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Quantitative Effect of the Pentafluorophenyl Ring on the Reactivity of Substituents

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The quantitative effect of the pentafluorophenyl ring on the reactivity of substituents (hydrogen, alkyl, aryl, carboxyl, amino, hydroxyl, and halogens) is surveyed. The efficiency with which fluorine atoms at different positions in the benzene ring influence a reaction centre is discussed. An analysis of the σ-constants of the pentafluorophenyl group is also given. A list of 106 references is included.

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I. INTRODUCTION

The chemistry of polyfluorinated aromatic compounds has developed rapidly during recent years[1-7]. One of the main lines of research in this field has been the study of reactions that involve nuclear substituents while leaving nuclear fluorine atoms unchanged.

The introduction of fluorine atoms instead of hydrogen atoms into an aromatic ring has a significant effect on the properties of substituents attached to the ring, which sometimes leads to reactions uncharacteristic of the corresponding hydrocarbon derivatives. No generalisations have been published on the quantitative effect of a polyfluorinated aromatic ring, in particular pentafluorophenyl, on the reactivity of atoms and groups, so that it is of interest to discuss the published information. Since the great majority both of synthetic papers and especially of papers on quantitative aspects of the effect of a polyfluorinated aromatic ring are concerned with pentafluoro-derivatives of benzene, the present Review will deal with the effect of the pentafluorophenyl ring on the reactivity of substituents attached to it. In several cases the effect of the pentafluorophenyl group is compared with those of other groups, e.g. mono-, di-, and poly-fluorophenyl, pentachlorophenyl, nitrophenyl, and trifluoromethyl†.

Since the effect of a pentafluorophenyl ring on a substituent varies with the nature of the latter (or its reactive centre)[9], a detailed study of this effect on key groups—such as alkyl, carbonyl, amino, nitro, etc.—may give information on the specific properties of polyfluorinated aromatic compounds. Here, therefore, we shall first discuss the effect for each specific group, and at the end of the Review attempt to generalise the data on the effect of the pentafluorophenyl ring.

† The effect of the trifluoromethyl group on the reactivity of functional groups has been reviewed[8].

II. HYDROGEN ATOMS

The electron-accepting properties of the fluorine atoms in fluorinated benzenes confer an acidic character on the carbon—hydrogen bonds, which is apparent e.g. in increased rates of isotopic exchange compared with benzene[10-12].

Table 1. Relative rates of exchange of deuterium and tritium at various positions in fluorobenzene and benzylidyne trifluoride with lithium cyclohexylamide in cyclohexylamine at 25°C.[11]

Compound	Rate relative to benzene	
	D	T
o-Deutero(tritio)fluorobenzene	6.3×10^5	3.4×10^5
m-Deutero(tritio)fluorobenzene	107	86
p-Deutero(tritio)fluorobenzene	11.2	9.1
m-Deutero(tritio)benzylidyne trifluoride	580	390

The data in Table 1 suggest that the acidity of the carbon—hydrogen bond will increase strongly as fluorine atoms accumulate in the benzene ring. The kinetic parameters of the base-catalysed exchange of tritium in polyfluorobenzenes (Table 2) show that *ortho*-fluorine atoms make the most significant contribution to the kinetic acidity of polyfluorobenzenes, and are followed by *meta*-fluorine atoms and finally the *para*-fluorine atom (by factors respectively of 260 000, 247, and only 23). The enhanced reactivity of pentafluorobenzene in comparison with *m*-difluorobenzene and 1,2,3,4-tetrafluorobenzene is due primarily to the difference in activation energy[13].

Results on the thermodynamic acidity of polyfluorobenzenes have been obtained by Streitwieser et al.[14] in a study of equilibria of the type

$$ArH + R^-Cs^+ \overset{K}{\rightleftarrows} Ar^-Cs^+ + RH$$

in cyclohexylamine, where ArH is a polyfluorobenzene, and RH an indicator hydrocarbon (Table 3).

Table 2. Rate constants and activation parameters of the exchange of tritium in polyfluorobenzenes in methanolic sodium methoxide at 40°C.[13]

Compound	Rate constant $10^4 k_2$, M^{-1} s^{-1}	Activation	
		energy ΔH^*, kcal mole^{-1}	entropy ΔS^*, e.u.
C_6HF_5	1360	18	—5.6
1,2,4,5-$C_6H_2F_4$	58	—	
1,2,3,5-$C_6H_2F_4$	5.6	—	
1,3-$C_6H_4F_2$	0.0061	27.9	1.9
1,2,3,4-$C_6H_2F_4$	0.0053	27.3	—0.3

It is interesting to compare results obtained on the kinetic and thermodynamic acidities of polyfluorobenzenes. Streitwieser et al.[14] evaluated the partial reaction rate factors for the exchange of deuterium in methanolic sodium methoxide (Table 2) or tritium in cyclohexylamine (CHA) (Table 1), as well as the equilibrium factors (Table 3) for fluorobenzenes, these being the difference between the thermodynamic acidities of benzene and of the fluorobenzene (Table 4). Good agreement between factors calculated from kinetic and from thermodynamic data is evident from Table 4.

Table 3. Thermodynamic acidity of polyfluorobenzenes and benzene in cyclohexylamine relative to 9-phenylfluorene (pK_a = 18.49).[14]

Compound	pK_a (at 34°C)	Indicator hydrocarbon (pK_a)
C_6HF_5	25.85	9-t-butylfluorene (24.23)
1,2,3,4-$C_6H_2F_4$	31.52	di-*p*-biphenylylmethane (30.83) triphenylmethane (31.45)
1,2-$C_6H_4F_2$	34.98	tri-*p*-tolylmethane (34.98)
C_6H_6	43	

The difference in thermodynamic acidity between benzene and pentafluorobenzene is easily calculated by means of these factors. Replacement of five hydrogen atoms in the benzene molecule by fluorine increases the equilibrium acidity (pK_a) of the carbon—hydrogen bond by 15.8—17.1. Approximately the same result was obtained from polarographic data for symmetrical organomercury compounds: values of pK_a for benzene, pentafluorobenzene, and pentachlorobenzene were respectively 37, 23, and 30.5.[15,16]

The considerably more acidic character of the carbon—hydrogen bond in pentafluorobenzene than in pentachlorobenzene is obviously due primarily to the strong inductive effect of fluorine atoms, which is the predominant factor in stabilising aryl anions whose lone electron pair is located in a σ-orbital. The acidic character of this bond in pentafluorobenzene is shown in its ability to react even with alkyl-containing Grignard reagents[17], which usually react only with compounds having $pK_a \leq 21$.[18]

The introduction of fluorine into an aromatic ring lowers the reactivity of the latter towards electrophilic reagents. Thus the rate of nitration of fluorobenzene in sulphuric acid at 25°C is lower than that of benzene by a factor of 8.5.[19] The electrophilic reactivity diminishes considerably with increase in the degree of fluorination of the aromatic ring (Table 5).[20-22]

Table 4. Partial rate and equilibrium factors for fluorobenzenes.

Position of fluorine	Partial rate factors		Equilibrium factors (Ref.14)
	MeONa—MeOH[a]	LiCHA—CHA (Refs.11,14)	
ortho-	5.25	5.43	5.7
meta-	2.07	1.95	2.3
para-	1.13	1.03	1.1

Quantum-chemical calculation of the electron density (allowing for π-and σ-charges) on the carbon atoms in the isomeric tetrafluorobenzenes and in pentafluorobenzene predicts the sequence

$$1,2,4,5\text{-}C_6H_2F_4 < 1,2,3,4\text{-}C_6H_2F_4 < C_6HF_5 < 1,2,3,5\text{-}C_6H_2F_4$$

of increasing reactivity towards electrophilic reagents[23].

Table 5. Rate constants of the sulphonation of polyfluorobenzenes in oleum (100.12% H_2SO_4) at 25°C.[22]

Compound	k, s^{-1}	Compound	k, s^{-1}
1,4-$C_6F_2H_4$	16.1	C_6F_5H	0.000512*
1,2,3,4-$C_6F_4H_2$	0.0079		

* Concentration of oleum 101.17%.

This sequence diverges somewhat from results for the sulphonation (Table 5) and nitration of polyfluorobenzenes[24]. The experimental reactivity sequence for electrophilic substitution in polyfluorobenzenes is

$$1,2,4,5\text{-}C_6H_2F_4 < C_6HF_5 < 1,2,3,4\text{-}C_6H_2F_4 \sim 1,2,3,5\text{-}C_6H_2F_4.$$

Thus deactivation of the aromatic ring towards electrophilic reagents depends on the positions and the number of fluorine atoms present. This is supported also by a study of the protiodesilylation and protiodestannylation of fluoroaryltrimethyl-silanes and -stannanes respectively (Table 6).[25] Additivity of the effects of the fluorine atoms is not observed in these processes (partly owing to steric acceleration of the reactions).

Polychlorobenzenes show a similar pattern: pentachlorobenzene is nitrated more rapidly than 1,2,4,5-tetrachlorobenzene by factors of ~4,[19] whereas the nitration of

Table 6. Relative rate of the protiodestannylation of fluoroaryltrimethylstannanes $ArSn(CH_3)_3$.[25]

Ar	k_{rel}	Ar	k_{rel}
Ph	1.0	*m*-FC_6H_4	0.22
p-FC_6H_4	0.93	C_6F_5	0.43
o-FC_6H_4	0.41		

chlorobenzene takes place correspondingly more slowly than that of benzene[19]. The variety of effects of the halogens in a polyhalogenated system obviously cannot be explained by the principle of additivity. Furthermore, pentafluorobenzene is inert towards nitric acid in 90% sulphuric acid, whereas pentachlorobenzene is nitrated under these conditions[19].

III. ALKYL AND ARYL GROUPS

The kinetic acidity of an α-C—H bond in toluene is enhanced by fluorine atoms in *ortho*- and *meta*-positions, but is diminished by a *para*-fluorine atom (Table 7).[26]

Table 7. Relative rates of exchange of substituted α-deuterotoluenes and α-tritiotoluenes $RC_6H_4CH_2D(T)$ with lithium cyclohexylamide in cyclohexylamine at 50°C.[26]

R	relative rate		
	ortho	*meta*	*para*
H	1	1	1
F	12	22	0.73
CF_3	—	60	180

The rate of deuterium exchange for α-deutero-2,5-difluorotoluene in cyclohexylamine at 25°C exceeds the corresponding rate for α-deuterotoluene by a factor of 350.[11] The strong acidifying effect of a *meta*-fluorine atom is obviously due to its inductive, electron-accepting effect, whereas a mesomeric, electron-donating effect is also exerted by *ortho*- and *para*-fluorine atoms. The superposition of these effects explains why a *p*-fluorine atom becomes a weak donor and destabilises the benzyl anion, whereas *o*-fluorine exerts a weaker acceptor effect than does *m*-fluorine[27]. The electron-donor character of a *p*-fluorine atom has been observed also in a study of the effect of substituents on the rate of alkaline cleavage of *para*- and *meta*-substituted benzyltrimethylstannanes[28].

The effect of *ortho*- and *para*-fluorine atoms on the acidity of an α-C—H bond in fluorotoluenes is similar to the effect of fluorine atoms on an α-carbanion centre in aliphatic systems, the "Hine effect".[29-33] If the carbanion is planar, *p*—*p* interaction between the lone electron pair of the fluorine atom and the lone pair of the negatively charged carbon atom leads to its destabilisation[29-33]. If, on the other hand, the carbanion is pyramidal, it is stabilised by the electron-accepting inductive effect of the α-fluorine atom[33,34]. Thus, in contrast to the *p*-fluorobenzyl anion, which is probably planar, the carbanion generated from 2-*p*-fluorophenyl-2-hydrohexafluoropropane is more stable than its analogue unsubstituted in the ring; in the absence of steric hindrance, this indicates the pyramidal geometry of such carbanions[35].

Thus it follows from the above data that the stability of fluoroarylated carbanions is determined primarily by the relation between the oppositely directed inductive and mesomeric effects of the fluorine atoms. Not only the type of hybridisation of the carbon atom with the lone electron pair but also steric factors preventing coplanarity of the benzene ring and the neighbouring carbanion centre are important for stabilisation of the carbanion. Thus the thermodynamic acidity of 2—6-pentafluorotoluene considerably exceeds that of toluene ($\Delta pK_a = 10$).[36] This can probably be explained by the existence of the pentafluorobenzyl anion in a conformation such that the adjacent carbanion centre, probably of sp^2 type, does not lie in the plane of the benzene ring (values of pK_a for $C_6H_5CH_3$, $C_6F_5CH_3$, *p*-$NO_2C_6H_4CH_3$, and *p*-$CF_3C_6H_4CH_3$ are respectively 35,[15] 25,[36] 26,[37] and 28 [36]). The stability of the pentafluorobenzyl anion is close to that of the *p*-nitrobenzyl anion, and exceeds that of the *p*-trifluoromethylbenzyl anion.

Table 8. Thermodynamic acidity of substituted methanes.

Methine acid	System	pK_a	Ref.
Ph_3CH	CHA-CsCHA*	31.5	38
	DMSO**	28	39
$(C_6F_5)_2CH—CH(C_6F_5)_2$	CHA	22.6	40
$(p\text{-}CH_3OC_6F_4)_3CH$	CHA	19.2	40
$(p\text{-}CH_3C_6F_4)_3CH$	CHA	17.8	40
$(C_6F_5)_3CH$	CHA	15.8	40
$(p\text{-}NO_2C_6H_4)_3CH$	DMSO	12.2	39
$(CF_3)_2CH$	CH_3ONa-CH_3OH	11	41
	***	7	16
Ph_2CH_2	CHA	33.1	38
	DMSO	28.6	42
$(C_6F_5)_2CH_2$	CHA	21.2	40
$(p\text{-}NO_2C_6H_4)_2CH_2$	C_2H_5OH-DMSO	15.85	43
$(CF_3)_2CH_2$	***	22	16

* CHA = cyclohexylamin(d)e.
** DMSO = dimethyl sulphoxide.
*** From polarography of mercury derivatives.

Table 8 compares the stabilities of polyfluorinated di- and tri-arylmethyl anions with those of their non-fluorinated analogues. Successive replacement of phenyl by pentafluorophenyl in a series of di- and tri-arylmethanes leads to an increase in the thermodynamic acidity (pK_a) of the α-C—H bond by 5—6. Roughly the same increase is produced by replacing phenyl by *p*-nitrophenyl. Trifluoromethyl has a greater acidifying effect than has phenyl, as can be seen from the values of pK_a for tris-trifluoromethylmethane and trispentafluorophenylmethane.

The triphenylmethyl anion, in which the α-carbon atom possesses hybridisation approximating to the sp^2 type[44], is a convenient model for revealing the inductive effects of substituents, since the benzene rings assume a propeller conformation (mean angle of deflection of ring 31.7°,[44] close to the 35° calculated theoretically[45]), which diminishes substantially their resonance interaction with the carbanion centre. This factor is most important for polyfluorinated triphenylmethyl anions‡, and is reflected

‡ It may be supposed that the mean angle of deflection of the pentafluorophenyl rings in the trispentafluorophenylmethyl anion will also be at least 31.7°.

in their enhanced thermodynamic stability in comparison with non-fluorinated analogues. However, transmission of the effect of a substituent by a conjugation mechanism is not completely excluded in polyfluorinated triarylmethyl anions: thus the introduction of an electron-donating substituent (methyl, methoxy) at a *para*-position in trispentafluorophenylmethane weakens the thermodynamic acidity of the corresponding methine acid. The contribution of each pentafluorophenyl group ($\Delta pK_a \simeq 5.2$) to the thermodynamic stability of the trispentafluorophenylmethyl anion, which is due predominantly to the inductive effect of the fluorine atoms, can be confirmed by calculation based on a different model, the 9-pentafluorophenylfluorenyl anion. Here the carbon atom with a lone pair of electrons is in the sp^2-hybrid state, but the pentafluorophenyl group should occur mainly in a conformation§ preventing resonance interaction of the fluorine atoms with the carbanion centre owing to steric repulsion of the hydrogen atoms at positions 1 and 8 in fluorene and the *ortho*-fluorine atoms of the pentafluorophenyl group. The differences ΔpK_a between the thermodynamic acidities of phenyl- and pentafluorophenyl-fluorenes have been calculated by means of the correlation[48] $pK_a = -4.557\sigma^* + 21.85$, representing the dependence of the thermodynamic acidity of 9-substituted fluorenes on the Taft induction constant σ^* of the 9-substituent. Substitution of the constant $\sigma^* \simeq 1.9$ for the pentafluorophenyl group[49] with the use of $pK_a = 18.6$ for 9-phenylfluorene[48] yields the difference $\Delta pK_a = 5.4$, which coincides with the contribution of the pentafluorophenyl group to the thermodynamic acidity of trispentafluorophenylmethane.

The possibility of varying the ratio of resonance and inductive effects of the pentafluorophenyl group has been shown for mesomeric carbanions of the type $[C_6F_5C^-RR']Na^+$, where R = R′ = $COOC_2H_5$, CN, COC_6H_5, etc.[50–53] It is significant that the carbon atom with the lone pair in these carbanions is usually in an sp^2-hybrid state, which favours resonance interaction of the fluorine atoms when the pentafluorophenyl group is coplanar with the carbanion centre. Depending on the relative parts played by the electron-accepting groups R and R′ in delocalisation of the negative charge and also on their spatial requirements, however, the conformation of the pentafluorophenyl group may change substantially, and hence also the relative contributions of resonance and inductive effects of this group. The influence of the fluorine atoms of the pentafluorophenyl group on the stability of mesomeric carbanions can be traced in the differences in acidity ΔpK_a = 0.5, 0.4, 0.1, and 0 for the series of *para*-substituted methine acids—$XC_6F_4CH(COOC_2H_5)_2$, $XC_6F_4CH(CN)COOC_2H_5$, $XC_6F_4CH(CN)C_6F_5$, and $XC_6F_4CH(CN)C_6H_5$—where X = H, F respectively. Whereas the *para*-fluorine atom acts as an acceptor in derivatives of polyfluorinated phenylmalonic acids, in polyfluorinated diarylacetonitriles replacing a *para*-hydrogen by fluorine either does not affect or diminishes pK_a, so that the *para*-fluorine atom is now a donor rather than an acceptor[53].

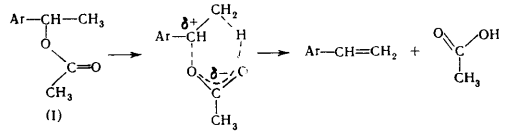
The thermodynamic acidities of various polyfluorinated carbonyl compounds and their non-fluorinated analogues show (Table 9) that the effect of the pentafluorophenyl group on the stability of mesomeric carbanions depends on the type of carbanion. Thus steric interaction between the two pentafluorophenyl groups in the carbanion from bispentafluorophenylmethyl phenyl ketone $(C_6F_5)_2CHCOC_6H_5$ deflects them from coplanarity, and the mesomeric carbanion is largely destabilised by the inductive effects of these groups. Whereas introduction of a phenyl group into deoxybenzoin $C_6H_5CH_2COC_6H_5$ leads to weakened thermodynamic acidity in diphenylmethyl phenyl ketone[54], bispentafluorophenylmethyl phenyl ketone is more acidic than is pentafluorodeoxybenzoin ($\Delta pK_a = 3.8$).

Table 9. Thermodynamic acidity of polyfluorinated carbonyl compounds and their non-fluorinated analogues with respect to 2,4-dinitrodiphenylamine in 1,2-dimethoxyethane.

Compound	pK_a	ΔpK_a per C_6F_5	Ref.
$PhCH(COOEt)_2$	14.2	1.4	50
$C_6F_5CH(COOEt)_2$	12.8		
$p\text{-}NO_2C_6H_4CH(COOEt)_2$	12.6	—	50
$PhCH_2COPh$	16.1	0.8	54
$C_6F_5CH_2COPh$	15.3		51
$C_6F_5CH_2COC_6F_5$	11.7		51
$Ph_2CHCOPh$	16.6	2.5	54
$(C_6F_5)_2CHCOPh$	11.5		52

The relation $\Delta pK_a = -0.077\delta_p + 14.508$ has been established[53] for polyfluoroarylated mesomeric carbanions $[C_6F_5C^-RR']Na^+$, where ΔpK_a is the difference between the thermodynamic acidities of non-fluorinated and fluorinated methine acids—C_6H_5CHRR' and C_6F_5CHRR'—and δ_p is the chemical shift (from trichlorofluoromethane as internal standard) of the *para*-fluorine atom in the pentafluorophenyl group of the fluorinated carbanion (in 1,2-dimethoxyethane as solvent). Since the chemical shift δ_p in pentafluorobenzene derivatives represents primarily the resonance effect of the substituent[23,55], the fractional destabilising effect of *ortho*- and *para*-fluorine atoms, expressed as the chemical shift δ_p in the fluorinated mesomeric carbanions, correlates with the difference in relative stability between non-fluorinated and fluorinated carbanions ΔpK_a. It follows from this correlation that, the greater the degree of conjugation of the pentafluorophenyl group with the carbanion centre (the greater the chemical shift δ_p), the smaller the difference in stability between the mesomeric carbanions of benzyl type containing phenyl or pentafluorophenyl groups.

Data have been obtained also on the effect of the pentafluorophenyl group on the positively charged benzyl carbon atom. In a kinetic study of the pyrolysis of α-methylfluorobenzyl acetates



(I)

(in the transition state the positive charge is concentrated mainly on the benzyl carbon atom) Taylor[56] found that the effects of fluorine atoms in the benzene ring were not additive. The acetate (I) with Ar = C_6F_5 is less reactive than that with Ar = C_6H_5 by a factor of 4.6, whereas a calculation based on additivity would indicate a factor of 7.75. The fact that the five fluorine atoms together are less strongly electron-accepting than if they had acted

§ The phenyl group in the 9-phenylfluorenyl anion is not coplanar with the carbanion centre, the angle of deflection being 30–39°.[46,47]

separately further confirms the peculiarity of the polyhalogenated system noted above in discussing the reactivity of incompletely fluorinated aromatic compounds.

Interesting results have been obtained by Taylor[57] in a study of the protiodetritiation of mon- and penta-fluorobiphenyls containing tritium in the *ortho*-, *meta*-, and *para*-positions of the non-fluorinated benzene ring (Table 10). In this typical electrophilic aromatic substitution the pentafluorophenyl group is primarily *para*—*ortho* orienting, although in comparison with the electronic effect of the phenyl group, of course, it quite strongly deactivates the aromatic ring towards electrophilic agents. Comparison of the observed partial rate factor of 0.0158 for the *para*-position in pentafluorobiphenyl with the calculated additive value of 0.044 also indicates a relative weakening of the electron-accepting power of the fluorinated phenyl group as fluorine atoms accumulate.

Table 10. Partial rate factors of the protiodetritiation of fluorinated biphenyls ArC_6H_4T.[57]

Ar	Position of tritium		
	ortho	*meta*	*para*
Ph	45	0.81	48
p-FC_6H_4—	—	—	26.3
o-FC_6H_4—	5.13	—	6.42
m-FC_6H_4—	4.25	—	4.65
C_6F_5—	0.0095	0.0053	0.0158

It is interesting to compare the above kinetic results on electrophilic reactions with data on the effect of the pentafluorophenyl group on the thermodynamic stability of carbonium ions of the triarylmethyl type. Successive replacement of phenyl by pentafluorophenyl in a triarylmethanol results in a decrease in stability (pK_{R^+}) of the corresponding polyfluorinated triarylmethyl cation by 3.2—4.0 (Table 11)[58-60]. About the same decrease in stability of the triphenylmethyl cation occurs on introduction of a *p*-nitro-group.

Table 11. Values of pK_{R^+} of substituted triarylmethanols.

Carbinol	pK_{R+}	Ref.	Carbinol	pK_{R+}	Ref.
Ph_3COH	— 6.63	61	$(4\text{-}NO_2C_6H_4)_3COH$	—16.27	61
$C_6F_5(Ph)_2COH$	—10.5	59	$(p\text{-}FC_6H_4)_3COH$	— 6.05	58
$(C_6F_5)_2PhCOH$	—13.7	59	$(m\text{-}FC_6H_4)_3COH$	—10.72	60
$(C_6F_5)_3COH$	—17.5	58	$(m,\ m\text{-}F_2C_6H_3)_3COH$	—14.2	60
	—17.7	60			
$(4\text{-}NO_2C_6H_4)Ph_2COH$	— 9.15	61	$(o,\ o\text{-}F_2C_6H_3)_3COH$	—11.12	60

The calculated additive value of pK_{R^+} for trispentafluorophenylmethanol, allowing for the values in Table 11, is −18.1, which agrees quite well with the experimental value. A possible explanation of the additivity of the effects of fluorine atoms in this equilibrium process, in contrast to the kinetics of the pyrolysis of aryl acetates and the kinetics of protiodetritiation, is that the requirement of the reaction centre for resonance stabilisation cannot be satisfied in polyfluorinated triarylmethyl cations of propeller structure¶. Nevertheless, in the transition state of the protiodetritiation of pentafluorobiphenyl, for example, the pentafluorophenyl group may approach coplanarity with the non-fluorinated benzene ring, which will increase the electron density at the *ortho*- and *para*-positions[57].

Table 12. Values of pK_{R^+} for trisperfluoroarylmethanols and triarylmethanols.

$(p\text{-}XC_6F_4)_3COH$ X	pK_{R+}^{60}	ΔpK_{R+} $[pK_{R+}(X) - pK_{R+}(H)]$	$(p\text{-}XC_6H_4)_3COH$ X	pK_{R+}^{61}	ΔpK_{R+} $[pK_{R+}(X) - pK_{R+}(H)]$
MeO	—11.3	5.8	MeO	+0.82	7.45
Me	—14.3	2.8	Me	—3.56	3.07
H	—17.1	0.0	H	—6.63	0.0
F	—17.7	—0.6	F	—6.05	0.58
CF_3	—25.8	—8.7	—	—	—

These considerations are supported by a comparison of the effects of *para*-fluorine atoms on the thermodynamic stability of trismono(and per)fluoroarylmethyl cations (Table 12). Whereas the introduction of *para*-fluorine atoms into the triphenylmethyl cation increases the stability of the carbonium ion $(p\text{-}FC_6H_4)_3C^+$ ($\Delta pK_{R^+} = 0.58$), the corresponding replacement of hydrogen by fluorine in the cation $(p\text{-}HC_6F_4)_3C^+$ leads to a diminution of stability in the cation $(C_6F_5)_3C^+$ (−0.6). Since values of ΔpK_{R^+} for all the substituents studied are lower with the polyfluorinated carbinols than with their non-fluorinated analogues, while the contribution of the three 2,3,5,6-tetrafluorophenyl groups to destabilisation of the cations remains about the same ($\Delta pK_{R^+} = 10.5—12.1$), good correlation is not observed between the pK_{R^+} for the polyfluorinated carbinols $(p\text{-}XC_6F_4)_3COH$ and the σ^+-constants of the substituents[60]. Filler et al. also suggested[60] the correlation

$$pK_a = 0.534\,pK_{R+} + 25.35$$

linking the pK_{R^+} of polyfluorotriarylmethanols and the pK_a of the corresponding triarylmethanes.

IV. CARBOXYL GROUP

The dissociation constants of fluorinated benzoic acids show (Table 13) that the effect of a fluorine atom on acidity depends on its position. Thus the acidity diminishes on passing from *ortho*- to *para*-derivatives. The electron-accepting influence of chlorine atoms is so much stronger than that of fluorine atoms that pentachlorobenzoic acid approaches 2,4,6-trinitrobenzoic acid in strength, whereas pentafluorobenzoic acid is only about as strong as 2,5-dinitrobenzoic acid. Additive calculation of pK_a for several polyfluorinated benzoic acids gives good agreement with experimental values. It must be noted that additivity of the effects of substituents in the benzene ring is not peculiar to fluorine atoms, but is exhibited by other substituents—both acceptor (chloro, bromo, nitro) and donor (methyl, hydroxy)[65].

¶ The calculated[45] angle of deflection of the benzene rings in the triphenylmethyl cation is 44°. The corresponding angle in the trispentafluorophenylmethyl cation may be assumed to be at least as large.

In connection with the additivity of the effects of fluorine atoms on the acidity of benzoic acids, Table 14 shows that the influence of a *para*-substituent R on acidity is about the same in the tetrafluorobenzene as in the benzene ring ($\Delta pK'_a \simeq \Delta pK''_a$), the contribution of the four fluorine atoms being almost identical for all the *para*-derivatives studied ($\Delta pK''_a = 2.25-2.39$). The form of the correlation dependence of pK_a on the σ_p-constants of the substituent is therefore the same for *para*-substituted benzoic acids as for their fluorinated analogues[63].

Table 13. Acidities of substituted benzoic acids ArCOOH.

Ar	pK_a expt.	Ref.	pK_a calc.	Ar	pK_a expt.	Ref.	pK_a calc.
Ph	4.20[a]	65	—	2, 3, 5, 6-F_4C_6H	1.50[a]	9	1.68
	5.78[b]	60	—		1.87[a]	63	
o-FC_6H_4	3.27[a]	62	—		1.84[c]	63	
m-FC_6H_4	3.87[a]	62	—	C_6F_5	1.48[a]	9	1.62
p-FC_6H_4	4.14[a]	62	—		1.75[a]	63	
	5.50[b]	60	—		1.67[c]	63	
2,6-$F_2C_6H_3$	2.31[a]	9	2.34		3.38[a,d]	64	
	3.92[b]	60	—	o-$NO_2C_6H_4$	2.17[a]	62	—
3,5-$F_2C_6H_3$	4.80[b]	60	—	2,4-$(NO_2)_2C_6H_3$	1.425[a]	65	—
2,3,4,5-F_4C_6H	2.71[a]	9	2.55	2,5-$(NO_2)_2C_6H_3$	1.62[a]	65	—
				2,4, 6-$(NO_2)_3C_6H_2$	0.65[a]	65	—
				2,6-$Cl_2C_6H_3$	1.594[a]	65	—
				C_6Cl_5	—		0.51[e]

[a] Determined in water at 25°C.

[b] Determined in 50% aqueous ethanol.

[c] Determined from shifts of infrared absorption band ν_{OH} (in carbon tetrachloride).

[d] Too high.[9]

[e] Calculated from data in Ref. 65.

Table 14. Acidities of *para*-substituted benzoic and 2,3,5,6-tetrafluorobenzoic acids.

p-RC_6H_4COOH R	pK'_a	Ref.	$\Delta pK'_a = pK'_{a(H)} - pK'_{a(R)}$	p-RC_6F_4COOH R	pK''_a [63,a]	$\Delta pK''_a = pK''_{a(H)} - pK''_{a(R)}$	$\Delta pK'''_a = pK'_a - pK''_a$
OH	4.53[a]	65	−0.33	OH	2.27	−0.4	2.26
Me	4.37[a]	65	−0.17	Me	2.00	−0.13	2.37
H	4.20[a]	65	0.0	H	1.87	0.0	2.33
	5.67[b]	8	0.0				
F	4.14[a]	62	0.06	F	1.75	0.12	2.39
Cl	3.98[a]	62	0.22	Cl	1.69	0.18	2.29
Br	3.97[a]	62	0.23	Br	1.66	0.21	2.31
CF_3	4.95[b]	8	0.72	CF_3	2.7[b60]	—	2.25
					1.44	0.33	—

[a] In water at 25°C.

[b] In 50% aqueous ethanol.

The influence of the pentafluorophenyl group on the acidity of the carboxy-group, accomplished through a system of double bonds, can be followed in *p*- and *m*-pentafluorophenylbenzoic acids (Table 15). The effects of a *para*-substituent R are about the same in benzoic and tetrafluorobenzoic acids ($\Delta pK'_a \simeq \Delta pK''_a$), except when R = C_6F_5. Whereas the effect of a *p*-pentafluorophenyl group on acidity is quite large on the fluorinated acid ($\Delta pK_a = 0.42$), the effect is very small on benzoic acid (+0.06). Such anomalous behaviour of *p*- and *m*-pentafluorophenylbenzoic acids may be attributed to the specific influence of the medium (75% methanol + 25% water), in which unexpected results have been obtained for other polyfluorinated substituents, e.g. perfluoroisopropyl[66].

Table 15. Acidities of *para*- and *meta*-substituted benzoic and tetrafluorobenzoic acids.

RC_6H_4COOH R	pK'_a	Ref	$\Delta pK'_a = pK'_{a(H)} - pK'_{a(R)}$	RC_6F_4COOH R	pK''_a	Ref.	$\Delta pK''_a = pK''_{a(H)} - pK''_{a(R)}$
H	6.05[a]	66	0.0	H	1.84[c]	63	0.0
	5.65[b]	67	0.0		—		—
m-Ph	5.57[b]	67	+0.08	—	—		—
p-Ph	5.66[b]	67	−0.01	p-Ph	1.88[d]		−0.04
m-C_6F_5	6.11[a]	66	−0.06	—	—		—
p-C_6F_5	5.99[a]	66	+0.06	p-C_6F_5	1.42[c]	63	+0.42
p-CF_3	5.30[a]	66	+0.75	p-CF_3	1.17[c]	63	+0.67
m-CF_3	5.31[a]	66	+0.74	—	—		—

[a] Determined in 75% methanol + 25% water at 39.8°C.

[b] Determined in 50% 2-butoxyethanol at 25°C.

[c] Determined from shifts of infrared absorption band ν_{OH} (in carbon tetrachloride).

[d] Calculated from data of Ref. 63 with $\delta_p = -0.01$ for the phenyl group[67].

Table 16. Acidities of some fluorinated arylacetic and α-amino-β-arylpropionic acids.

RCH_2COOH R	pK_a expt.	Ref.	$RCH_2CH(NH_3^+)COO^-$ R	pK_a expt.	Ref.
Ph	4.31[a]	62	Ph	2.16[c]	69
o-FC_6H_4	4.07[a]	9	o-FC_6H_4	2.12[c]	69
m-FC_6H_4	4.13[a]	68	m-FC_6H_4	2.10[c]	69
p-FC_6H_4	4.22[a]	68	p-FC_6H_4	2.13[c]	69
2,3,5,6-F_4C_6H	3.47[a]	9	—	—	
C_6F_5	3.48[a]	9	C_6F_5	1.88[a]	9
	3.43[b]			1.93[b]	
COOEt	3.35[a]	62			

[a] In water at 25°C.

[b] Calculated by an additive scheme.

[c] In 0.1 *N* NaCl at 24°C.

Sheppard[66] suggested the alternative explanation that the decrease in acidity of *p*- and *m*-pentafluorophenylbenzoic acids is due to $p-\pi$ donation of unshared electrons of the *ortho*-fluorine atoms to the π-system of the adjacent non-fluorinated ring. However, the existence of such an effect of fluorine atoms in the biphenyl system is doubtful, for *o*-fluorotritiobenzene and 2-fluoro-4′-tritiobiphenyl undergo protiodetritiation at almost the same rate, although the latter reaction would have been the more rapid in the presence of $p-\pi$ donation[57].

The acidity of carboxylic acids falls, of course, when the substituent and the carboxyl are separated by one or especially several methylene groups. The substituent, in particular a pentafluorophenyl group, will then have only an inductive effect on the reaction centre. Table 16

shows that the effects of fluorine atoms at different positions in the benzene ring, exerted through methylene bridges on the acidity of carboxylic acids, fit well into an additive scheme of calculation of pK_a for the pentafluorophenyl group, whose total electron-accepting power is comparable with that of the ethoxycarbonyl group.

V. AMINO-GROUP

The pK_a values of the fluorinated conjugate acids of anilines show (Table 17) that the acidity of the conjugate acid of pentafluoroaniline can be calculated additively from the pK_a values for the conjugate acids of monofluoroanilines. The predominant contribution to the acidity is made by the *ortho*-fluorine atoms, while the *meta*-fluorine atoms have rather less effect. In polyfluoroanilines greater acceptor effects are exerted by a *p*-bromine atom and by 2,4-chlorine atoms than by fluorine atoms at these positions. The total electron-accepting effect of the five fluorine atoms on the acidity of the conjugate acids of anilines can be compared with that of an *o*-nitro-group; trifluoromethyl has a considerably smaller effect.

Table 17. Acidities of substituted conjugate acids of anilines $ArNH_3^+$ (in aqueous sulphuric acid at 25°C).

Ar	pK_a expt.	Ref.	Ar	pK_a expt.	Ref.
Ph	4.58	62	4-Br—2,3,5,6-F_4C_6	−0.93	70
o-FC_6H_4	3.20	62	2,4-Cl_2—3,5,6-F_3C_6	−1.28	70
m-FC_6H_4	3.59	62	*p*-$NO_2C_6H_4$	1.02	62
p-FC_6H_4	4.65	62	*o*-$NO_2C_6H_4$	−0.29	62
C_6F_5 *	−0.28	9	2,5-$(CF_3)_2C_6H_3$	+0.38	70
	−0.36	70	*p*-$CF_3C_6H_4$	2.6	62
				2.93	9
			m-$CF_3C_6H_4$	3.5	62

* Calculated additive value of $pK_a = -0.18$.

Table 18. Acidities of conjugate acids of *NN*-dimethylanilines $RC_6H_4NH(CH_3)_2^+$ (in 45% aqueous dioxan at 25°C).

R	pK_a	Ref.	R	pK_a	Ref.
H	4.14	66	*p*-CF_3	1.56	71
m-C_6F_5	2.64	66	*m*-$CF(CF_3)_2$	1.79	71
p-C_6F_5	2.33	66	*p*-$CF(CF_3)_2$	1.33	71
m-CF_3	2.06	71			

The conductance through a system of conjugated bonds of the effect of the pentafluorophenyl group on the ionisation of the conjugate acids of amines has been estimated only for *m*- and *p*-pentafluorophenyl-*NN*-dimethylanilines, since it is difficult to estimate the basicity of the anilines because of their sparing solubility in aqueous systems[66]. Table 18 shows that the electron-accepting effect of both *m*- and *p*-pentafluorophenyl groups on the ionisation of the conjugate acids of *NN*-dimethylaniline is considerably smaller than that for perfluorinated alkyl groups, which parallels the effects observed in the ionisation of substituted benzoic acids (Table 15). The greater electron-accepting effect of the *para*- than of the *meta*-group can be attributed to non-coplanarity of the benzene rings and a consequent diminution in the effect of conjugation of the pentafluorophenyl group[57].

Table 19. Acidities of conjugate acids of some amines (in water at 25°C).

$RCH_2NH_3^+$ R	pK_a	Ref.	$RCH_2CH(NH_3^+)COO^-$ R	pK_a	Ref.
Ph	9.3	62	Ph	9.12	69
C_6F_5	7.7	72		9.09	8
COOEt	7.7	72	*o*-FC_6H_4	9.01	69
COOMe	7.66	62	*m*-FC_6H_4	8.98	69
CHF_2	7.5	72	*p*-FC_6H_4	9.05	69
CF_3	5.7	72	C_6F_5	8.47	9
	5.87	73		8.55 *	

* Calculated by an additive scheme[9].

The inductive effect of the pentafluorophenyl group on the ionisation of conjugate acids of amines can conveniently be traced in systems in which the group is separated from the reaction centre by a methylene bridge (Table 19). Such systems are characterised by additivity of the effects of fluorine atoms at different positions in the ring, as noted above for carboxylic acids of the type $Ar[CH_2]_nCOOH$ (Table 16). The pentafluorophenyl group is comparable in its inductive effect with such groups as alkoxycarbonyl and difluoromethyl, but weaker than trifluoromethyl.

VI. HYDROXY-GROUP

Fluorinated phenols and aromatic alcohols may be expected to be more acid than their non-fluorinated analogues, in view of the electron-accepting inductive effect of the pentafluorophenyl group. Table 20 gives data on the effect of aromatically bound fluorine atoms on the acidity of phenols, with for comparison the effects of a nitro-group and chlorine atoms. Additivity of the effects of fluorine atoms at different positions in the benzene ring is evident for phenols, as for benzoic acids and anilines, the main contribution to the acidity of pentafluorophenol being made by the *ortho*-fluorine atoms, and a rather smaller contribution by the *meta*-atoms, while a *para*-fluorine atom has almost no effect on the acidity of phenol.

Table 20. Acidities of substituted phenols ArOH (in water at 25°C).

Ar	pK_a	Ref.	Ar	pK_a	Ref.
Ph	9.98	62	C_6Cl_5	5.26	75
o-FC_6H_4	8.81	62		4.82	76
	8.71	74			
m-FC_6H_4	9.28	62	*p*-$NO_2C_6H_4$	7.15	62,76
	9.21	74	2,4-$(NO_2)_2C_6H_3$	4.07	77
p-FC_6H_4	9.95	52			
	9.91	63			
C_6F_5	5.53	75			
	5.76 *	9			
	6.21 *				

* Calculated by additivity from data in Refs. 62 and 74.

The electron-accepting power of the pentachlorophenyl group is considerably stronger than that of the pentafluorophenyl group, because fluorine atoms at *ortho*- and *para*-positions are more efficient than are chlorine atoms

in supplying electron density by a mechanism of conjugation to the reaction centre. The effect of the pentafluorophenyl group on the acidity of the hydroxyl exceeds that of *p*-nitrophenyl and approaches that of 2,4-dinitrophenyl.

Table 21. Acidities of some fluorinated alcohols.

RCH_2OH R	pK_a	Ref.	$RR'R''COH$ R	R'	R''	pK_a	Ref.
Ph	15.4*	78	Ph	CF_3	CF_3	8.80	81
	15.44*	78	C_6F_5	CF_3	CF_3	7.90	81
	14.86*	49	C_6F_5	C_6F_5	CF_3	9.20	81
m-FC_6H_4	14.47*	49	C_6F_5	C_6F_5	C_6F_5	~11	81
p-FC_6H_4	14.95*	49	CF_3	CF_3	CF_3	5.4	80
C_6F_5	13.30*	49	C_6F_5	CF_3	$C(CF_3)(C_6F_5)OH$	8.85	81
CF_3	12.37	79	CF_3	CF_3	$C(CF_3)_2OH$	5.95	82
	12.8	80					

* Calculated value.

As a consequence of the electron-accepting inductive effect of fluorine atoms, fluorinated aromatic alcohols are more acidic than their non-fluorinated analogues (Table 21). The trifluoromethyl group has a stronger acidifying action on alcohols than has the pentafluorophenyl group. It is noteworthy that the latter group makes different contributions to the acidities of primary and of tertiary alcohols: whereas the difference between the pK_a values of benzyl and pentafluorobenzyl alcohols is 1.5, the corresponding difference between the tertiary alcohols $C_6H_5C(CF_3)_2OH$ and $C_6F_5C(CF_3)_2OH$ is only 0.9. If one trifluoromethyl group in perfluoro-t-butyl alcohol is replaced by pentafluorophenyl, the acidity (pK_a) of the alcohol falls by 2.5. When two trifluoromethyl groups are replaced, the acidity of the alcohol falls by only 1.9 (per pentafluorophenyl group). Further substitution produces almost no change in the contribution of a pentafluorophenyl group to the acidity of the alcohols, since the difference in pK_a between trispentafluorophenylmethanol and perfluoro-t-butyl alcohol is ~5.6, which gives ~1.9 per pentafluorophenyl group.

VII. HALOGENS

Whereas the introduction of fluorine atoms into an aromatic ring lowers its reactivity towards electrophilic reagents (Section II), the reactivity of the polyfluorinated aromatic ring towards nucleophilic reagents is sharply increased[4,7]. Results for the reaction of mono-, di-, and poly-fluorobenzenes with methanolic sodium methoxide show (Table 22) that the rate of nucleophilic substitution increases significantly with the accumulation of fluorine atoms. The position of these atoms relative to the reaction centre is extremely important: thus the rate of nucleophilic substitution is least in 1,2,4,5-tetrafluorobenzene among its isomers, owing to $I-\pi$ repulsion of the *para*-fluorine atom in the transition state (an intermediate structure of the Wheland type is the least stable)[88,89]. As with aromatic electrophilic substitution (Section II) the effects of the fluorine atoms in polyfluorobenzenes on nucleophilic substitution are not additive: the calculated rates are higher than the experimental values. Thus the accumulation of fluorine atoms in the benzene molecule leads to a relative slowing down of nucleophilic aromatic substitutions on the one hand, and to a relative increase in the rate of electrophilic aromatic substitutions on the other. Quantum-mechanical calculation of the electron density (allowing for π- and σ-charges) on the carbon atoms bearing fluorine in polyfluorobenzenes predicts the reactivity sequence

$$C_6H_2F_4 > 1,2,3,4\text{-}C_6H_2F_4 > 1,2,4,5\text{-}C_6H_2F_4;\ C_6HF_5 > C_6F_6$$

towards nucleophilic reagents[23]. This corresponds satisfactorily to experimental results allowing for the statistical factor for hexafluorobenzene.

Table 22. Rates of nucleophilic substitution of fluorine in certain fluorinated benzenes on reaction with methanolic sodium methoxide at 50°C.

Compound	Rate constant k_2, $M^{-1}\,s^{-1}$		Ref.
	expt.	calc. additively[a]	
C_6H_5F	$2.16\cdot10^{-12}$	—	83
m-$C_6H_4F_2$	$7.25\cdot10^{-10}$[b]	$1.0\cdot10^{-9}$	—
p-$C_6H_4F_2$	$7.95\cdot10^{-12}$[b]	—	—
1,2,4,5-$C_6H_2F_4$	$< 10^{-8}$	$1.29\cdot10^{-7}$	13
1,2,3,4-$C_6H_2F_4$	$1.8\cdot10^{-6}$	—	13
1,2,3,5-$C_6H_2F_4$	$4.9\cdot10^{-6}$	—	13
C_6HF_5	$0.866\cdot10^{-4}$		85
	$1.0\cdot10^{-4}$	$5.76\cdot10^{-4}$	86
	$0.795\cdot10^{-4}$		87
C_6F_6	$3.01\cdot10^{-4}$	$2.12\cdot10^{-3}$	85
	$3.16\cdot10^{-4}$		87

[a] Contributions of fluorine atoms to reaction velocity calculated from rate constants for mono-, di-, and tetrafluorobenzenes: $F_o = 35$; $F_m = 467$; and $F_p = 3.68$.

[b] Rates calculated by means of suggested[84] Hammett correlation equations.

Table 23. Comparative kinetic data for nucleophilic substitutions of certain halogenated benzenes with sodium methoxide.

Compound	Solvent	Relative rate at		Activation energy, kcal mole^{-1}	lg *A*	Ref.
		50°C	60°C			
C_6HF_5	MeOH	—	1	22.6	11.2	87
		—	1	22.9	11.4	86
		1	—	20.2	9.6	85
	dioxan–MeOH (5:1 by vol.)	1	—	19.0	10.5	85
C_6F_6*	MeOH	—	0.65	21.4	11.0	87
		—	0.90	22.4	11.0	86
		0.58	—	20.4	10.2	85
	dioxan–MeOH (5:1 by vol.)	0.87	—	19.7	11.6	85
C_6Cl_5F	MeOH	—	26	18.9	10.2	87
		39	—	18.9	10.3	85,89
C_6Cl_6*	MeOH	—	$3.5\cdot10^{-3}$	22.0	10.1	87
p-$FC_6H_4NO_2$	MeOH	—	28	20.1	11.0	90
o-$FC_6H_4NO_2$	MeOH	—	19	19.9	10.7	91

* Relative rate allowing for statistical factor.

Table 23 gives the relative rates and kinetic parameters of the reactions of halogenated benzenes with sodium methoxide. The relative lability of a fluorine atom in hexafluorobenzene is closely similar to that of the *para*-fluorine atom in pentafluorobenzene, owing to the approximately equal difference in stabilities of both ground and

transition states for these compounds[89]. The lower mobility of a fluorine atom in hexafluorobenzene than in pentachlorofluorobenzene shows that the five fluorine atoms are less strongly accepting than are the five chlorine atoms, since $I-\pi$ repulsion is greater for a fluorine atom than for a chlorine atom[89]. Effective participation of *p*-electrons of lone pairs on fluorine atoms in destabilising the carbanion type of transition state obviously reverses the sequence of the halogens observed in the stability of polyhalogenated aryl anions (Section II). Table 23 shows that the total electron-accepting effect of five fluorine atoms and five chlorine atoms is close to that of a nitro-group *ortho* or *para* to a halogen.

Table 24. Rates of nucleophilic substitution of *para*-fluorine atom in compounds *p*-RC_6H_4F (k_2') and C_6F_5R (k_2'') with methanolic sodium methoxide at 50°C.

R	Reaction rate constants k_2' and k_2'' ($M^{-1}\,s^{-1}$) and their ratios					
	k_2'*	$\frac{k_2'(R)}{k_2'(H)}$	k_2''	Ref.	$\frac{k_2''(R)}{k_2''(H)}$	$\frac{k_2''}{k_2'}\cdot 10^5$
NO_2	$2.4\cdot10^{-3}$	$1.11\cdot10^9$	$3.09\cdot10^2$	86	$3.09\cdot10^6$	1.28
CN	$3.02\cdot10^{-5}$	$1.4\cdot10^7$	$3.95\cdot10^1$	85	$3.95\cdot10^5$	13.1
CF_3	$4.36\cdot10^{-7}$	$2.02\cdot10^5$	3.70	85	$3.70\cdot10^4$	84.7
Cl	$1.23\cdot10^{-10}$	$5.7\cdot10^1$	$1.74\cdot10^{-3}$	86	$1.74\cdot10^1$	141
F	$7.95\cdot10^{-12}$	3.69	$3.16\cdot10^{-4}$	87	3.16	397
H	$2.16\cdot10^{-12}$	1	$1.0\cdot10^{-4}$	86	1	463

* Rates calculated by proposed[84] Hammett correlation equation.

Since additivity is lacking in the effect of fluorine atoms on the rate of nucleophilic substitution, it is of interest to examine comparative data on the effect of a substituent on the rate of substitution of a *para*-fluorine atom in fluorinated and in non-fluorinated benzene derivatives. Table 24 shows that the transmissibility of the effect of the substituent R from the *para*-position to the reaction centre is different for compounds of types *p*-RC_6H_4F and C_6F_5R, since the ratios $k_2'(R)/k_2'(H)$ and $k_2''(R)/k_2''(H)$ are unequal. On the other hand, the contribution of the four fluorine atoms at positions 2, 3, 5, and 6 vary for different substituents R, which is responsible for differences in the ratio k_2''/k_2'. It follows from this analysis of the rates of nucleophilic substitution of the *para*-fluorine atom in compounds *p*-RC_6H_4F and C_6F_5R that the electron-accepting effects of substituents such as nitro, cyano, and trifluoromethyl are weaker in polyfluorinated compounds than in their non-fluorinated analogues, whereas the effects of weakly accepting substituents (chloro and especially fluoro) are quite close with the two types of compounds. Therefore no correlation is observed between the rates ($\lg k$) of the reactions of sodium methoxide with substituted pentafluorobenzenes and the σ_p-constants of the substituents[86]. A satisfactory correlation is obtained if σ_p^--constants are used for strongly accepting substituents, and σ_p-constants for weakly accepting substituents[84,92,93].

Table 25 shows that the relative rates of nucleophilic substitution of the *para*-fluorine in pentafluorobenzene derivatives C_6F_5R are considerably dependent on the reagent and the solvent[92-98]. The rates with charged nucleophiles (methoxide and phenoxide ions) exceed the rates with uncharged nucleophiles (piperidine). The influence of the solvent helps to explain the differing reactivities of polyfluorinated benzenes. Table 26 shows that methanol has a slight effect on the rate of reaction of the substituted pentafluorobenzenes with piperidine, especially when R = C_6F_5.[93] The probable reason is solvation by methanol of the substrates in initial and transition states, that of the fluorine atoms tending to lower the accepting power of the pentafluorophenyl group (Table 29). Weakening of the acceptor character of this group in 75% methanol has been noted earlier in connection with the acidity of benzoic acids (Table 15).

Table 25. Relative rates of nucleophilic substitution of *para*-fluorine atom in substituted pentafluorobenzenes C_6F_5R as function of reagent and solvent.

R	Relative rates (C_6HF_5 = 1)						
	MeONa — MeOH, 50°	Ref.	MeONa–dioxan–MeOH, 50°C (Ref.85)	piperidine–MeOH, 50°C (Ref.93)	piperidine–dioxan, 50°C (Ref.93)	piperidine–*n*-hexane, 50°C (Ref.93)	C_6F_5ONa–$CH_3CON(CH_3)_2$ 106°C (Ref.95)
H	1		1	1	1	1	1
Me	0.438	86	0.0737	—	—	—	—
F[a]	0.58	85	0.87	0.326	0.235	0.373	0.91
	0.66	87					
Cl	17.4	86	—	5.02	3.5	8.5	32
Br	19.9	85	16.1	—	—	—	39
C_6F_5	—		—	$4.18\cdot10^2$	$5.49\cdot10^2$	$3.63\cdot10^3$	$7.3\cdot10^2$
COOMe	—		—	$8.85\cdot10^3$	—	$6.16\cdot10^3$	$2.9\cdot10^3$[b]
CF_3	$4.28\cdot10^4$	85	—	$1.375\cdot10^4$	$4.46\cdot10^3$	$1.63\cdot10^4$	$2.4\cdot10^4$
	$5.25\cdot10^3$	86					
COOMe	—		—	$3.25\cdot10^4$	$8.36\cdot10^3$	$2.77\cdot10^4$	—
NO_2	$3.09\cdot10^6$	86	—	—	—	—	—

[a] Allowing for the statistical factor of 6.

[b] For the ethoxycarbonyl group.

Table 26. Effect of solvent on rate of reaction of substituted pentafluorobenzenes C_6F_5R with sodium methoxide and piperidine[85,86,93,94].

Solvent	Relative rate of substitution of *p*-fluorine at 50°C*.									
	Me	H	COO–	F	Cl	Br	C_6F_5	COOMe	CF_3	COMe
	with sodium methoxide									
Methanol	1	1	1	1	—	1	—	1	—	—
Dioxan–methanol (5:1 by vol.)	6.73	46.1	47.6	69.7	—	37.5	—	—	—	—
	with piperidine									
n-Hexane	—	1	—	1	1	—	1	1	1	1
Methanol	—	5.11 (15)	—	4.46 (12)	3.02 (19)	—	0.59 (2)	7.35 (14)	4.3 (6)	6.0 (22)
Dioxan	—	43.6 (40)	—	27.5 (34)	17.3 (29)	—	6.6 (11)	—	11.9 (22)	13.1 (24)

* Parentheses enclose relative rates of substitution of the *para*-fluorine at 100°C.[93]

An interesting solvent effect has been detected in the reaction of hexafluorobenzene[93] or methyl pentafluorobenzoate[94] with sodium methoxide in methanol or in a binary methanol–benzene mixture (Table 26). Addition of benzene to methanol diminishes the reaction velocity, probably owing to weakening of electrostatic interaction of the reagent and the fluorine atoms *ortho* to the reaction centre (breakdown of the so called "built-in solvation") and the steric retarding effect of the methanol-solvated fluorine atoms located *ortho* to the reaction centre[93]. The solvation of these atoms increases their bulk and

intensifies their steric interaction with the substituent. Probably for this reason the Hammett correlations for the reactions of substituted pentafluorobenzenes with piperidine are satisfied with poorer indices in methanol than in aprotic solvents (Table 27).[92,93]

The effects of the fluorine atoms in the polarographic reduction of pentafluorohalogenobenzenes are satisfactorily additive[99]. Whereas their contributions to the half-wave reduction potentials of pentafluorophenyl bromide and iodide decrease in the sequence $o > m > p$, in the case of the chloride and hexafluorobenzene the contributions are independent of the positions of the fluorine atoms in the benzene ring. These results suggest that the mechanism of the electrochemical detachment of fluorine and chlorine is different from that for bromine and iodine in pentafluorohalogenobenzene derivatives[100].

Several quantitative data have been published on the reactions of polyfluorinated aromatic compounds with radical agents. Thus the ratio of the rate constants for the phenylation of hexafluorobenzene and benzene by phenyl radicals generated by the decomposition of benzoyl peroxide is 0.44. The rate-determining stage of the process is probably addition of the phenyl radical to the aromatic substrate with formation of a radical σ-complex[101].

Table 27. Correlation between the rate constants of the reactions of substituted pentafluorobenzenes C_6F_5R with nucleophilic reagents and the σ_p^--constants of the substituents.

Reagent	Solvent	Temp., °C	ρ	r	s	$-\lg k_0$	Ref.
Piperidine	n-hexane	50	5.4	0.989	0.33	7.10	92,93
		100	4.8	0.990	0.27	6.15	
Piperidine	dioxan	50	4.9	0.992	0.29	5.66	92,93
		100	4.4	0.994	0.22	4.58	
Piperidine	methanol	50	5.8	0.986	0.41	6.57	92,93
		100	4.8	0.991	0.27	4.98	
Na methoxide	methanol	50	5.3	0.993	0.34	3.89	92,93
		100	4.7	0.994	0.29	1.94	
Na methoxide*	16% methanol + 84% dioxan	50	6.9	0.999	0.08	2.34	84
		100	6.1	0.998	0.18	0.51	
Na pentafluorophenoxide	*NN*-dimethylacetamide	106	5.7	0.986	0.34	—	92,93

* Correlation with σ_m^--constants.

VIII. EFFECTIVENESS OF FLUORINE ATOMS

The effectiveness of fluorine atoms at different positions of the pentafluorophenyl group in influencing the reaction centre can be assessed both from thermodynamic data (ratio of ΔpK_a values for pentafluorophenyl- and *m*-fluorophenyl-benzene derivatives) and from kinetic data (ratio of reaction rate constants for these derivatives) (Table 28).

Table 28. Relative effects of fluorine atoms on reactivity of pentafluorobenzene derivatives.

No.	Reaction	Solvent	Temp., °C	$\frac{\Delta pK_a(C_6F_5\text{—Ph})}{\Delta pK_a(m\text{-}FC_6H_4\text{—Ph})}$	$\frac{k(C_6F_5)}{k(m\text{-}FC_6H_4)}$	Sequence of effects	Additivity F atoms	Ref.
1	$ArT+MeOH \xrightarrow{MeONa} ArH+CH_3OT$	MeOH	40	7.62	—	$o>m>p$	yes	13,14
2	$ArT+NH_2C_6H_{13} \xrightarrow{LiNHC_6H_{13}} ArH+\underset{\displaystyle T}{\underset{\vert}{N}}HC_6H_{13}$	$NH_2C_6H_{13}$	25	8.1	—	$o>m>p$	yes	11,14
3	$ArH+R^-Cs^+ \rightleftarrows Ar^-Cs^++RH$	$NH_2C_6H_{13}$	34	7.44	—	$o>m>p$	yes	14
4	$ArF+CH_3ONa \rightarrow ArOCH_3+NaF$	MeOH	50	—	$4.27\cdot10^5$	$m>o>p$	no	[a]
5	$ArCl+2e \rightarrow ArH$	DMF	25	4.77[b]	—	$p\sim o\sim m$	yes	99
6	$ArBr+2e \rightarrow ArH$	DMF	25	6.45[b]	—	$o>m>p$	yes	99
7	$ArI+2e \rightarrow ArH$	DMF	25	6.95[b]	—	$o>m>p$	yes	99
8	$ArC(CF_3)_2OCH_2CH\text{—}CH_2+(n\text{-}Bu)_2NH \rightarrow ArC(CF_3)_2OCH_2\text{—}\underset{\displaystyle OH}{\underset{\vert}{CH}}\text{—}CH_2NBu_2$ (O bridge)	$C_5H_{11}OH$	60	—	1.85	$o>m\sim p$	no	102
9	$ArSnMe_3 \xrightarrow{HClO_4} ArH$	H_2O, MeOH	50	—	1.34	$p>o>m$	no	25
10	$ArSnMe_3 \xrightarrow{H_2SO_4} ArH$	H_2O, AcOH	50	—	$6.84\cdot10^{-4}$	$p>o>m$	no	25
11	$Ar\text{—}CH(Me)\text{—}OCOMe \rightarrow ArCH=CH_2+MeCOOH$	—	352	—	0.364	$p>m\sim o$	no	56
12	$Ar\text{—}C_6H_4T\text{-}p \xrightarrow[CF_3COOH]{HClO_4} Ar\text{—}Ph$	H_2O	70	—	$3.49\cdot10^{-3}$	$p>o>m$	no	57
13	$Ar\text{—}C_6H_4T\text{-}o \xrightarrow[CF_3COOH]{HClO_4} Ar\text{—}Ph$	H_2O	70	—	$2.56\cdot10^{-3}$	$o>m$	no	57
14	$Ar_3COH \underset{}{\overset{+H^+}{\rightleftarrows}} Ar_3C^++H_2O$	H_2SO_4, H_2O	25	2.81[c]	—	$p\gg o>m$	yes	60
15	$ArCOOH+H_2O \rightleftarrows ArCOO^-+H_3O^+$	H_2O	25	7.65	—	$o>m>p$	yes	9
16	$ArCH_2COOH+H_2O \rightleftarrows ArCH_2COO^-+H_3O^+$	H_2O	25	4.6	—	$o>m>p$	yes	9
17	$ArCH_2\underset{\displaystyle NH_2}{\underset{\vert}{C}}H\text{—}COOH \rightleftarrows ArCH_2\underset{\displaystyle \underline{\underline{NH_3^+}}}{\underset{\vert}{C}}H\text{—}\underline{COO^-}$	H_2O	25	<u>4.67</u>	—	$m\sim o\sim p$	yes	9
18				<u>4.64</u>	—	$m\sim o\sim p$	yes	9
19	$Ar\overset{+}{N}H_3+H_2O \rightleftarrows ArNH_2+H_3O^+$	H_2O, H_2SO_4	25	4.91	—	$o>m>p$	yes	9
20	$ArCH_2\overset{+}{N}H_3+H_2O \rightleftarrows ArCH_2NH_2+H_3O^+$	—	—	3.9	—		—	49
21	$ArOH+H_2O \rightleftarrows ArO^-+H_3O^+$	H_2O	25	6.36	—	$o>m>p$	yes	9
22	$ArCH_2OH+H_2O \rightleftarrows ArCH_2O^-+H_3O^+$	—	—	4.0	—	$m>p$	—	49

[a] Present work. [b] Ratio of differences in half-wave potentials $-E_{\frac{1}{2}}$. [c] Ratio of values of ΔpK_{R^+}.

These ratios show that the effects of *o*-, *m*-, and *p*-fluorine atoms depend on the nature of the reaction centre[9]. The efficiencies of the fluorine atoms in the pentafluorophenyl group are about the same—*o* > *m* > *p*—for reactions 16—18, 20, and 22 (Table 28), since they are governed solely by the inductive effect of the pentafluorophenyl group. The same sequence applies to reactions 1—3, 6, 7, 15, 19, and 21, in which the electron-accepting inductive character of the fluorine atoms also prevails. With all these reactions the effects of the

Table 29. σ-Constants of substituents.

Reaction series	Solvent	Temp. °C	Substituent	σ-Constants of substituent								Ref.
				σ_m	σ_p	σ_m^+	σ_p^+	σ_p^-	σ^*	σ_I	σ_R^0	
1	2	3	4	5	6	7	8	9	10	11	12	13
pK_a	75% CH_3OH —	39.8	C_6F_5	−0.12	−0.03	—	—	—	—	—	—	66
m-, *p*-RC_6H_4COOH	25% H_2O		CF_3	+0.48	+0.48	—	—	—	—	—	—	66
	50% butoxyethanol	25	Ph	+0.06	−0.01	—	—	—	—	—	—	67
pK_a	CCl_4	—	C_6F_5	—	+0.45	—	—	—	—	—	—	— a
m-,*p*-RC_6F_4COOH			Ph	—	−0.01	—	—	—	—	—	—	— a
			CF_3	—	+0.70	—	—	—	—	—	—	— a
pK_a	H_2O	25	C_6F_5	—	—	—	—	—	2.0	—	—	— b
RCOOH			Ph	—	—	—	—	—	0.6	—	—	78
			CF_3	—	—	—	—	—	2.6	—	—	78
pK_a	H_2O	25	C_6F_5	—	—	—	—	—	—	0.31	—	9
RCH_2COOH			Ph	—	—	—	—	—	—	0.10	—	103
			CF_3	—	—	—	—	—	—	0.42	—	103
			COOEt	—	—	—	—	—	—	0.34	—	103
pK_a	45% dioxan	25	C_6F_5	+0.34	+0.41	—	—	—	—	—	—	66
m-,*p*-$RC_6H_4\overset{+}{N}H(Me)_2$	+ 55% water		CF_3	+0.48	+0.60	—	—	—	—	—	—	71
pK_a { $RRC(CF_3)OH$	H_2O	25	C_6F_5	—	—	—	—	—	1.3	—	—	81
pK_a { $RC(CF_3)_2OH$			C_6F_5	—	—	—	—	—	0.9	—	—	81
			Ph	—	—	—	—	—	0.26	—	—	— c
			CF_3	—	—	—	—	—	2.6	—	—	80
Rate of detritiation	H_2O	70	C_6F_5	—	—	+0.285	+0.255	—	—	—	—	57
$RC_6H_4T \xrightarrow[CF_3COOH]{HClO_4}$ RPh			Ph	—	—	+0.012	−0.2	—	—	—	—	57
Rate of nucleophilic substitution	n-hexane	50	C_6F_5	—	—	—	—	0.66	—	—	—	— d
$RC_6F_5 + NHC_5H_{10} \longrightarrow$			CF_3	—	—	—	—	0.74	—	—	—	92,93
		100	C_6F_5	—	—	—	—	0.66	—	—	—	— d
$\longrightarrow$ *p*-$RC_6F_4NC_5H_{10}$	dioxan	50	C_6F_5	—	—	—	—	0.60	—	—	—	— d
		100		—	—	—	—	0.57	—	—	—	
	MeOH	50	C_6F_5	—	—	—	—	0.48	—	—	—	— d
		100		—	—	—	—	0.47	—	—	—	
Rate of nucleophilic substitution	$CH_3CON(CH_3)_2$	106	C_6F_5	—	—	—	—	0.50	—	—	—	— d
$RC_6F_5 + C_6F_5ONa \longrightarrow$				—	+0.42	—	—	—	—	—	—	95
			CF_3	—	—	—	—	0.74	—	—	—	92,93
$\longrightarrow$ *p*-$RC_6F_4OC_6F_5$				—	+0.58	—	—	—	—	—	—	95
^{19}F n.m.r.	CF_3Cl	—	C_6F_5	+0.26	+0.27	—	—	—	—	0.25	0.02	66
m-,*p*-RC_6H_4F			C_6Cl_5	+0.23	+0.24	—	—	—	—	0.25	−0.01	66
			Ph	+0.04	0	—	—	—	—	0.08	−0.09	104
			CF_3	+0.44	+0.49	—	—	—	—	0.39	0.10	71
^{19}F n.m.r.	CF_3Cl	—	C_6F_5	—	—	—	—	—	—	0.15	0.00	66
RC_6F_5			Ph	—	—	—	—	—	—	−0.03	−0.07	66
			CF_3	—	—	—	—	—	—	0.33	0.01	66
^{19}F n.m.r.												
C_6F_5RXY			C_6F_5	+0.22	—	—	—	—	—	—	—	105
^{35}Cl n.q.r.			C_6F_5	—	—	—	—	—	1.93	—	—	49
				—	—	—	—	—	—	—	−0.12	— e

a Calculated from data of Ref. 63.

b Calculated by means of the equation[78,63]

$$pK_a\ (RCOOH) = -1.795\ \sigma^*(R) + 5.275\ ,$$

$$pK_a\ (C_6F_5COOH) = 1.67\ .$$

c Calculated by means of the equation[80]

$$pK_a = -1.44\ \Sigma\sigma^* + 16.67\ ,$$

with pK_a = 8.80 for $C_6H_5C(CF_3)_2OH$ [81] and σ* = 2.6 for the trifluoromethyl group[80].

d Calculated from data of Refs. 92 and 93.

e Calculated by means of the equation

$$\sigma_R^0 = (-2.44 + 0.0521\ \nu + 0.132\ pK_a)\ ,$$

from data of Ref. 106 with pK_a = 3.48 for $C_6F_5CH_2COOH$ [9] and ν = 35.76 MHz for $C_6F_5CH_2Cl$.[49]

fluorine atoms of the pentafluorophenyl group exhibit satisfactory additivity. Such additivity may thus be expected in nucleophilic reactions such as 1, 2, 3, 6, and 7 and in the dissociation of various acidic groups, e.g. reactions 15—22, involving a transition state or intermediate product without a significant contribution by *p*-electrons of lone pairs on the fluorine atoms, when the predominant stabilising effect will be the electron-accepting inductive effect in the sequence $o > m > p$.

The distribution of negative charge in the intermediate σ-complex in nucleophilic substitutions (reaction 4 in Table 28) depends to a considerable extent on the position of the fluorine atoms in the ring, since the participation of *p*-electrons of the fluorine atoms in this process is very substantial. Here, therefore, the stabilising effects of the fluorine atoms vary in the sequence $m > o > p$, and are non-additive.

Reaction 8 (Table 28) probably involves formation of a hydrogen bond between the reagent and an *ortho*-fluorine atom of the substrate, which accelerates the reaction[102]. In this case, of course, additivity of the effects of the fluorine atoms cannot be expected.

Electrophilic reactions such as 9—14 (Table 28), involving transition states or intermediate compounds with a significant contribution by *p*-electrons of lone pairs on fluorine atoms, exhibit the sequence $p > o > m$, corresponding to the predominant contribution by the positive conjugation effect of *ortho*- and *para*-fluorine atoms in the benzene ring. As with aromatic nucleophilic substitution, the effects of the fluorine atoms in the pentafluorophenyl group are not additive. An exception is reaction 14, for reasons discussed above (Section III).

Directly opposite requirements must obviously be met for resonance stabilisation of the σ-complexes in nucleophilic and in electrophilic aromatic substitution. Hence the former reactions become relatively slower (Section VII), and electrophilic substitutions relatively faster (Section II), than the additive rates to be expected with increasing degree of fluorination of the benzene ring.

IX. ANALYSIS OF σ-CONSTANTS OF PENTAFLUOROPHENYL GROUP

Quantitative data on the electronic effects of the pentafluorophenyl group can be derived as various σ-constants from thermodynamic measurements of pK_a or reaction velocities, as well as from the fluorine-19 n.m.r. chemical shifts of the corresponding pentafluorobiphenyl derivatives. Table 29 gives various σ-constants of the pentafluorophenyl group obtained for various reaction series. These data show that, with respect to its inductive effect (σ_m, σ^*, and σ_I constants), this group is a strong electron-accepting substituent in comparison with phenyl, but is weaker than trifluoromethyl. Its electron-accepting inductive effect is closely similar to those of ethoxycarbonyl and pentachlorophenyl. It is significant that the σ_I^*-constants of the pentafluorophenyl and phenyl groups, obtained from the ionisation constants of tertiary alcohols[81], are only about one-third of the analogous σ^*-constants deduced from the ionisation constants of carboxylic acids, and that the σ^*-constant in a tertiary alcohol containing two pentafluorophenyl groups is larger than that in the corresponding alcohol containing only one such group[81]. This effect (Section VI) may be attributed to $p-\pi$ interaction of trifluoromethyl groups and the benzene ring, which weakens the acceptor properties of phenyl and pentafluorophenyl groups[71]. Introduction of a second pentafluorophenyl group into the tertiary alcohol weakens the $p-\pi$ interaction owing to the increased *I*-effect of the field due to this group. It is significant that chlorine-35 nuclear quadrupole resonance has revealed an increase in the electron-accepting *I*-effect of pentafluorophenyl also in compounds of the type C_6F_5CHClR (R = Cl, CH_3, $COOC_2H_5$, C_6F_5).[49] The change in ^{35}Cl n.q.r. frequency in the compound $C_6F_5CHClCF_3$ might give information on the $p-\pi$ interaction of trifluoromethyl and pentafluorophenyl groups. The value of the σ_I-constant for the latter (and other groups) deduced from the fluorine-19 n.m.r. shifts of the pentafluorophenyl ring are usually 0.1 below the corresponding values obtained by Taft's method[66]. Nevertheless, Taft's method for estimating the σ-constants of a substituent, involving the ^{19}F n.m.r. chemical shifts of monofluorobenzene derivatives[104], will give values close to the σ-constants determined from other reaction series.

The σ_m-constants are smaller than the σ_p-constants for various reaction series, although it would appear that the opposite relation should apply, since the resonance effect of pentafluorophenyl expressed as the σ_R^0-constant is very slight. However, this last constant disregards direct polar conjugation of the substituent with the reaction centre, which is very important for the pentafluorophenyl group, as the preceding discussion has shown, for instance, in electrophilic and nucleophilic aromatic substitutions. It is highly probable that a constant effect of a *p*-pentafluorophenyl group cannot be expected, expressed as a narrow range of values of the σ_p-constant: rather a considerable range may be expected depending on the conditions of stabilisation of the transition state or the intermediate compound in various reactions. Whereas the values σ_m and σ_m^+ lie in the range 0.22—0.34, the corresponding range for σ_p, σ_p^+, and σ_p^- is 0.255—0.66. The relation $\sigma_m^+ > \sigma_p^+$ reflects the effective resonance participation of the pentafluorophenyl group in the distribution of positive charge in electrophilic reactions[57].

The very low values of the σ_m- and σ_p-constants derived from the ionisation of benzoic acids in 75% aqueous methanol, and also the decrease in the σ_p^--constant obtained from the correlation with the rate constants of nucleophilic aromatic substitution in methanol[92,93], are due (Section VII) to solvation by the alcohol of the fluorine atoms in the pentafluorophenyl group, which becomes less strongly accepting.

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Thus the survey of the effect of the pentafluorophenyl ring on the reactivity of various functional groups has revealed an interesting combination of acceptor and donor properties of the fluorine atoms, which interact specifically with various functional groups. The effects of the pentafluorophenyl group connected predominantly with $p-p$ interaction of the fluorine atoms and the reaction centre are especially interesting.

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