3$, are very close (2.60[45], 2.73[14], 2.68[14], and 2.72 D[51]). The values of μ_{int} for *p*-amino(trifluoromethyl)benzene and *p*-amino(perfluoro-t-butyl)benzene (0.42[45] and 0.30 D[51]) show that the direct polar conjugation between the CF_3 and NH_2 groups is somewhat more pronounced than between $C(CF_3)_3$ and NH_2.

Like the CF_3 group, all the perfluoroalkyl groups are *meta*-directing in electrophilic substitution reactions (nitration, bromination)[14,51].

In order to account for the greater deactivation of the *para*-position compared with the *meta*-position by the CF_3, C_2F_5, and $CF(CF_3)_2$ substituents, for which $\sigma_m < \sigma_p$, Sheppard[14] put forward the hypothesis of p-π interaction of the p electrons of the fluorine atoms of the perfluoroalkyl groups with the π electrons of the aromatic ring. Such interaction results in an electron shift, which partially compensates the powerful inductive effect of the substituents in the *meta*-position, while the *para*-position is greatly deactivated.

A number of objections have been made to the hypothesis of p-π interaction. Dewar[72] noted that the p-π interaction has no chemical analogies and that a shift of π electrons to the *meta*-position as a result of a conjugation effect is unlikely. Stock and coworkers[73], Smith and Menger[74], and Holtz[68] failed to observe such p-π conjugation in model compounds.

We established[51] that the $C(CF_3)_3$ group does not exhibit a conjugation effect although in the presence of p-π interactions the nine fluorine atoms in the β-position should be equivalent to the three fluorine atoms of the CF_3 group, according to Sheppard's hypothesis, and should lead to similar values of the σ_R constants of these substituents. Theoretical calculations of the distribution of electrons and of bond orders in the trifluoromethylbenzene molecule also failed to confirm the hypothesis of $p - \pi$ interaction[50]. Thus the hypothesis has not been confirmed by theoretical and experimental studies[30,50,68].

The results of studies on the electronic nature of trifluoroalkyl groups discussed above lead to the conclusion that the electron-accepting inductive effect of these substituents, which is transmitted both via σ bonds and through space (field effect) is most important in their electronic influence. The conjugation effect of these groups is small and is mainly caused by hyperconjugation.

On gradual substitution of hydrogen atoms in the methyl group by fluorine, the electron-accepting properties of the substituents become more pronounced—the σ_m, σ_p, σ_I, and σ_R constants increase and their sign changes from negative to positive (Tables 2 and 3).

When fluorine atoms are introduced into the CH_3 group, the σ_I constant does not increase in proportion to their number. The "saturation effect" is particularly marked for chloro-, bromo-, and iodo-derivatives. As a result of this effect, the σ_I constants of the $CHCl_2$ and CCl_3 groups and of the $CHBr_2$ and CBr_3 groups hardly differ. Another anomaly is that the σ_I constants of the CH_2X and CHX_2 groups do not decrease in the sequence X = F, Cl, Br, and I, although the electronegativity of the halogens decreases on passing from fluorine to iodine. These anomalies may be related to the different field effects of the CH_2X, CHX_2, and CX_3 groups. When X = Cl, Br, and I, the CH_2X and CHX_2 groups cannot rotate freely about the bond with the aromatic ring owing to steric hindrance, in contrast to the analogous fluorine-containing substituents, and occupy fixed positions. The angle θ (see above) between the C–X bond and the line joining the centre of this bond to the fluorine atom in the *meta*-position (from the chemical shifts of which the σ_I constants are determined) will be smaller than the average statistical angle for freely rotating fluorine-containing groups.

Table 3. σ constants for halogenoalkyl groups[47,48].

Substituent	σ_I	σ_R	Substituent	σ_I	σ_R	Substituent	σ_I	σ_R
CH_3[11]	−0.08	−0.15						
CH_2F[a]	0.13	−0.02	CHF_2[a]	0.26	0.06	CF_3	0.39	0.10
CH_2Cl	0.14[11,b]	−0.03[11, 50, c]	$CHCl_2$	0.29[d]	0.02[49, 50, e]	CCl_3	0.29[f]	0.02[g]
CH_2Br	0.14[h]	−0.03[i]	$CHBr_2$	0.29[j]	0.02[49, k]	CBr_3	0.25[l]	0.02[n]
CH_2I	0.14[n]	−0.04	CHI_2	0.26	0.00	Cl_3	—	—
CH_2CF_3[a]	0.14	−0.05	$CH(CF_3)_2$	—	—	$C(CF_3)_3$[a]	0.55	0.00
CH_2CN[49]	0.26	−0.08	$CH(CN)_2$[49]	0.55	−0.03	$C(CN)_3$[49]	0.98	0.01

Other data: [a]Table 2; [b]0.15,[50,55] 0.16,[49] and 0.17;[10,11] [c]0.04;[49] [d]0.28,[10] 0.30,[49] and 0.31;[50] [e]0.04;[10] [f]0.30[49] and 0.31;[50] [g]0.03;[49,50] [h]0.16[10,49,50] and 0.18;[75] [i]−0.02;[49,50] [j]0.26[50] and 0.30;[49] [k]0.03;[50] [l]0.26;[49,50] [m]0.03;[49,50] [n]0.16.[75]

The field effect of the CH_2X and CHX_2 substituents, where X = Cl, Br, and I, depends on $\cos\theta$, increases for this reason, and leads to an increase of the σ_I constants.

The accumulation of the large chlorine and bromine atoms at the same carbon atom in the CCl_3 and CBr_3 groups leads to an increase of the bond angles  or  and hence to an increase of the angle θ and a decrease of the field effect. This may be the reason for the appearance of the "saturation effect".

The angle θ in the $C(CF_3)_3$ substituent must be smaller than for CBr_3 and for the $C(CN)_3$ group θ should be smaller still, the steric hindrance to the rotation of this group is low and the valence angles apparently do not change, so that saturation is not observed for the $C(CN)_3$ group and the latter exhibits a very high inductive effect.

The conjugation constants for halogenoalkyl substituents are small. In terms of its conjugation effect, the CH_2F group is still not an electron donor and its σ_R constant is negative, while the CHF_2 and CF_3 substituents are electron acceptors on the basis of this effect.

On passing from fluorine to iodine in the series of substituents CH_2X, the electron-donating conjugation effect increases slightly, while the electron-accepting effect of the CHX_2 and CX_3 groups decreases.

The CH_2F and CH_2Cl groups are very similar as regards their electronic properties. Their directing effect in electrophilic substitution reactions is the same—they are

predominantly *ortho*, *para*-directing substituents. In the nitration of benzyl fluoride the ratios of the *p*-, *m*-, and *o*-isomers correspond to 54, 28, and 18%,[76] while the corresponding proportions for benzyl chloride are 52.5, 32, and 15%.[77] The directing effects of other partly fluorinated alkyl groups in electrophilic substitution reactions have not been investigated.

IV. PERFLUOROACYL GROUPS (COR_F)

The σ constants of the $C(=O)F$, $COCF_3$, and COC_3F_7[2] groups have been determined by ^{19}F NMR (Table 4). The $COCF_3$ and COC_3F_7 groups are much more powerful electron-accepting substituents, in terms of both their inductive and conjugation effects, than the analogous non-fluorinated acyl groups. In terms of the σ_p constants, they resemble the nitro-group ($\sigma_p = 0.78$)[10]. This is because, under the influence of the perfluoroalkyl substituents at the carbon atom of the carbonyl group, the positive charge increases appreciably and the inductive effect and capacity of the carbonyl group of the perfluoroacyl substituents become much more marked. The latter should also exhibit the effect of direct polar conjugation with electron-donating groups. It can be estimated from the σ_p^- constants. We calculated it from the correlation equation of Swain and Lupton[18]. σ_p^- for the $COCF_3$ group was found to be 1.22 (the corresponding values for the O_2 and $COCH_3$ groups are 1.27 and 0.8).[10]

Table 4. σ constants of perfluoroacyl groups.

Substituent	σ_m	σ_p	σ_I	σ_R
COF[2,11]	0.55	0,70	0,39	0,31
$COCF_3$[2,14]	0.63	0.80	0.47[a]	0.33
COC_3F_7[b]	0.63	0,79	0.46	0.33
COH[10,B]	0.43	0.52	0,25	0.27
COCl[10,B]	0.53	0.69	0,38	0.31
$COOC_2H_5$[10,C]	0.20	0.30	0.11	0.19
$COCH_3$[10,C]	0.28	0.38	0.18	0.20

Other data: [a]0.45;[11] [b]calculated from δ_m^F and δ_p^F (Sheppard[14]) data; [c](F).

In electrophilic substitution reactions, for example in nitration, the $COCF_3$ group exhibits predominantly a *meta*-directing effect[78].

The substitution of the hydrogen atom in the aldehyde group by fluorine leads to an increase of the electron-accepting inductive effect and of the conjugation effect. However, the fluoroformyl group has smaller σ constants than the $COCF_3$ group. This is because the fluorine atom exhibits, apart from a powerful electron-accepting inductive effect, an electron-donating conjugation effect. The latter is much smaller than for the ethoxy-group in the $COOC_2H_5$ substituent. For this reason, the COF group is a stronger electron-accepting substituent than $COOC_2H_5$. The constant σ_p^- for the COF group is also somewhat smaller than for $COOC_2H_5$, amounting to 1.09.

V. NITROGEN- AND PHOSPHORUS-CONTAINING SUBSTITUENTS (N – R_F, P – R_F)

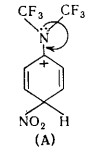
The electronic properties of the substituents in which the CF_3, COF, $COCF_3$, and SO_2CF_3 groups are linked to the nitrogen atom have been investigated (Table 5). The replacement of the methyl by trifluoromethyl in the dimethylamino-group converts this powerful electron-donor into an electron-acceptor, whose σ_m and σ_p constants are close to those of the trifluoromethyl group. However, the inductive effect contributes most to the electronic influence of the $N(CF_3)_2$ group. Its conjugation effect is close to zero owing to the withdrawal of the free electron pairs of the nitrogen atom by the trifluoromethyl groups. For the same reason, di(trifluoromethyl)aniline and its derivatives do not exhibit basic properties and do not form salts with acids[79,82].

Table 5. σ constants for nitrogen-containing substituents (^{19}F NMR method).

Substituent	σ_m^a	σ_p^a	σ_I	σ_R
NH_2[10]	−0.23	−0,47	0.01	−0,48
$N(CH_3)_2$[10]	−0.17	−0,44	0,10	−0,54
$N(CF_3)_2$[2,79,b]	0,49	0.50	0,49	0,01[c]
$NHCOCH_3$[80]	0.17	0,05	0.28	−0,22
$NHCOCF_3$[80]	0.37[d]	0.27[d,e]	0.46[f]	−0.19[f]
$NHSO_2CH_3$[80]	0,32	0.21	0,42	−0.21
$NHSO_2CF_3$[80]	0.44	0.39	0.49	−0.10
$N(CH_3)COCH_3$[80]	0,31	0,26	0.36	−0.10
$N(CH_3)COCF_3$[80]	0.41	0,39	0,43	−0,04
$N(CH_3)SO_2CH_3$[80]	0.29	0,24	0.34	−0.10
$N(CH_3)SO_2CF_3$[80]	0.46	0.44	0.48	−0.04
$N(COCH_3)_2$[80]	0.35	0.33	0.37	−0,04
$N(SO_2CH_3)_2$[80]	0,47	0.49	0,45	0.04
$N(SO_2CF_3)_2$[80]	0.75	0,80	0.70	0.10
$N(CF_3)COF$[79]	0.56	0,56	0,56	0.00
$N(COF)_2$[79]	0.58	0,57	0.58	−0.01
$N{=}C(CF_3)_2$[2]	0.29	0.23	0.35	−0.12
$N{=}N{-}CF_3$[80]	0.56	0.68[g]	0,44	0.24
$N{=}N{-}C_6H_5$[10]	0.23	0.27	0.19	0.08

Other data: [a]calculated from σ_I and σ_R; [b]$\sigma_m = 0.40$, $\sigma_p = 0.53$, $\sigma_I = 0.29$, $\sigma_R = 0.23$ (B),[14] $\sigma_m = 0.47$, $\sigma_p = 0.53$, $\sigma_I = 0.44$, and $\sigma_R = 0.06$ (A)[14]; [c]0.13 (i.r.)[23]; [d]$\sigma_m = 0.30$ and $\sigma_p = 0.12$ (B)[81]; [e]0.13 (C)[21]; [f]$\sigma_I = 0.38$ and $\sigma_R = -0.15$;[10] [g]0.74 (C)[21].

However, in electrophilic substitution reactions the $N(CF_3)_2$ group still behaves as an *ortho*, *para*-directing substituent. In the nitration of di(trifluoromethyl)aniline the proportions of the *para*-, *ortho*-, and *meta*-isomers are 92.4, 5.6, and 1.9%, while in the bromination reaction the corresponding proportions are 94.9, 0.3, and 1.7%.[79] Under the influence of electrophilic agents, the free electron pair at the nitrogen atom is probably nevertheless involved in conjugation and stabilises the transition state (A):



(A)

We estimated by two methods the constants σ_p^+ and σ_R^+, which determine the directing effect of the substituents

in electrophilic substitution reactions. The constants $\sigma_p^+ = 0.42$ and $\sigma_R^+ = 0.07$ were calculated for the $N(CF_3)_2$ group by the equation of Swain and Lupton[18].

The constant σ_R^+ was determined by another method, using the correlation equation $\mu_{int} = 1.10\ (\sigma_R - \sigma_R^+)$ derived by the present authors, for the compounds *p*-$XC_6H_4NO_2$, where X = NMe_2, NH_2, OH, Br, or SCH_3.[24] The dipole moments of *p*-$NO_2C_6H_4N(CF_3)_2$ and $C_6H_5N(CF_3)_2$ are 1.80 and 2.69 D,[79] $\mu_{int} = 0.40$ D, $\sigma_R^+ = 0.13$, and $\sigma_p^+ = 0.36$. The two methods yielded similar negative values of σ_R, and $\sigma_p^+ < \sigma_m$. Consequently the $N(CF_3)_2$ group should be *ortho*, *para*-directing, in agreement with experimental data.

The replacement of the hydrogen atom in the amino-group by $COCH_3$, SO_2CH_3, $COCF_3$, and SO_2CF_3 groups leads to an increase of the electron-accepting inductive effect and a decrease of the conjugation effect. However, the latter still retains its electron-donating character. Thus, even the $NHSO_2CF_3$ group is *ortho*, *para*-directing[83]. A change in the sign of the constant σ_R is observed only when two methane- or trifluoromethane-sulphonyl groups are introduced at the nitrogen atom. The σ_m and σ_p constants of the $N(SO_2CF_3)_2$ substituent resemble those of the nitro-group. Nitration of di(trifluoromethylsulphonyl)aniline yields a mixture of *meta*- and *para*-nitro-isomers in proportions of 8 : 1.[83] The $N(SO_2CH_2)_2$ group is predominantly *ortho*, *para*-directing[84].

The electrophilic constants σ_R^+ and σ_p^+ of the $N(SO_2CF_3)_2$ group, calculated by the method of Swain and Lupton[18], are 0.04 and 0.74. The positive value of the σ_R^+ constant indicates a *meta*-directing effect of this substituent. Thus the directing effect of the amino-group in electrophilic substitution reactions involving an aromatic ring was altered for the first time only by introducing at the nitrogen atom two powerful electron-accepting CF_3SO_2 groups[83].

There are linear relations[21,80] between the σ_p and σ_I constants of the NHR group on the one hand and the corresponding constants of the substituents R, where R = $COCF_3$, SO_2CF_3, and other acyl groups, on the other; they are expressed by the equations

$$\sigma_p(NHR) = 0.49\,\sigma_p(R) - 0.13 \text{ and } \sigma_I(NHR) = 0.38\,\sigma_I(R) - 0.23.$$

It is interesting to note that the $N(CH_3)R$ groups, where R = $COCH_3$, SO_2CH_3, or SO_2CF_3, are weaker electron donors in terms of their conjugation effects than the corresponding NHR groups, although the introduction of the electron-donating methyl group in place of a hydrogen atom should have resulted in the opposite effect[80]. The explanation is probably that the $N\langle^{CH_3}_{R}$ groups are displaced from the plane of the benzene ring owing to steric hindrance, which reduces the degree of conjugation between the free electron pair at the nitrogen atom and the ring π electrons.

The $N(CF_3)COF$ and $N(COF)_2$ substituents are somewhat stronger electron acceptors than $N(CF_3)_2$ due to the greater contribution of the inductive component. The trifluoromethylazo-group $-N{=}N{-}CF_3$ is a powerful electron-accepting substituent, approaching in this respect the nitro-group and greatly superior in its electron-accepting influence to the $-N{=}NC_6H_5$ group. In terms of its conjugation effect, the $-N{=}C(CF_3)_2$ substituent is an electron donor. This group is probably not located in the plane of the benzene ring and the free electron pair at the nitrogen atom is involved in conjugation with the aromatic ring.

The phosphorus-containing groups $P(CH_3)_2$ and $P(CF_3)_2$ are less effective electron-accepting substituents than their nitrogen-containing analogues. The inductive effects of the corresponding substituents are close and the conjugation effects of the phosphorus-containing groups indicate more pronounced electron-accepting properties than those of the nitrogen-containing groups (Tables 5 and 6). The σ_I and σ_R constants of the $P(CF_3)_2$ group virtually correspond to those of the nitro-group.

Table 6. σ constants for fluorine-containing substituents.

Substituent	σ_m^a	σ_p^a	σ_I	σ_R
$P(CH_3)_2$ [85]	0.05	0.03	0.08	−0.05
$P(CF_3)_2$ [85]	0.60	0.69	0.50	0.19
$P(CF_3)(C_6H_4F)$[b]	0.44	0.47	0.41	0.06

[a]calculated from σ_I and σ_R (F) data; [b]σ_I and σ_R calculated from δ_m^F and δ_p^F.[85]

The involvement of the free *d* orbitals of the phosphorus atom in conjugation with the π electrons of the aromatic ring is characteristic of phosphorus-containing substituents. The presence of electron-accepting groups at the phosphorus atom, such as CF_3, leads to a decrease of the size and diffuseness at the *d* orbitals, which makes their overlapping with the π electron cloud of the ring more effective and increases the electron-accepting character of the conjugation of the substituent. The replacement of one of the CF_3 groups by an aromatic ring with more marked electron-donating properties makes the conjugation effect of the $P(CF_3)(C_6H_4F)$ group much weaker than for $P(CF_3)_2$. Linear relations have been found for substituents of the type PX_3, where X = F, CF_3, CN, and other groups, whereby the constants of the substituents PX_2 can be calculated from the values of σ_I and σ_R for X:[85]

$$\sigma_I(PX_2) = 0.78\,\sigma_I(X) + 0.47\,\sigma_R(X) + 0.15;\quad \sigma_R(PX_2) = 0.44\,\sigma_I(X) + 0.08\,\sigma_R(X) - 0.03.$$

VI. OXYGEN-CONTAINING GROUPS (O–R_F)

The σ constants of fluorinated oxygen-containing groups are listed in Table 7. The replacement of three hydrogen atoms in the OCH_3 group by fluorine atoms greatly increases its electron-accepting inductive effect and decreases the electron-donating conjugation effect. However, the σ_R constant of the OCF_3 group is still negative, in contrast to all the known substituents of the type $X(CF_3)_n$. All the σ constants of the OCF_3 group resemble most closely those of the chlorine atom. Like the latter, the OCH_3 group is an *ortho*, *para*-directing substituent[97,98], but in the nitration and bromination of phenyl trifluoromethyl ether only the *para*-isomers are formed in yields of 91 and 82% respectively[99,100].

The *para*-directing influence of the trifluoromethoxy-group can be accounted for by the stabilisation of the transition state by the electron-donating conjugation effect of this group. The *ortho*-position relative to the OCF_3 group is deactivated, as in fluorobenzene, by the powerful electron-accepting inductive effect. The σ_I constant of the OCF_3 group is closer to that of fluorine than chlorine.

Table 7. σ constants for oxygen-containing groups.

Substituent	σ_m			σ_p			σ_I			σ_R		
	B	A	F*	B	A	F*	B	A	F	B	A	F
OCH_3 [10]	0.12		0.08	−0.27	−0.27	−0.14	0.30 [86]		0.25	−0.57 [86]		−0.43
OCH_2F [a]			0.20			0.02			0.37			0.35
$OCHF_2$	0.31 [86]		0.33	0.18 [86]	0.11 [88]	0.21	0.44 [86]		0.45 [87,89]	−0.24 [86]		−0.24 [89, b, c]
OCF_3 [52–54, 10, d]	0.35[e]	0.47 [90]	0.46	0.32[f]	0.27 [90, g]	0.37	0.40	0.50 [90]	0.55	−0.07 [i]	−0.23 [90]	−0.18 [j]
OCH_2Cl [87]			0.25			0.08			0.41			−0.33
$OCHCl_2$ [87]			0.38			0.26			0.49			−0.23
$OCCl_3$ [87]			0.43			0.34			0.51			−0.17
OCF_2CF_3 [90, k]		0.48			0.28			0.52				
OCF_2CHF_2 [90]	0.34	0.43		0.25	0.21		0.39	0.45		−0.14	−0.25	
OCF_2CHFCl [91]	0.35			0.28			0.42			−0.12	−0.25	
$OCOCH_3$ [10]	0.39		0.17	0.31		0.06			0.27			−0.21
$OCOCF_3$ [92]			0.56			0.46			0.65			−0.19
OSO_2CF_3 [93,94]	0.56		0.80	0.53	0.49 [88]	0.90	0.58		0.70	−0.05		0.20
OSF_5 [2,95]				0.44								
 [52]				0.36[l]								

*Calculated from σ_I and σ_R data.

Other data: [a]approximate values, σ_R = −0.31 (i.r.)[87]; [b]−0.27;[87] [c]−0.23 (i.r.)[87]; [d]σ_m = 0.40, σ_p = 0.26, σ_I = 0.36, and σ_R = −0.15(P)[10]; [e]0.38;[2,14] [f]0.35;[2,14,19] [g]0.25;[88] [i]−0.04[2] and −0.17;[11] [j]−0.19 [87] and −0.25 (i.r.)[22,23]; [k]σ_m = 0.43, σ_p = 0.21, σ_I = 0.42, and σ_R = −0.17(ρ);[90] [l]0.21(Dy).[96]

On gradual substitution of the hydrogen atoms in the OCH_3 group by fluorine, the σ_I constants increase regularly approximately by 0.1 and the absolute values of the σ_R constants decrease on average by 0.08 (according to ^{19}F NMR). The saturation effect is hardly observed. The inductive effects for analogous chlorinated groups also increase on accumulation of chlorine atoms, but a marked saturation effect is shown. Compounds containing the OCH_2F substituent have not so far been obtained but its σ constants have been calculated (Table 7).

Like OCF_3, the $OCHF_2$ group is an *ortho*, *para*-directing substituent[101]. However, since the inductive effect of the $OCHF_2$ group is smaller, the *ortho*-position in the difluoromethylphenyl ether molecule is less deactivated in relation to electrophilic substitution reactions than in phenyl trifluoromethyl ether, but is nevertheless more deactivated than in anisole. Thus nitration of anisole yields a mixture of *ortho*- and *para*-isomers in proportions of 1 : 2,[102] nitration of difluoromethylphenyl ether gives the corresponding proportion of 1 : 2.6,[101] while phenyl trifluoromethyl ether is nitrated only in the *para*-position.

Methoxy- and fluoromethoxy-groups are irregular substituents[24]. The methoxy-group has a group moment of 1.28 D[41] and an angle $\theta = 72°$,[41] the substituent constituting the positive end of the dipole. The fluorinated groups $OCHF_2$ and OCF_3 have group moments of 2.46[103] and 2.27 D[104] (2.36 D[90]) and angles θ of 137°30′[103] and 154°[104] (160°[24]). When the hydrogen atoms are replaced by fluorine in the methoxy-group, the angle gradually increases, the direction of the group moment approaches the direction of the C_{aryl}–O bond, and the substituent becomes the negative end of the dipole.

The conjugation effect of the OCH_3, OCH_2F, $OCHF_2$, and OCF_3 substituents depends on whether they are located in the plane of the aromatic ring or whether they are displaced from it under the influence of their steric interaction with the hydrogen atoms in the *ortho*-positions. It has been shown by quantum-mechanical calculations[87] that the π electron density in the *para*-position of the benzene ring depends on the angle between the planes of the benzene ring and C_{aryl}–OR. For the OCH_3, OCH_2F, $OCHF_2$, and OCF_3 substituents, these angles are 18°, 56°, 90°, and 90° respectively. With increase of the angle, the electron-donating properties of the substituents diminish, but still persist even when the angle is 90°.

The OCF_2CF_3, OCF_2CHF_2, and OCF_2CHFCl substituents have σ constants close to those of the OCF_3 group. The trifluoroacetoxy-group exhibits a more powerful electron-accepting inductive effect than the $OCOCH_3$ substituent and even OCF_3, while they all have virtually identical electron-donating conjugation effects.

As was to be expected, among all the known groups OR the OSO_2CF_3 group is the most powerful electron acceptor[84,93] and has the highest σ_I constant. Nevertheless in electrophilic substitution reactions the group is an *ortho*, *para*-directing substituent[93]. The OSF_5 group behaves similarly[95].

VII. SULPHUR- AND SELENIUM-CONTAINING GROUPS ($S-R_F$, $Se-R_F$)

According to ^{19}F NMR data, on passing from the methoxy- to the methylthio-group, the electron-accepting inductive effect diminishes by a factor of two, while the electron-donating conjugation effect decreases approximately by a factor of three (Tables 7 and 8). The methylthio-group exhibits inductive and conjugation effects which are almost of the same magnitude but have the opposite signs. The introduction of three fluorine atoms sharply enhances the electron-accepting properties of the methylthio-group. The inductive effect increases appreciably, being only slightly inferior to that of the ECF_3 group, while the conjugation effect of the trifluoromethylthio-group changes direction and becomes an electron-accepting effect, in contrast to that of the oxygen analogue. As a result, the σ_m constants of the OCF_3 and SCF_3 groups are very close and the σ_p constant of the SCF_3 group shows that it is a much more powerful electron-accepting substituent than OCF_3.

Successive substitution of the hydrogen atoms of the SCH_3 group by fluorine results in a gradual increase of the electron accepting inductive effect, while the conjugation effect changes from electron-donating for the SCH_3 and

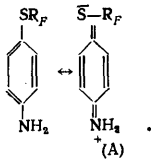
Table 8. σ constants for sulphur- and selenium-containing substituents.

Substituent	σ_m			σ_p			σ_I			σ_R		
	B	A	F*	B	A	F*	B	A	F	B	A	F
SCH_3 [86,89]	0.15		0.05	0.00		−0.03	0.19		0.13	−0.19		−0.16
SCH_2F [89]			0.23			0.20			0.27			−0.07
$SCHF_2$ [86,89]	0.33		0.34	0.36[a]	0.48 [88]	0.35	0.31		0.33	0.07		0.02
SCF_3 [10,52—54,b]	0.36 [105,c]	0.46 [90]	0.53	0.46[a]	0.64 [90, e]	0.56	0.30[f]	0.40 [90]	0.44[g]	0.17	0.22 [90]	0.16[i]
SCF_2CF_2H [90]	0.38[k]	0.42		0.47[j]	0.61		0.29	0.37		0.20	0.21	
$SOCH_3$ [10]	0.52		0.49	0.49		0.49	0.52		0.49			0.00
$SOCHF_2$ [89, j]			0.70		0.93 [88]	0.76			0.65			0.11
$SOCF_3$ [19, 53, 54, 88]	0.63	0.76 [2]	0.74	0.69	1.05[m]	0.80	0.60	0.70 [2]	0.67	0.11	0.32 [2]	0.13
SOF [107]			0.74			0.83			0.66			0.17
SOCl [107]			0.75			0.82			0.68			0.14
SO_2CH_3 [10,89]	0.60	0.66 [88]	0.56	0.72	1.09 [88]	0.64	0.62 [90]		0.48	0.16 [90]	0.51 [90]	0.16
SO_2CH_2F [89]			0.66		1.17 [88]	0.77			0.55			0.22
SO_2CHF_2 [86,89, n]	0.75	0.87 [88]	0.73	0.86	1.44 [88]	0.87	0.70[o]		0.59	0.19		0.28
SO_2CF_3 [52—54, p]	0.76	0.98 [88]	0.88[r]	0.96	1.63 [88]	1.04[s]	0.64[t]	0.84 [90]	0.73 [89, u]	0.32[v]	0.73 [90]	0.31 [89]
$SO_2CF_2CHF_2$				1.01[w]								
SO_2CF_2CHFCl				0.98[w]								
$SO_2CF_2CHFCF_3$				1.03[w]								
SO_2F [2]	0.98	0.99	0.88	1.08	1.54	1.01	0.88	0.87	0.75	0.21	0.59	0.26
SO_2Cl [10]			0.92			1.04			0.80			0.24
CH_2SCF_3 [108]	0.12		0.15	0.15		0.12	0.11		0.19[x]	0.04		−0.07[y]
$CH(SCF_3)_2$ [47]			0.44			0.43			0.44			0.01[z]
$C(SCF_3)_3$ [47]			0.50			0.52			0.49			0.03[aa]
CH_2SOCF_3 [108]			0.25			0.24			0.26			−0.02
$CH_2SO_2CF_3$ [108]	0.29		0.29	0.31		0.31	0.28		0.28	0.03		0.03
$SeCF_3$ [109]	0.32		0.44	0.38[bb]	0.53 [88]	0.46	0.28		0.42	0.10		0.04
$SeOCF_3$ [111]			0.81			0.86[cc]			0.76			0.10
SeO_2CF_3 [111]			1.08			1.21			0.96			0.25

*Calculated from σ_I and σ_R.

Other data: [a]0.34;[105] [b]σ_m = 0.43, σ_p = 0.57, σ_I = 0.39, and σ_R = 0.14(P)[90]; [c]0.37 [106] and 0.40;[90] [d]0.42 [106] and 0.50;[90,105] [e]0.91;[88] [f]0.31;[90] [g]0.42;[2,71] [i]0.00 (i.r.)[22,23]; [j]σ_m = 0.54 and σ_p = 0.58;[105] [k]0.39;[106] [l]0.45;[106] [m]10.7;[2] [n]σ_m = 0.76 and σ_p = 0.84(B)[105]; [o]0.65;[86] [p]σ_m = 0.92, σ_p = 1.36, σ_I = 0.84, and σ_R = 0.49(P)[90]; σ_m = 0.76 and σ_p = 0.93(Dy)[19]; [r]0.90;[2] [s]1.06;[2] [t]0.62;[2] [u]0.75 [2] and 0.78;[107] [v]0.22;[2] [w]method (C); [x]0.21;[49] [y]−0.06;[49] [z]0.00;[49] [aa]0.04;[49] [bb]0.38(Dy)[110]; [cc]0.63(Dy)[110].

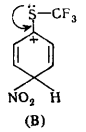
SCH_2F groups to electron-accepting for the $SCHF_2$ and SCF_3 substituents. The interaction of a sulphur atom with the aromatic ring is of a dual nature: it is an electron-donating $(3p - 2p)\pi$ interaction with charge transfer to the ring and an electron-accepting $(3d - 2p)\pi$ interaction with charge transfer from the ring to the vacant *d* orbitals of the sulphur atom. Electron-accepting substituents at the sulphur atom tend to increase the interaction involving the *d* orbitals of sulphur. The electron-accepting $(3d - 2p)\pi$ conjugation occurs when the *para*-position relative to the fluoroalkylthio-group contains electron-donating substituents, for example the amino-group.



As fluorine atoms accumulate in the methylthio-group, the $(3d - 2p)\pi$ conjugation becomes more marked and the contribution of the resonance structure (A) gradually increases, as can be seen from the increase of μ_{int} in the series of substituents $SCH_3 < SCHF_2 < SCF_3$ (0.27, 0.46, and 0.68 D)[103,104]. The group moments and the angles θ between the direction of the dipole moment and the Caryl–S bond of the above substituents also gradually increase (μ = 1.34[104], 2.48,[103] and 2.50 D[104]; θ = 77.5°,[24] 137°,[103] and 156°[24,104]). The change in the angle θ shows that the electrons in the SCH_3 group are displaced to the benzene ring ($\theta < 90°$), while in fluorinated groups the opposite shift obtains.

The electron-donating $(3p - 2p)\pi$ conjugation decreases on accumulation of fluorine atoms in the methylthio-group. This is evident from a comparison of the μ_{int} for the corresponding *p*-nitro-derivatives, which diminishes on passing from SCH_3 to $SCHF_2$ and SCF_3 (θ_{int} = 0.78, 0.48, and 0.21 D respectively).[103,104]

In electrophilic substitution of an aromatic ring, the SCF_3 group is *ortho*, *para*-directing. Thus nitration of phenyl trifluoromethyl sulphide results in the formation of 65% of the *p*-nitro-isomer and 35% of the *o*-nitro-isomer[112]. This is probably due to the stabilisation of the transition state (B) by $(3p - 2p)\pi$ conjugation with the electron pair of the sulphur atom:



(B)

An approximate estimate of the electrophilic conjugation constant σ_R^+ of the SCF_3 group from data for μ_{int} for the interaction with a nitro-group (see above) yields 0.09. The negative value of the constant is also consistent with the *ortho*, *para*-directing influence of the substituent. The electronic influence of the SCF_2CF_2H group hardly differs from that of the SCF_3 group.

When the SCF_3 group is converted into $SOCF_3$ and SO_2CF_3, there is a marked enhancement of the electron-accepting properties of the substituent. We have established[52,113] that the CF_3SO_2 group is one of the most powerful electron acceptors. The σ constants of this substituent greatly exceed those of the nitro-group. The strength of the $SOCF_3$ group is close to that of the nitro-group.

In contrast to SCF_3, the $SOCF_3$ and SO_2CF_3 groups are *meta*-directing. Nitration of phenyl trifluoromethyl sulphoxide yields 90% of the *m*-nitro-isomer and only 5% of the *p*-nitro-isomer[114] and nitration of phenyl trifluoromethyl sulphone results in the formation of the *m*-nitro-isomer alone[113].

When the hydrogen atoms in the $SOCH_3$ and SO_2CH_3 groups are replaced successively by fluorine, the inductive and conjugation effects gradually increase. The σ constants of the SO_2CH_2F group correspond to those of the nitro-group and the constants of the SO_2CHF_2 group are actually higher.

More marked electron-accepting properties of the SO_2CF_3 and SO_2CHF_2 substituents compared with those of the nitro-group are observed also in nucleophilic substitution reactions involving the aromatic ring. Thus the introduction of the SO_2CF_3 group in place of the nitro-group in the 4-position of 1-halogeno-2,4-dinitrobenzenes increases the rate of substitution of fluorine and chlorine in the reactions with aniline by a factor of 10 and 40 respectively[115].

When *p*-nitrophenyl trifluoromethyl and *p*-nitrophenyl difluoromethyl sulphones react with sodium alkoxides, the weaker electron-accepting substituent (the nitro-group) is preferentially substituted by the alkoxy-group[116-118]. In *p*-nitrophenyl trifluoromethyl sulphoxide the weaker electron-accepting $SOCF_3$ group is replaced.

The group moments of the SCF_3, $SOCF_3$, and SO_2CF_3 substituents gradually increase and are 2.50, 3.88, and 4.32 D, while the angles θ are 156°, 143°, and 167°.[104] The angles θ increase in the series of substituents SO_2CH_3, SO_2CH_2F, SO_2CHF_2, and SO_2CF_3: 117°,[24] 136°,[113] 152°,[103] and 167°,[104] while the group moment passes through a minimum: 4.73,[24] 4.04,[119] 4.08,[103] and 4.32 D.[104] The vibration frequencies (ν_{as}) of the SO bond[120] gradually increase in the above series of substituents: 1334, 1342, 1358, and 1380 cm^{-1}.

The σ_I constants for the SCF_3, $SOCF_3$, and SO_2CF_3 groups were also determined from the pK_a data for the corresponding substituted acetic acids and the σ_p constants were determined from the pK_a for the phenylacetic acid derivatives[108]. These results are close to the values of σ_I and σ_p constants obtained by ^{19}F NMR. It was found that trifluoromethylthioacetic acid is approximately 65 times, trifluoromethylsulphoxyacetic acid is 500 times, and trifluoromethylsulphonylacetic acid is 750 times stronger than acetic acid[108]. The last acid is the strongest of all known monosubstituted acetic acids.

The σ constants determined by different methods for powerful electron-accepting substituents, for example SO_2CHF_2 and SO_2CF_3, show differences. This is probably due to a contribution by the direct polar conjugation between these substituents and the reaction centre (the fluorine atom and the hydroxy- and amino-groups). The σ_R constants of the SCF_3, $SOCF_3$, and SO_2CF_3 groups determined by ^{19}F NMR include a definite contribution by polar conjugation as for other powerful electron-accepting substituents. Correlations whereby it is possible to determine the constants σ_R^0 free of the contribution by direct polar conjugation have been found by comparing the σH, $\sigma^{13}C$, and σ^F chemical shifts[121]. The σ_R^0 constants of the SCF_3, $SOCF_3$, and SO_2CF_3 groups are 0.01, 0.09, and 0.20; they are appreciably smaller than the σ_R = 0.06, 0.13, and 0.31 found by ^{19}F NMR.

The basicity of the anilines *p*-$NH_2C_6H_4SO_2R$ decreases markedly as fluorine atoms accumulate in the substituents. Thus pK_a = 1.48, 1.28, 0.51, and −0.02 for R = CH_3, CH_2F, CHF_2, and CF_3.[88] *p*-Trifluoromethylsulphonylaniline is the weakest base among all the known *p*-substituted anilines.

The enhancement of the electron-accepting influence of the substituents with increase of the number of fluorine atoms in the OCH_3, SCH_3, $SOCH_3$, and SO_2CH_3 groups is clearly shown in the ESR spectra of the radical-anions obtained by the reduction of the corresponding substituted nitrobenzenes. The splitting constants a_N for the nitrogen atoms of the nitro-groups and the reduction half-wave potentials $E_{1/2}$ decrease steadily as the electron-accepting properties of the substituent become more pronounced[122].

Transmission of the electronic effects of substituents in an aromatic ring to the OCF_3, SCF_3, and SO_2CF_3 groups was observed by ^{19}F NMR from the change in the chemical shifts of the fluorine atoms in these groups. It was found that the electronic influence is transmitted most effectively via the sulphur atom and with greater difficulty via the oxygen atom of the SO_2 group[123]. A similar behaviour was observed in a study of the shifts of the C–F stretching vibration frequencies in the infrared spectra of compounds of the type $XC_6H_4OCF_3$, $XC_6H_4SCF_3$, and $XC_6H_4SO_2CF_3$.[124,125]

When one hydrogen atom in the methyl group is replaced by the SCF_3, $SOCF_3$, or SO_2CF_3 groups, the inductive effect becomes of the electron-accepting type and the conjugation effect changes sign only for the $CH_2SO_2CF_3$ group. As the SCF_3 groups accumulate at the carbon atom, the inductive effect becomes increasingly of the electron-accepting type and a saturation effect is observed, as for chloro- or bromo-methyl groups. The conjugation effect becomes of the electron-accepting type only for the $C(SCF_3)_3$ group.

The SOF and SO_2F substituents have σ constants close to those for the SOCl and SO_2Cl groups. The SO_2F group is a much more effective electron-accepting substituent than SOF. The latter hardly differs in the values of the σ constants from the $SOCF_3$ group. The SO_2F substituent has a σ_I constant close to that of the SO_2CF_3 group, but its σ_R constant is somewhat smaller, probably owing to the electron-donating conjugation effect of the fluorine atom.

The electron-accepting inductive effect decreases in the series of substituents with Group VI elements $OCF_3 > SCF_3 > SeCF_3$, the values for the last two being very close, as for the corresponding methyl derivatives[109]. In contrast to the trifluoromethoxy-group, which exhibits an electron-donating conjugation effect, the SCF_3 and $SeCF_3$ groups have positive σ_R constants owing to the involvement in conjugation of the vacant *d* orbitals of the sulphur and selenium atoms. The more diffuse 4*d* orbitals of selenium show a smaller tendency towards $(p-d)\pi$ conjugation than the 3*d* orbitals of the sulphur atom and therefore the $SeCF_3$ groups exhibit a weaker electron-accepting conjugation effect than SCF_3. A similar phenomenon was observed on comparing the SCH_3 and $SeCH_3$ substituents[109]. The dipole moment of the interaction between $SeCF_3$ and the amino-group in the *para*-position (μ_{int} = 0.43 D)[126] is somewhat smaller for the same reason than that for the interaction between SCF_3 and NH_2 groups (μ_{int} = 0.68 D)[104].

Owing to the smaller tendency of the selenium atom towards $(4p-2p)\pi$ conjugation, the $SeCF_3$ substituent does not show electron-donating properties, in contrast to the

SCF_3 group, even when a nitro-group is present in the *para*-position (μ_{int} = 0.01 D)[126]. The group moment of the $SeCF_3$ substituent is 2.48 D (2.50 D for SCF_3) and its vector forms an angle $\theta = 140°$ with the C_{aryl}–Se bond[116] ($\theta = 156°$ for SCF_3).

Thus the SCF_3 and $SeCF_3$ substituents with bivalent sulphur and selenium have similar electronic properties; the substituents containing atoms of these elements in the quadrivalent ($SOCF_3$ and $SeOCF_3$) and hexavalent (SO_2CF_3 and SeO_2CF_3) states differ more markedly.

The $SeOCF_3$ and SeO_2CF_3 substituents have higher σ_I constants and somewhat lower σ_R constants than the corresponding sulphur-containing groups. This is probably due to the greater contribution of polar structures of the type $CF_3\overset{O}{\overset{\|}{S}}e^+-O^-$, which results in a high positive charge on the selenium atom and a decrease of the multiplicity of the Se–O bond. The study of the dipole moments confirms this hypothesis. The group moments of the $SeOCF_3$ (4.13 D)[127] and SeO_2CF_3 (5.37 D)[127] substituents are higher than for the sulphur-containing groups (3.88 and 4.32 D respectively), while the μ_{int} for interaction with electron-donating substituents are lower. For example, μ_{int} is 0.97 D for *p*-$NH_2C_6H_4SeOCF_3$,[127] 1.11 D for the sulphur analogue[104], 0.18 D for *p*-$CH_3C_6H_4SeO_2CF_3$,[127] and 0.78 D for the analogous sulphone[104].

As for the SCF_3 and $SeCF_3$ groups, the angles θ in the $SeOCF_3$ and SeO_2CF_3 substituents (128° and 151°)[127] are smaller by approximately 15° than for the sulphur-containing groups. The electron-accepting influence of the $SeOCF_3$ and SeO_2CF_3 substituents, characterised by the σ_m and σ_p constants, is much greater than that of the analogous $SOCF_3$ and SO_2CF_3 groups. In terms of its inductive effect, SeO_2CF_3 is an even more powerful electron acceptor than the SO_2CN and $N^+(CH_3)_3$ groups (σ_I = 0.94[107] and 0.93[10] respectively).

VIII. UNSATURATED FLUORINATED GROUPS

The vinyl group has σ constants close to zero. On replacement of a hydrogen atom in such groups by CF_3 and SO_2CF_3, unsaturated groups are formed with electron-accepting properties, albeit considerably weakened by the introduction of the vinylene group (Table 9). The inductive effect decreases particularly markedly.

A correlation has been found between the σ_I constants of the CH=CHX and X substituents[10]: σ_I (*trans*-CH=CHX) = 0.01 + 0.41 σ_I(X). The decay of the inductive effect transmitted via the vinyl group is smaller by a factor of approximately two than via two methylene groups. This suggests that the inductive effect is transmitted not only via σ bonds but also via π bonds. In these unsaturated systems the I_π effect probably plays a certain role.

The σ_R constants of the CH=CHX and X groups are also linearly related: σ_R (*trans*-CH=CHX) = −0.03 − 0.96 σ_R(X). Comparison of the coefficients of σ_I(X) and σ_R(X) shows that the conjugation effect is more effectively transmitted via the vinyl unit than the inductive effect.

In the *cis*-isomer of the group $CH=CHCF_3$ the σ_I and σ_R constants are smaller than for the *trans*-isomer. This is probably because, owing to steric hindrance, the CH = $CHCF_3$ group in the *cis*-isomer is partly displaced from the plane of the benzene ring.

The σ_m and σ_p constants of the CH = $CHSO_2CF_3$ group resemble those of the CF_3 group. The ethynyl group is a more powerful electron acceptor than the vinyl group and the replacement of its hydrogen atom by a CF_3 group leads to the substituent $C{\equiv}CCF_3$ with more powerful electron-accepting properties than those of the $CH=CHCF_3$ group. The *trans*-$CF=CF-CF_3$ group has the same σ constants as the $C{\equiv}C-CF_3$ group. Thus the replacement of hydrogen atoms in the substituent $CH=CHCF_3$ by fluorine atoms is equivalent to the conversion of a double bond into a triple bond. The σ constants of the $CF=CFCF_3$ and $C{\equiv}CCF_3$ substituents are very close to those of the CF_3 group.

Table 9. σ constants for unsaturated fluorinated substituents.

Substituent	σ_m		σ_p		σ_I		σ_R	
	B	F*	B	F*	B	F	B	F
$CH=CH_2$ [10]		0.00		−0.02	0.05[11]	0.01		−0.03
CF_3 [10]	0.43	0.44	0.54	0.49	0.41	0.38	0.13	0.10
$CH=CH-CF_3$-*trans* [10, 53, 54]	0.22[a]	0.23	0.20[b]	0.27	0.23[c]	0.19[d]	−0.03[e]	0.08[f]
$CH=CH-CF_3$-*cis* [2,71]	0.16	0.15	0.29	0.17	0.14	0.12	0.14	0.05
SO_2CF_3 [10]	0.76	0.88	0.96	1.04	0.64	0.73	0.32	0.31
$CH=CH-SO_2CF_3$-*trans* [10, 53, 54, g]		0.44		0.56		0.31		0.25
$CH=CH-NO_2$ [10, 11]	0.34	0.41	0.26	0.39	0.38	0.24		0.15
$CF=CF-CF_3$-*trans* [10, 53, 54, i]		0.37		0.44		0.30		0.14
$C{\equiv}CH$ [10]		0.12	0.28	0.16		0.08		0.08
$C{\equiv}C-CF_3$ [10, 53, 54]	0.41	0.39	0.51	0.47	0.35	0.31	0.17	0.16
C_6H_5 [10, 11]	0.06	0.04	−0.01	−0.01	0.10	0.08	−0.10	−0.09
C_6F_5 [129, i]	−0.12	0.26	−0.03	0.27		0.25		0.02
C_6Cl_5 [129]		0.25		0.24		0.25		−0.01

*Calculated from σ_I and σ_R.

Other data: [a]0.20;[2,71] [b]0.34;[2,71] 0.23 (C)[21], 0.23 (Dy)[19,128], and σ_p^- = 0.34 (A);[88] [c]0.17;[2,71] [d]0.20;[2,71] [e]0.16;[2,71] [f]0.07;[2,71] [g]σ_{p^-} = 0.83 (A)[88]; [h]0.45 (C)[21]; σ_p^- = 0.65 (A)[88]; [i]σ_m = 0.34 and σ_p = 0.41 (DA).[129]

The group moments of the substituents increase in the series $CH=CHCF_3 < CF=CFCF_3 < C{\equiv}CCF_3 < CH=CHSO_3CF_3$, amounting to 2.79, 3.06, 3.38 and 4.93 D respectively[130,131]. As a result of the increase of the length of the dipole, these values exceed the group moments of CF_3 and SO_2CF_3 (2.51[132] and 4.32 D[104]). The dipole moments for the interaction with an amino-group in the *para*-position are 0.85, 0.94, and 2.71 D for the substituents $CH=CHCF_3$, $CH=CFCF_3$, and $CH=CHSO_2CF_3$ respectively and also exceed the μ_{int} for substituents without vinyl groups (μ_{int} = 0.49 and 1.46 D for CF_3 and SO_2CF_3).[130,131]

Despite the fact that the fluorine-containing unsaturated groups are electron-accepting in terms of their σ_m and σ_p constants, they are *ortho*, *para*-directing in electrophilic substitution reactions involving the aromatic ring[133], like other substituents of the type CH=CH–X, where X = NO_2, COOH, or $\overset{+}{N}(CH_3)_3$. Thus nitration of the compounds C_6H_5R results in a mixture of nitro-isomers having the following composition[133]:

R	*ortho*	*meta*	*para*
$CH=CH-CF_3$	46.5	3.5	50.0
$CF=CF-CF_3$	26.5	7.5	66.0
$CH=CH-SO_2CF_3$	27.0	15.0	58.0

Nitration of β-trifluoromethanesulphonylstyrene yields a considerable amount of the *meta*-isomer. This is because the SO_2CF_3 group, which has the highest σ_R constant, withdraws electrons from the *ortho*- and *para*-positions of the benzene ring and counteracts the formation

of the energetically favourable *ortho*- or *para*-quinonoid transition complex.

The pentafluorophenyl group, which we shall also consider in this section, should exhibit powerful electron-accepting properties. Indeed pentafluorophenol and pentafluorobenzoic acid exhibit much stronger acid properties (pK_a = 5.5 and 3.4)[129] than phenol and benzoic acid (pK_a = 9.98 and 4.2).[37] However, it has been found by ^{19}F NMR that the electron-accepting inductive effect of the C_6H_5 group is small and the conjugation effect is close to zero[129] The explanation is that the pentafluorobenzene ring in *m*- and *p*-$FC_6H_4C_6F_5$, which were used to determine the σ constants, is displaced from the plane by an appreciable angle. The electronic properties of the C_6Cl_5 group are very close to those of C_6F_5.

IX. SUBSTITUENTS WITH FLUORINE ATOMS LINKED TO HETEROATOMS (EF_n)

The σ constants for substituents of the type EF are listed in Table 10 in order of increasing Group number of the element. All groups of the type EF_n are powerful electron-accepting substituents in terms of both inductive and conjugation effects. The inductive effect of the EF_n group with the maximum number of fluorine atoms increases with the atomic number.

Table 10. σ constants for EF_n substituents (from ^{19}F NMR data).

Substituent		σ_m	σ_p	σ_I	σ_R
Group III	BF_2[2]	0.32	0.48	0.16	0.32
Group IV	CF_3[47, 48]	0.44	0.49	0.39	0.10
	CCl_3[47, 48]	0.30	0.31	0.29	0.02
	CBr_3[47, 48]	0.26	0.27	0.25	0.02
	SiH_3[a]	0.05	0.10	0.01	0.09
	SiF_3[135, 2]	0.54	0.66	0.42	0.24
	$SiCl_3$[135]	0.48	0.56	0.39	0.17
	$SiBr_3$[135]	0.48	0.57	0.39	0.18
	GeF_3[135]	0.85	0.97	0.74	0.23
	$GeCl_3$[135]	0.71	0.79	0.63	0.16
	$GeBr_3$[135]	0.66	0.73	0.59	0.14
Group V	PF_2[71, 85]	0.48	0.59	0.38	0.21
	PCl_2[71, 85]	0.53	0.61	0.45	0.16
	PF_4[71, 85]	0.63	0.80	0.45	0.35
Group VI	SF_3[2, 71]	0.70	0.80	0.60	0.20
	SF_5[2, 136, б]	0.59	0.62	0.55	0.07
Group VII	IF_2[137]	0.85	0.83	0.86	−0.03
	ICl_2[137]	1.10	1.11	1.08	0.03
	IF_4[137]	1.07	1.15	1.00	0.15
	$I(OCOCH_3)_2$[137]	0.85	0.88	0.82	0.06
	$I(OCOCF_3)_2$[137]	1.28	1.34	1.22	0.12

Other data: [a]Calculated from δF;[134] [b]σ_m = 0.61(B), 0.63(A), and 0.61(P), σ_p = 0.68(B), 0.86(A), and 0.70(P), σ_I = 0.55(B), 0.56(A), and 0.53(P), and σ_R = 0.11(B), 0.27(A), and 0.12(P)[2,136].

Despite the fact that boron is less electronegative than carbon, under the influence of fluorine atoms the BF_2 group exhibits an electron-accepting inductive effect[2]. The higher σ_R constant of this substituent can be explained by the presence of a vacant *p* orbital in the boron atom to which the π electrons of the aromatic ring are displaced.

The σ_I constants gradually increase in the series of substituents with Group IV elements $CF_3 < SiF_3 < GeF_3$.[135] In the first two groups they are very close but on passing to GeF_3 the σ_I constant increases sharply. This is probably due to the increase of the polarity of the Ge–F bond with increase of the contribution of ionic structures of the type $ArGeF_2F^-$. The higher negative charges on the fluorine atoms in the SiF_3 and GeF_3 groups than in the CF_3 group are confirmed by the fact that the ^{19}F NMR signals for the first two groups are located in a higher field relative to trifluoromethylbenzene[135].

The σ constants of substituents with Group IV elements linked to chlorine and bromine atoms also increase on passing from carbon to silicon and germanium but their σ_I constants are lower than those of the fluorine analogues. This is because E–F bonds are the most polar[135]

The values of σ_R for the $SiHal_3$ and $GeHal_3$ groups greatly exceed the σ_R for the $CHal_3$ groups. This increase of the conjugation effect is accounted for by the involvement of the *d* orbitals of silicon and germanium in $(d-p)\pi$ conjugation. It is shown to the greatest extent in aryltrifluorosilanes and aryltrifluorogermanes where electron withdrawal by fluorine atoms promotes an increase of the $(d-p)\pi$ conjugation.

The dipole moment of phenyltrifluorosilane (2.77 D)[138] is higher than that of phenyltrichlorosilane (2.41 D)[138] and trifluoromethylbenzene (2.51 D)[132] which is consistent with the more marked electron-accepting properties of the SiF_3 group. It is also indicated by the increase of the dipole moment in the sequence $C_6H_5Si(CH_3)_2F < C_6H_5Si(CH_3)F_2 < C_6H_5SiF_3$ (1.70, 2.55, and 2.72 D respectively)[139].

In electrophilic substitution reactions, for example in chlorination in the presence of $FeCl_3$, the $Si(CH_3)_3$ group is predominantly *ortho*, *para*-directing, activating the benzene ring. On gradual substitution of the methyl groups in $Si(CH_3)_3$ by fluorine atoms, the content of the *meta*-isomer in the reaction products increases, reaching 72% for the SiF_3 group, while the reactivity decreases by a factor of 1000 compared with the $Si(CH_3)_3$ group.[140,141]

The PF_2 group is a substituent with somewhat weaker electron-accepting properties than $P(CF_3)_2$.[85] The reason for this is the occurrence in the PF_2 group of an interaction between the *p* electrons of the fluorine atom and the *d* orbitals of the phosphorus, which acts in the opposite direction. In the PCl_2 substituent the $(p-d)\pi$ interaction between the chlorine and phosphorus atoms is weaker and therefore the electron-accepting inductive effect of the PCl_2 group is somewhat higher than that of the PF_2 group.

An increase of the number of fluorine atoms at the phosphorus atom leads to an increase of the constants σ_I and σ_R. The PF_4 group is one of the most powerful electron-accepting phosphorus-containing substituents. The pronounced electron-accepting effects of the PF_2 and PF_4 groups can be explained by the interaction of the π electrons of the aromatic ring with the vacant *d* orbitals of phosphorus, which become compact under the influence of the fluorine atoms and overlap fairly effectively with the *p* orbitals of the carbon atoms in the benzene ring[85]

Similar phenomena are observed in the SF_3 and SF_5 substituents. However, the conjugation effect of the SF_5 group proved to be smaller than that of SF_3 despite the higher number of fluorine atoms. Two *d* orbitals of the sulphur atom in the SF_5 group are involved in the formation of σ bonds and the remaining three vacant *d* orbitals, which have higher energies, are to a considerable degree saturated by the electrons of the five fluorine atoms and probably interact less effectively with the π electrons of the benzene ring. Only one *d* orbital of the SF_3 and PF_4 substituents is involved in the formation of σ bonds and

the remaining four vacant *d* orbitals interact fairly effectively both with fluorine atoms and with the π electrons of the aromatic ring[107].

Among all the substituents of the EF_n type investigated, only the SF_5 group is extremely resistant to hydrolysis. Nitration of phenylsulphur pentafluoride yields 80% of the *m*-nitro-isomer. The group moment of CF_5 is 3.44 D and μ_{int} for the interaction with an amino-group in the *para*-position is 0.6 D.[136]

Table 10 shows that groups with tervalent or quinquevalent iodine interact with an aromatic ring mainly via the inductive mechanism. The very high σ_I constants are probably due to the high polarity of the bonds between the iodine atom and halogen atoms or acyloxy groups. The ICl_2 and $I(OCOCF_3)_2$ groups, in which the contributions by the structures I^+Cl^- and $I^+(OCOCF_3)^-$ should be maximal, have the highest σ_I constants.

The accumulation of fluorine atoms at the iodine atom leads to an increase of the inductive effect and a considerable increase of the conjugation effect. The involvement of vacant *d* orbitals in substituents with a pentacovalent iodine atom in conjugation with the π electrons of the benzene ring is probably more effective than in the IF_2 and ICl_2 groups[137].

X. FLUORINE-CONTAINING SUBSTITUENTS WITH METAL ATOMS

Fluorine-containing substituents with a mercury atom have now been investigated (Table 11)[142]. The electronic properties of mercury-containing substituents are largely determined by their inductive effects. The constants σ_I of these substituents depend very markedly on the nature of the solvent. The lower the polarity of the solvent the higher the σ_I constant. The increase of the σ_I constants on passing from dichloroethane (DCE) to chloroform can probably be accounted for by the tendency of chloroform to form hydrogen bonds with electron-accepting groups linked to the mercury atom[143]. Mercury has vacant 6*p* orbitals and therefore solvents such as tetrahydrofuran (THF) may be coordinated to mercury atoms, which leads to a sharp decrease of the constants σ_I. For the same reason, the σ_R constants, determined by the interaction of the 6*p* orbitals of mercury with the ring π electrons, fall almost to zero in THF. The presence of electron-accepting substituents at the mercury atom (CN, CF_3, SCF_3) promotes the overlapping of the mercury 6*p* orbitals with the 2*p* electrons of the carbon atom in the benzene ring—$(6p - 2p)\pi$ interaction and an electron-accepting conjugation effect. The *p* electrons of the fluorine atom in the HgF substituent are displaced to the 6*p* orbitals of the mercury atom and probably further to the benzene ring, which leads to a weak electron-donating conjugation effect of this substituent.

Table 11. σ constants for substituents with a mercury atom (from ^{19}F NMR data).

Substituent	σ_I			σ_R		
	$CHCl_3$	DCE	THF	$CHCl_3$	DCE	THF
HgF[142]		0.34	0.18		−0.01	−0.01
HgCl[143]	0.31		0.17	0.04		0.01
$HgCF_3$[142]	0.27	0.16	0.06	0.05	0.03	0.01
HgCN[143]	0.23		0.07	0.11		0.02
$HgSCF_3$	0.37	0.32	0.18	0.05	0.04	0.02
$HgOCOCH_3$[143]	0.38		0.16	0.02		0.00
$HgOCOCF_3$[143]	0.48	0.37	0.22	0.04	0.03	0.00

XI. INDUCTIVE CONSTANTS σ^+ OF FLUORINE-CONTAINING SUBSTITUENTS IN ALIPHATIC COMPOUNDS

Taft's σ^+ constants[9], obtained mainly from the dissociation constants of aliphatic acids by means of the equation

$$\lg \frac{K}{K_0} = \rho^*\sigma^*$$

are used to characterise the inductive effect of substituents. Very exact correlations are achieved between the pK_a of R–COOH acids and the $\sigma^+(R)$ when two equations are employed[144]—for saturated acids [Eqn. (I)] and for unsaturated acids with an sp^2 hybridised carbon atom linked to the COOH group [Eqn. (II)]:

$$pK_a = -1.700\,\sigma^*(R) + 4.644\,, \qquad (I)$$

$$pK_a = -1.795\,\sigma^*(R) + 5.275\,. \qquad (II)$$

A similar equation [Eqn. (III)] has been found also for aliphatic alcohols of the type RCH_2OH:[144]

$$pK_a = -1.316\,\sigma^*(R) + 15.74\,. \qquad (III)$$

Table 12. Inductive constants σ^* for fluorine-containing substituents.

Substituent	σ^*	Substituent	σ^*
CH_3	0[9]	OCF_3	3.42[d]
F	3.10[10, 28]	SCF_3	2.74[d,e]
CH_2F	1.10[9, a]	$SOCF_3$	4.17[d,e]
CHF_2	2.05[9, b]	SO_2CF_3	4.55[d,e]
CF_3	2.60[10, 28, c]	NO_2	3.90[10]
CH_2CF_3	0.92[9]	$CH=CH_2$	0.57[144, f]
$CH_2CH_2CF_3$	0.32[9]	$CF=CH_2$	1.53[g]
$CH_2CH_2CH_2CF_3$	0.12[9]	$CH=CF_2$	1.17[g]
$CH(CF_3)_2$	1.34[51]	$CF=CF_2$	1.94[g,h]
$C(CF_3)_3$	1.48[51]	$CCl=CCl_2$	2.26[g]
CH_2SCF_3	0.99[108]	$CH=CHCF_3$	1.07[g]
CH_2SOCF_3	1.50[108]	$CH=CHCCl_3$	1.19[146]
$CH_2SO_2CF_3$	1.61[108]	C_6H_5	0.60[9]
$COCF_3$	3.70[145]	C_6F_5	1.10[147]
$N(CF_3)_2$	3.05[d]		

[a] 1.17;[144] [b] 2.00;[144] [c] 2.61;[147] [d] calculated from Eqn. (4); [e] calculated from Eqn. (V) for SCF_3, $SOCF_3$, and SO_2CF_3 groups (experimental values 2.77, 4.20, and 4.50); [f] 0.56[147] and 0.65;[148] [g] calculated from the pK_a for unsaturated acids[57] with the aid of Eqn. (II); [h] 1.73.[149]

The effects of substituents are additive in alcohols with the structure R′R″R‴COH, hydroxylamines R′R″R‴CNHOH, and oximes R′R″C=NOH.[145,146] However, on gradual substitution of the hydrogen atoms in the methyl group of acetic acid by fluorine or chlorine atoms or CF_3 groups, a "saturation effect" is observed instead of additivity[10,51].

The σ^* constants can also be calculated from Eqns. (IV) and (V):[10]

$$\sigma^* = 6.23\,\sigma_I \qquad \text{(IV)}$$

and

$$\sigma^*(R) = 2.8\,\sigma^*(CH_2R)\,. \qquad \text{(V)}$$

Table 12 lists the constants σ^* for fluorine-containing substituents found by the methods indicated. The σ^* for certain groups without fluorine are listed for comparison.

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The data obtained for the σ constants made it possible to derive correlation equations whereby one can estimate the electronic properties of new substituents the σ constants of which are still unknown. For example, the σ constants of fluorine-containing substituents of the type XCF_3 and $XCHF_2$ may be determined from the σ constants of XCH_3 substituents[10,53,54,89]:

$$\sigma_I(XCF_3) = \sigma_I(XCH_3) + \begin{cases} 0.20 & (n=2) \\ 0.10 & (n=3) \\ 0.06 & (n=4) \end{cases};$$

$$\sigma_c(XCF_3) = \begin{cases} 0.88\,\sigma_R(XCH_3) + 0.19 & (n=2) \\ 1.05\,\sigma_R(XCH_3) + 0.08 & (n=3) \end{cases};$$

$$\sigma_R(XCHF_2) = 0.71\,\sigma_I(XCH_3) + 0.28$$

where X are various elements or groups of atoms and n is the number of bonds between the benzene ring and the CF_3 or CH_3 group.

The electronic properties of fluorine-containing substituents incorporating only 12 of the elements in the Periodic System have now been investigated. Nevertheless many relations useful to chemists have been discovered; these are already being used and will undoubtedly find wider applications in various branches of organic chemistry.

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