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Polyfluorinated Arenonium Ions

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This novel type of arenonium ions plays a key role in the isomerisation and electrophilic reactions of aromatic compounds. Methods for their generation, the investigation of their electronic structure by means of fluorine-19 nuclear magnetic resonance, and the influence of structural factors on their relative stability are discussed. Results on the chemical reactions of polyfluorinated arenonium ions, opening up paths for their synthetic use, are summarised. A list of 74 references is included.

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I. INTRODUCTION

A most important stage in studying the mechanism of the reactions of aromatic compounds with electrophilic agents, which has been responsible for a recently established and extremely fertile direction of research in this field, has been the development of methods for generating long-lived arenonium ions that in some degree model intermediate species in these reactions. The progress made[1] has provided an experimental basis for earlier views on the intermediate formation of σ-complexes during electrophilic reactions of aromatic compounds and has revealed the role of isomerisation of these species as one factor governing the dependence of the final result on the reaction conditions; in particular, the isomeric composition of the reaction products depends on the contribution made to the total change by addition of an electrophilic species to a substituted aromatic ring carbon atom (*ipso*-reactions[2]).

ipso-Reactions with electrophilic agents have recently been studied in particular on aromatic polyfluoro-compounds. The immense possibilities for the synthesis of diverse polyfluorinated compounds opened up by the discovery of reactions of this type (those between aromatic polyfluoro-compounds and nitrating reagents have been reviewed[3]) and the trend to their directed use have made necessary a more profound study of the reaction mechanism.

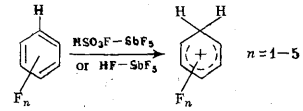
The mechanism of *ipso*-electrophilic reactions of aromatic polyfluoro-compounds suggested initially involves addition of the electrophilic species at a position in the aromatic ring occupied by such an electronegative substitutent as a fluorine atom[3]. The arenonium ion assumed to be formed possesses structural characteristics that are extremely unfavourable for its stability: it contains a large number of fluorine atoms at positions in the unsaturated portion at which the substituent plays no effective part in charge delocalisation by a conjugation mechanism (non-resonance positions†), and also two electronegative substituents together at an sp^3-hybridised site. At the time at which this scheme was proposed stable arenonium ions having such characteristics were unknown. Therefore the generation of ions of this type under "long-lived" conditions, with the aim of demonstrating the very possibility of their existence, would provide one of the most fundamental pieces of experimental evidence in support of the scheme. Results thus obtained are obviously of value not only in studying the chemistry of aromatic polyfluoro-compounds: they are important for understanding the properties of carbocations—species that have a fundamental role in organic chemistry.

† We shall regard as resonance positions those that are involved in delocalisation of the positive charge when the distribution of π-electron density is described in terms of limiting ("resonance") structures.

II. GENERATION OF POLYFLUORINATED ARENONIUM IONS

1. Protonation of Partly Fluorinated Aromatic Compounds

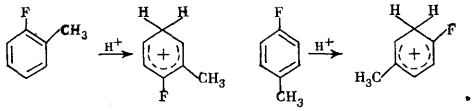
The first polyfluorinated arenonium ions were obtained by this reaction, which was most widely used in the initial state of development of the chemistry of these species (during 1967–1968). The weak basicity of aromatic polyfluoro-compounds required the use of a "superacid"—a solution of antimony(V) fluoride in fluorosulphuric acid—to achieve a sufficient degree of protonation. Both hydrogen and fluorine-19 nuclear magnetic resonance spectroscopy were used to record the formation of benzenonium ions having two hydrogen atoms as geminal substituents[4–6] when incompletely substituted fluorinated benzenes were dissolved in this acid system:



The orientation of addition of the proton then corresponds to decrease in stability of the arenonium ions as the position of the fluorine atom in the unsaturated part varies in the sequence *para* > *ortho* ≫ *meta*. *o*-Difluorobenzene, 1,2,3,4- and 1,2,4,5-tetrafluorobenzenes, and pentafluorobenzene are hardly protonated at all in this acid system, owing to the strong destabilisation of arenonium ions by a *meta*-fluorine atom. Protonation of these compounds required the use of a stronger acid—a solution of antimony(V) fluoride in hydrofluoric acid—but hexafluorobenzene is not protonated even in this case[7]. Such difficulty of *ipso*-protonation according to the position occupied by a fluorine atom is consistent with subsequent quantum-chemical calculations of the relative stability of fluorobenzenonium ions[8].

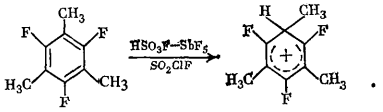
Fluorine-containing methylbenzenes are also protonated at unsubstituted positions[5,6,9]. In cases in which the *ortho*–*para* orienting effects of methyl group and fluorine atom do not coincide the fluorine atom in the resulting arenonium ion

is located in a resonance position, predominantly *para*, while the methyl group occupies the non-resonance *meta*-position[5]:



Because of the high rate of interconversion of isomeric arenonium ions corresponding to protonation of aromatic compounds the above rules apply to equilibrium proportions of isomers. However, isomeric ions differ in the nature of the substitutents at two or more positions, so that the relative effects of substituents at any one of them on the stability of the ion cannot be assessed. Therefore the orientation involved in the protonation of *o*- and *p*-fluorotoluenes cannot be interpreted as indicating that a fluorine atom has a stronger stabilising influence than a methyl group in the resonance arrangement. Determination of the relative stabilising effects of these substituents by comparing the relative stabilities of arenonium ions differing in the substituent at only one position (Section III) has shown that the methyl group has the stronger stabilising influence.

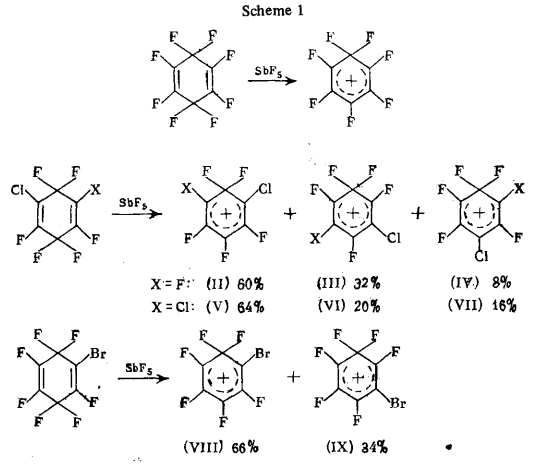
The only example of an aromatic polyfluoro-compound that is completely substituted in the ring and is converted into an arenonium ion on protonation is trifluoromesitylene. In this case, however, a benzenonium ion is formed in which all the fluorine atoms are located in the unsaturated portion[5]:



The above examples show that the arenonium ions containing a fluorine atom attached to an sp^3-hybridised carbon atom cannot be obtained by the protonation of aromatic fluoro-compounds. Such ions have been obtained by using less traditional methods of generating arenonium ions.

2. Action of Antimony(V) Fluoride on Polyfluorinated Dihydro-aromatic Compounds

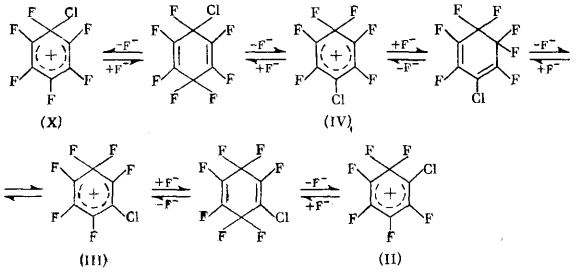
Scheme 1



An approach made earlier to obtain alkyl cations[10,11] has proved useful for generating polyfluorinated arenonium ions having fluorine atoms in an sp^3-hybride node: a fluoride anion is detached by antimony(V) fluoride from the corresponding precursor, in the present case from the polyfluorinated dihydro-aromatic compound. The perfluorobenzenonium ion (I) and its analogues (II)–(IX) containing chlorine or bromine atoms in the unsaturated portion have been generated from polyfluorinated cyclohexadienes in antimony(V) fluoride[12,13] and in sulphuryl chloride fluoride[14–16]. Scheme 1 gives for these analogues the equilibrium proportions established in antimony(V) fluoride solution at 20–40 °C.

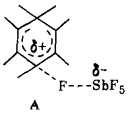
Ions containing a *p*-chloro-substitutent cannont be formed directly from percursors. Their presence in the reaction mixtures indicates the possibility of interconversion of isomeric ions, which apparently occurs by a series of reversible transformations of benzenonium ions into cyclohexadienes[13,14]. The equilibrium character of the proportions given in Scheme 1 is supported by formation of the ion (IV) and of the 1-chlorohexafluorobenzenonium ion (X) in the proportions 9 : 1 when antimony(V) fluoride acts on 3-chloroheptafluorocyclohexa-1,4-diene in sulphuryl chloride fluoride at −90 °C (the latter ion (X) is generated also by the chlorination of hexafluorobenzene—see below). With rise in temperature to −40° C the ion (X) is converted into (IV), which at −20 °C is in turn converted into the ions (II) and (III), between which the above relation is established. The sequence of interconversions of chlorohexafluorobenzenonium ions when the solution "thaws out" (Scheme 2) indicates the greater ease of addition of a nucleophilic species at the *para*-position in the benzenonium ion [transition from (X) to (IV)] than at an *ortho*-position [conversion of (IV) into (III) and then into (II)], and may well represent the relative electrophilic strengths of the two resonance positions in the cyclohexadienyl fragment[14].

Scheme 2



It follows from the above results that between −90 and −80 °C the addition of a fluoride ion at the *para*-position and hence also the isomerisation of polyfluorinated arenonium ions are slow processes. This means that the proportions in which isomers are formed at these temperatures are kinetically controlled. The action[17] of antimony(V) fluoride on hexafluoro-1-halogenocyclohexa-1,4-dienes in sulphuryl chloride fluoride at −90 °C yields the corresponding hexafluoro-2- and -3-halogenobenzenonium ions in the proportions 1 : 2 and 1 : 3 when the halogen is respectively chlorine and bromine; these differ from the equilibrium proportions of the same ions (Scheme 1) established at −60 °C. In the case of the chloro-compounds complete equilibrium involving the isomer (IV) is established at −20 °C.[17]

If the transition state corresponding to the detachment of a fluoride anion from a cyclohexadiene molecule is assumed to be of the type



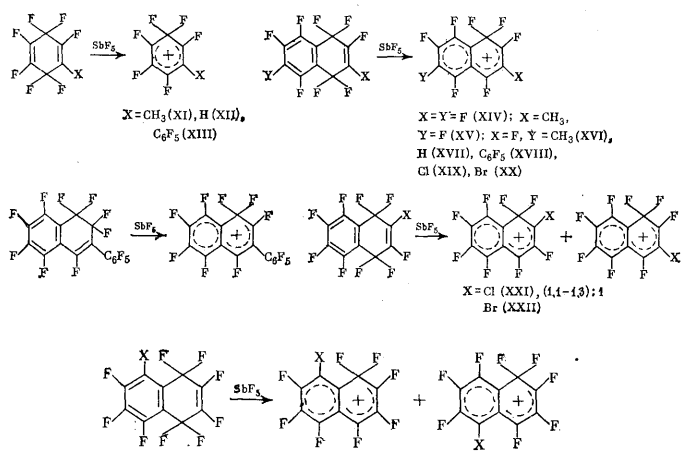
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the discrepancy between the kinetically controlled and the equilibrium ratios of isomeric ions may indicate that the increase in the positive charge in the cyclohexadienyl system accompanying transformation of the transition state into an

arenonium ion leads to a change in the relative stabilising effects of *o*- and *m*-halogeno-substitutents with respect to the sp^3-hybridised carbon atom[17].

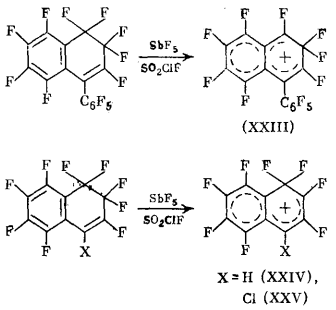
The ions 1,1,2,4,5,6-hexafluro-3-methylbenzenonium (XI),[18] 1,1,2,3,4,6-hexafluorobenzenonium (XII),[16] perfluoro-3-phenylbenzenonium (XIII),[19] and perfluoro-1-naphthalenonium (XIV)[12,13] and many of its substituted analogues[17-19] have been generated by the action of antimony(V) fluoride on the corresponding polyfluorinated cyclohexadienes (Scheme 3).

Scheme 3



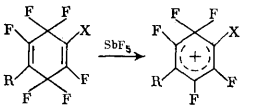
The formation of ions (XI), (XV), and (XVI) corresponds to the tendency mentioned in subsection 1 for the methyl group to occupy a non-resonance position if that will make a resonance arrangement of the fluorine atom possible[18]. This also partly explains the preferential non-resonance orientation of the pentafluorophenyl group. In the latter case, however, another possible factor is that resonance involvement of the pentafluorophenyl group in charge delocalisation is apparently diminished by its non-coplanarity with respect to the remainder of the ion, which causes steric interaction of fluorine atoms situated near together[19,20].

The net effect of these factors is that, with a pentafluorophenyl group substituted on an α-carbon atom in the cyclohexadienyl fragment of a naphthalenonium ion, the napthalen-2-onium ion (XXIII) is formed[21], whereas naphtalen-1-onium ions are usually more stable than naphthalen-2-onium ions[1] (cf. formation of the ions (XXIV) and (XXV) from the corresponding precursors[22]):



The relative stabilising effects of so closely related substituents as the halogen atoms are apparently very sensitively dependent on the structure of the arenonium ion, primarily on the distribution of positive charge in it (cf. the above data on the discrepancy between kinetically controlled and equilibrium proportions of halogenohexafluorobenzenonium ions). This is evident e.g. in the conclusion from the equilibrium ratios of isomeric 1,1-difluorobenzenonium and 1,1-difluoronaphthalen-1-onium ions that a chlorine or a fluorine atom in a cyclohexadienyl fragment occupies preferentially a resonance position (predominance of the ions (II), (V), (XIII), (XXI), and (XXII) over their isomers), whereas halogen atoms in a β-position in the benzene fragment of naphthalen-1-onium ions are characterised by the opposite tendency (ions (XIX) and (XX)—see above).

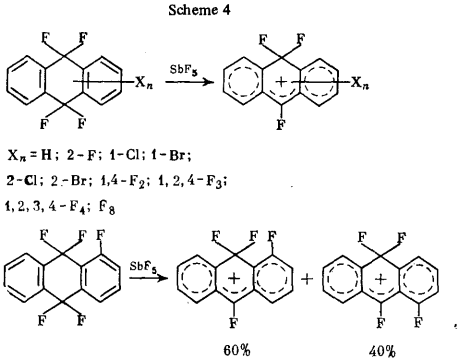
The possibility of generating 5-R-pentafluoro-2-halogenobenzenonium ions (R = CH_3, H) from the corresponding cyclohexadienes was predicted from the above results and then realised[15]:



R = CH_3, X = Cl, Br, CH_3; R = H, X = Cl, Br, H, CH_3 .

The action of antimony(V) fluoride in sulphur dioxide at −20 °C on 9,9,10,10-tetrafluoro-9,10-dihydroanthracenes yields the 9,9,10-trifluoroanthracenonium ion and the corresponding halogen derivatives, including polyfluorinated analogues[23,24] (Scheme 4).

Scheme 4



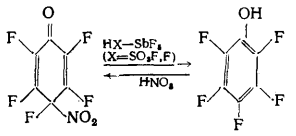
The predominance of the 1-X-9,9,10-trifluoroanthracenonium ions (X = F, Cl, Br) over their 4-X-isomers is obviously a consequence of the occurrence in the latter of destabilising interaction between halogen atoms present in the spatially contiguous resonance positions 4 and 10.

3. Protonation of Polyfluorinated Cyclohexadienones

Cyclohexadienones are conjugated bases of hydroxyarenonium ions, and their protonation has long been used to generate the latter. Koptyug et al.[1] have obtained by this method several hydroxyarenonium ions containing an electronegative atom or group (F, Cl, Br, OH, OCH_3, $OCOCH_3$, NO_2) attached to an sp^3-hybridised carbon atom.

This method has been used to generate polyfluorinated arenonium ions containing as geminal substitutents not only fluorine but also other halogen atoms[25-27]. Ions of the latter type simulate intermediate species in the electrophilic *ipso*-halogenation of aromatic polyfluoro-compounds at positions occupied by fluorine atoms. The ability, revealed by these examples, of chlorine and bromine atoms to be retained at an sp^3-hybrid atom of an arenonium ion in a geminal position with respect to a fluorine atom has served as experimental basis for the generation of polyfluorinated arenonium ions by the direct electrophilic halogenation of aromatic polyfluoro-compounds (below).

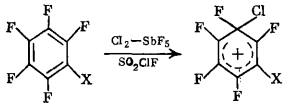
In attempts to generate an arenonium ion containing a nitro-group as substituent located geminally with respect to a fluorine atom, in contrast, pentafluoro-4-nitrocyclohexa-2,5-dien-1-one when dissolved in the systems $HSO_3F-SbF_5-SO_2$ and $HF-SbF_5-SO_2ClF$ is converted into pentafluorophenol, with the dependence of the degree of conversion on the quantity of the pentafluoride corresponding to a stoichiometric ratio of two moles of the latter per mole of the ketone. In the absence of antimony(V) fluoride the reaction does not take place, but nor does protonation of the ketone[28]. Thus introduction of antimony pentafluoride into the system leads to reversal of the *ipso*-nitration of pentafluorophenol[28,29], which may be due to involvement of a nitronium cation in specific complex formation in such systems:



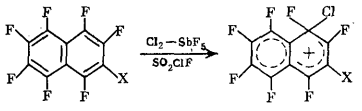
4. Action of Electrophilic Agents on Aromatic Polyfluoro-compounds

Generation of arenonium ions by direct electrophilic attack on aromatic compounds is obviously the most fundamental method for experimental testing of the generally accepted schemes of interaction between aromatic compounds and electrophilic agents. For a long time arenonium ions corresponding to reactions involving addition of an electrophile to an aromatic ring by means of an electronegative heteroatom could not be generated in this way[1]. Success was achieved independently by groups of workers headed by Olah in the USA [30] and by Koptyug in the USSR,[31-33] who used polymethylated aromatic compounds as substrates and strong protic acids as media. These researches, as well as the above results on the fixation of polyfluorinated hydroxyarenonium ions with chlorine and bromine atoms as substituents geminal with respect to a fluorine atom, initiated attempts to generate polyfluorinated arenomium ions by the direct electrophilic halogenation of aromatic polyfluoro-compounds.

The action of molecular chlorine and antimony(V) fluoride on aromatic polyfluoro-compounds in sulphuryl chloride fluoride between −80 and −60 °C forms polyfluorinated 1-chloro-1-fluoroarenonium ions[14,34,35]:

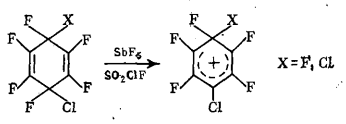


X = F, CH_3, C_6F_5



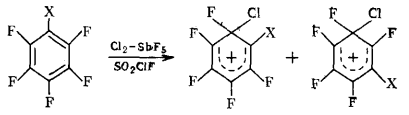
X = F, H, CH_3

With respect to the reaction mechanism, an alternative to direct electrophilic attack on the polyfluoro-aromatic ring would be addition of molecular chlorine on chlorine fluoride followed by reaction between the resulting cyclohexadienes containing a chlorofluoromethylene group and antimony(V) fluroide. Such a possibility is refuted, at least for the chlorination of hexafluorobenzene, by the abstraction of a fluoride anion from the halogenated methylene group when antimony(V) fluoride acts on cyclohexadienes of the above type[14]:



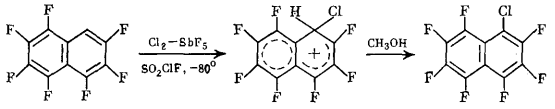
In most of the above cases of the chlorination of aromatic polyfluoro-compounds the orientation of addition of the chlorine cation is consistent with the relative stability of the isomeric polyfluorinated 1,1-difluorobenzenonium and 1,1-difluoronaphthalenonium ions formed by the action of antimony(V) fluoride on polyfluorinated cyclohexadienes or dihydronaphthanlenes (Section III). The only exception is the chlorination of chloro- and bromo-pentafluorobenzenes, with preferential formation of 3-X-1-chloropentafluorobenzenonium ions (X = Cl, Br). Since there are grounds for supposing that at least with polyfluorinated 1-chloro-1-fluorobenzenonium ions, such orientation corresponds to the equilibrium ratios of the isomeric ions (in virtue of the ease of migration of the chlorine atom—Section III), this exception indicates a change in the relative stability of 2- and 3-X-substituted isomers (X = Cl, Br) on passing from 1,1-difluorobenzenonium ions to their 1-chloro-1-fluoro-substituted analogues (Scheme 5). Such a change may be due both to increase in steric strain in the 2-X-isomer with increase in the bulk of the geminal substitutent and to change in the distribution of electron density in the unsaturated portion of the ion under the influence of change in the electronic effect of the substituent at the sp^3-hybridised atom[28,36].

Scheme 5



X = Cl:	33%	67%
X = Br:	20%	80%

Pentafluorobenzene and 1-H-heptafluoronaphthalene are chlorinated under the above conditions at the unsubstituted position. However, whereas in the former case only chloropentafluorobenzene is formed, in the latter a rare example of formation of an arenonium ion corresponding to substitution of hydrogen could be observed:



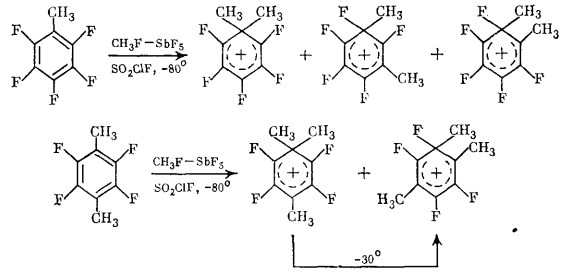
(XXVI)

The chief product of methanolysis of a solution containing this ion is 1-chloroheptafluoronaphthalene. The comparative stability of the ion (XXVI) with respect to detachment of a proton is apparently due to steric hindrance caused by *peri*-interaction when a chlorine atom is situated in the plane of the naphthalene ring system[35].

Attempts have also been made to generate arenonium ions by electrophilic bromination and nitration of aromatic polyfluoro-compounds. Bromination has proved successful with pentafluorotoluene, addition of which to a solution of bromine and antimony(V) fluoride in sulphuryl chloride fluoride at −60 °C forms a 1-X-3 methylpentafluorobenzenonium ion, in which X appears from the chemical shifts of atoms in its immediate vicinity to be a bromine atom[22,36]. However, formation of polyfluorinated arenonium ions could not be detected from the ^{19}F n.m.r. spectra in the action on polyfluorinated

benzenes of nitrating systems containing nitronium fluoroborate or nitrosyl chloride together with fluorosulphuric acid or antimony pentafluoride in sulphur dioxide or sulphuryl chloride fluoride, which recalls the above unsuccessful attempts to generate the 4-hydroxy-1-nitropentafluorobenzenonium ion by protonating the corresponding nitrocyclohexadienone[28].

Scheme 6



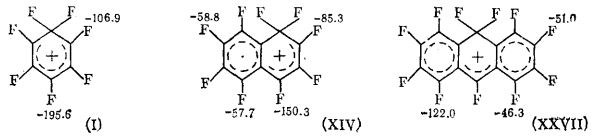
It has recently been discovered that the complex of fluoromethane and antimony(V) fluoride is able to methylate aromatic polyfluoro-compounds at positions occupied by either a fluorine atom or a methyl group, with formation of the corresponding arenonium ions[37]. This method has been used to generate 1,1-, 1,2-, and 1,3-dimethylpentafluorobenzenonium ions in sulphuryl chloride fluoride at −80 °C. The methylation of tetrafluoro-*m*-xylene under similar conditions occurs predominantly at a position occupied by a methyl group, and to a less extent at position 5 occupied by a fluorine atom. With tetrafluoro-*p*-xylene approximately equal quantities of 1,1,4- and 1,2,5-trimethyltetrafluorobenzenonium ions are formed. When the temperature of the solution rises from −80 to −30 °C, the ion containing two geminal methyl groups isomerises with migration of one of them to an adjacent position (Scheme 6).

III. PROPERTIES OF POLYFLUORINATED ARENONIUM IONS

1. Nuclear Magnetic Resonance Spectra and Structure

A most important experimental advance making a considerable contribution to the development of research on polyfluorinated carbocations and on arenonium ions in particular is the possibility of using ^{19}F n.m.r. spectroscopy to detect the formation and study the electronic structure of these species. The great sensitivity of the degree of shielding of fluorine nuclei to structural characteristics of a molecule, producing a change in the chemical shifts of fluorine atoms δ_F over a range of $\sim 10^{-6}$, makes this method a powerful tool for determining the structure of molecules containing fluorine. Furthermore, the predominantly π-electronic character of the variation in shielding of fluorine atoms in series of structurally similar unsaturated compounds makes it theorectically possible to use δ_F values to characterise the influence of structural factors, in particular of substituents quite remote from the given fluorine atom, on the π-electron density distribution. The spin–spin coupling constants between fluorine nuclei are also extremely informative.

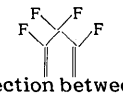
Despite the admittedly approximate character of such an approach, there are grounds for supposing that it gives a qualitatively correct picture of the dependence of the delocalisation of positive charge in polyfluorinated carbocations on their structure. This is indicated, for example, by the decrease in $\Delta\delta_F$ in the series of arenonium ions[14,22,23]



(I) (XIV) (XXVII)

i.e. with gradual increase in extent of the π-electron system (here $\Delta\delta_F$ is the chemical shift of a fluorine atom in the arenonium ion relative to the corresponding fluorine atom in the polyfluoroaromatic precursor, which in this case corresponds to formal removal of one of the geminal fluorine atoms as a cation). The relations between the $\Delta\delta_F$ values for different fluorine atoms in each of these arenonium ions correspond qualitatively with quantum-chemical calculations of the distribution of π-electron density in fluorine-containing arenonium ions[38]. Finally, the $\Delta\delta$ values for fluorine atoms and the carbon atoms to which they are attached in these three ions vary in parallel, in conformity with the equation $\Delta\delta_C = 0.135\,\Delta\delta_F$. Such a correlation apparently indicates that the ratio between the fractional charges on carbon and fluorine atoms remains approximately constant for a given cyclic C–F group, despite variation within wide limits in the degree of delocalisation of the charge[39].

An analysis[40] of $\Delta\delta_F$ values# in a series of arenonium ions generated by protonation of partly fluorinated benzenes[4,7] leads to the conclusion that accumulation of fluorine atoms in the unsaturated part of the ion is apparently accompanied by a redistribution of electron density involving increase in the electron deficiency of the *para*-position but diminution in the deficiency at the *ortho*-positions. Comparison of $\Delta\delta_F$ values for protonated pentafluorobenzene[7] and for the ion (I)[14] shows that replacement of hydrogen by fluorine atoms at an sp^3-hybridised site leads to further increase in the fractional positive charge at the *para*-position, so that the π-electronic structure of ion (I) can be represented to a first approximation by the limiting structure



(B)

The existence of a connection between $\Delta\delta_F$ values of the type of π-electron density distribution reveals the tempting prospect

These tendencies are supported by quantum-chemical calculations[38].

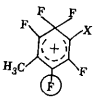
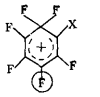
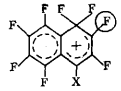
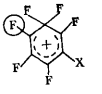
The existence of a connection between $\Delta\delta_F$ values and the type of π-electron density distribution reveals the tempting prospect of elucidating the relations between the electronic effects of substituents. The Table gives values of $\Delta\delta_F$ for series of polyfluorinated arenonium ions differing in the nature of a substituent in a given position. Inspection of these data indicates that the ratio of the $\Delta\delta_F$ values for structurally similar polyfluorinated arenonium and hydroxyarenonium ions is consistent with the generally accepted relation between the electron-donor resonance effects of the hydroxy-group and the fluroine atom. Yet the dependence of $\Delta\delta_F$ for an *o*-fluorine atom in the cyclohexadienyl fragment on the nature of the substitutent X in series of 4-X-hexafluorobenzenonium (X = F, Cl), 4-X-2,3,5,6-tetrafluorobenzenonium (X = F, Cl, Br, H), and 4-X-octafluoronaphthalen-1-onium (X = F, Cl, H)

This analysis is based on an assignment of signals, somewhat different from that of Ref.7, in the ^{19}F n.m.r. spectra of several of the ions.

ions conforms to electron-donor effects of halogens located in the resonance *para*-position diminishing on the whole in the sequence Br > Cl > F.[13,17,20]

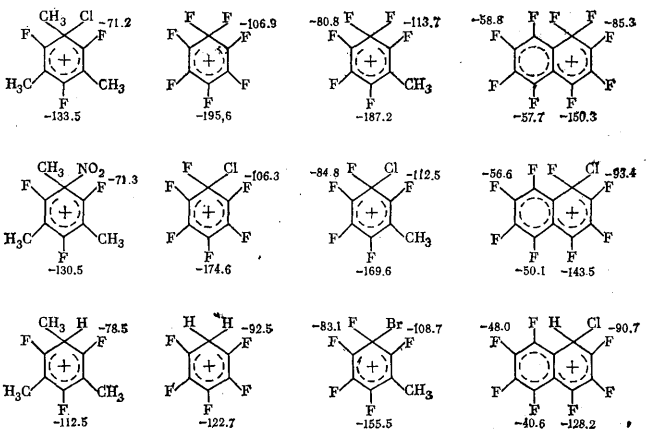
The same laws are revealed by a comparison of $\Delta\delta_F$ values for *p*-fluorine atoms in the cyclohexadienyl fragment of 2-X-hexafluorobenzenonium (X = F, Cl, Br),[13,16] 2-X-5-R-pentafluorobenzenonium (R = CH_3: X = F, Cl, Br; R = H: X = F, Cl, Br, H),[15] and 2-X-octafluoronaphthalen-1-onium (X = F, Cl, Br)[13,17] ions. In 2-X-substituted benzenonium ions, however, substituents X located in resonance positions have different effects on $\Delta\delta_F$ for chlorine atoms in the other two resonance positions, *para* and *ortho*. As the electronic structure of polyfluorinated benzenonium ions closely resembles a limiting structure of type (B), it may be supposed that the relation between the π-electronic effects of substituents X should be evident in the influence of the nature of X on the value of $\Delta\delta_F$ for the *para*-fluorine atom, not for the fluorine atom located in the other *ortho*-position, especially as it coincides qualitatively with the effect of *p*-X-substituents on the shielding of the fluorine atoms in other resonance positions in 4-X-hexafluorobenzenonium[13] and 4-X-2,3,5,6-tetrafluorobenzenonium[20] ions, as well as polyfluorinated arylmethyl cations[41].

Values of $\Delta\delta_F$ for polyfluorinated arenonium ions[15,20,22,25] (for the circled fluorine atom in each formula).

Arenonium ion	X	$\Delta\delta_F$, ppm	Arenonium ion	X	$\Delta\delta_F$, ppm
	F	−106.9		F	−187.2
	Cl	−88.5		Cl	−170.5
	OH	−64.2		Br	−164.7
	H	−96.3			
	F	−92.5		H	−185.6
	Cl	−84.8		F	−186.8
	Br	−81.7		Cl	−170.8
	H	−89.1		Br	−164.8
	F	−85.3		F	−106.9
	Cl	−71.0		Cl	−93.7
	OH	−59.8		Br	−89.6
				H	−83.1
	F	−195.6			
	Cl	−173.9			
	Br	−165.7			

It is extremely important whether the sequence Br > Cl > F of variation in the influence of halogen atoms on the shielding of fluorine atoms in resonance positions actually represents the relation between their resonant electron-donor effects (the influence of *p*-halogen atoms in non-fluorinated benzenonium ions on the $\delta_{^{13}C}$ values of ring *ortho*-carbon atoms is characterised by an analogous series[42]. Indeed, although all halogen atoms exert a greater shielding effect than does a hydrogen atom, which corresponds to predominance of the electron-donor resonance component in their total electronic effects, differences in effects of halogen atoms may be connected mainly with their inductive effects[43] (see discussion of these results in Ref. 44). Sufficiently accurate results obtained by quantum-chemical calculations on the ions are necessary to solve this problem. The influence of substituents in non-resonance positions in the unsaturated part of polyfluorinated arenonium ions on the shielding of fluorine atoms in remote resonance positions is represented by the sequence CH_3 > H > Br > Cl > F, which coincides qualitatively with the generally accepted relation between their inductive effects[15].

Scheme 7



Important data have been obtained on the effects of substituents at the sp^3-hybridised site on the distribution of electron density in, and on the stability of, arenonium ions. The laws governing the reactions of aromatic compounds with various electrophiles[45] and also the actual possibility of generating the arenonium ions that are intermediate species in such reactions may depend on this effect. Such information can be obtained in a series of polyfluorinated arenonium ions by comparing $\Delta\delta_F$ values for ions formed by the protonation of pentafluorobenzene[7,20], the protonation, nitration, and halogenation of trifluoromesitylene[5,31], the halogenation of aromatic polyfluoro-compounds[14,33], and the action of antimony(V) fluoride on polyfluorinated cyclohexadienes[15,20,22]. The data in Scheme 7, illustrating the variation in $\Delta\delta_F$ in series of arenonium ions differing in the nature of the geminal substituents, indicate that decrease in electronegativity of a geminal substituent is accompanied by increase in shielding of the $F_{(4)}$ atom in benzenonium or of $F_{(4)}$, $F_{(5)}$, and $F_{(7)}$ atoms in naphthalen-1-onium ions, which apparently represents diminution in the fractional positive charge in the corresponding C−F groups. It is reasonable to expect an accompanying increase in the fractional positive charge at the *ortho*-position and hence the deshielding of *o*-fluorine atoms. This does actually occur in a series of benzenonium ions generated from trifluoromesitylene. Analogous changes are observed in the ^{13}C n.m.r. spectra of polymethylated benzenonium ions differing in the nature of substitutents at the sp^3-hybridised site[45]. In the remaining series, however, no unambiguous correspondence is observed between variation in $\Delta\delta_F$ for an *o*-fluorine atom and the electronegativity of a substituent at an sp^3-hybrid site. The apparent reason is that changes in $\Delta\delta_F$ observed for *o*-fluorine atoms are largely due to variation in the shielding effect of geminal substituents that is transmitted directly through space. Analogous laws are observed with variation in the nature of geminal substituents in polyfluorinated hydroxyarenonium ions[26].

The $\Delta\delta_F$ values for fluorine atoms at non-resonance positions in the unsaturated part of arenonium ions and also at the sp^3-hybridised site apparently do not reflect the character of the distribution of positive charge. It is sufficient to mention that the signals of geminal fluorine atoms are displaced upfield on passing from polyfluorinated dihydro-aromatic compounds to the corresponding polyfluorinated

arenonium ions[13], which may be due to change specific to this process in the so called van der Waals contribution to the shielding constant[46]. Fluorine atoms at non-resonance positions in the unsaturated part of ions are apparently subject to the deshielding influence of fluorine atoms at neighbouring resonance positions, which bear considerable fractions of the positive charge. This is most likely due to a downfield shift in the signals of fluorine atoms at non-resonance positions relative to the corresponding signals in the ^{19}F n.m.r. spectra of the precursors[13]. An analogous explanation was given for the mutually deshielding influence of *peri*-fluorine atoms in polyfluorinated anthracenonium ions[23].

Even in the early work on the generation of polyfluorinated arenonium ions by the protonation of polyfluorobenzenes[4-6], and later by the action of antimony(V) fluoride on polyfluorinated cyclohexadienes or dihydronaphthalenes[12,13], it had already been shown that *o*- and *p*-fluorine atoms in a cyclohexadienyl fragment are characterised by unusually large absolute values of the spin–spin coupling constants between them, far exceeding those of J_{FF} for similarly oriented fluorine atoms in neutral compounds[47]. This phenomenon was interpreted qualitatively[13], in view of the close similarity of the π-electron system to a limiting structure of type (B), on the basis of effective interaction between the *o*- and *p*-fluorine atoms by a mechanism of conjugation.

From analogous considerations a similar increase in J_{FF} values in polyfluorinated naphthalenonium and anthracenonium ions relative to neutral compounds may be expected for the interaction between fluorine atoms in other resonance positions. In fact values of $J^{5,7}_{FF} \approx 50$ Hz are observed for naphthalene-1-onium ions[13], $J^{2,4}_{FF}$ 35–40 Hz for anthracen-9-onium ions[23], and $J_{FF} = 20-25$ Hz for the interaction of $F_{(2)}$ and $F_{(4)}$ with $F_{(5)}$ and $F_{(7)}$ in naphthalen-1-onium ions[18]. It is significant that the interaction between the spatially contiguous $F_{(3)}$ and $F_{(4)}$ atoms in polyfluorinated benzenonium ions corresponds to values of $J^{3,4}_{FF} = 25-30$ Hz only slightly exceeding those of J^{ortho}_{FF} for neutral fluoro-aromatic compounds[47], whereas the interaction of $F_{(2)}$ with $F_{(3)}$ is characterised by values $J^{2,3}_{FF} = 4-6$ Hz typical of the interaction of vicinal fluorine atoms located at a double bond in a cycloalkene[48], which is consistent with the close similarity of the cyclohexadienyl fragment in a polyfluorinated arenonium ion to the structure (B).

The above generalisations suggest that values of J_{FF} for interaction between fluorine atoms in resonance positions should be extremely sensitive to the type of the delocalisation of positive charge in arenonium ions. In conformity with this a parallelism in the variation of J_{FF} values and chemical shifts of the corresponding fluorine atoms is observed for polyfluorinated arenonium ions[13,23] and also the related arylmethyl cations[41]. From this point of view it is reasonable that the interaction of *peri*-fluorine atoms in naphthalen-1-onium and anthracene-9-onium ions corresponds to values of $J_{FF} = 130-150$ Hz,[13,23] since in neutral derivatives of naphthalene and anthracene such interaction is characterised by values of 60–80 Hz.[49,50] When a hydroxy-group, which exerts a stronger electron-donor effect than does a fluorine atom, is introduced into a resonance position in a polyfluorinated benzenonium or naphthalenonium ion, values of J_{FF} for interaction between fluorine atoms involved in resonance charge delocalisation decrease significantly, as is to be expected[27].

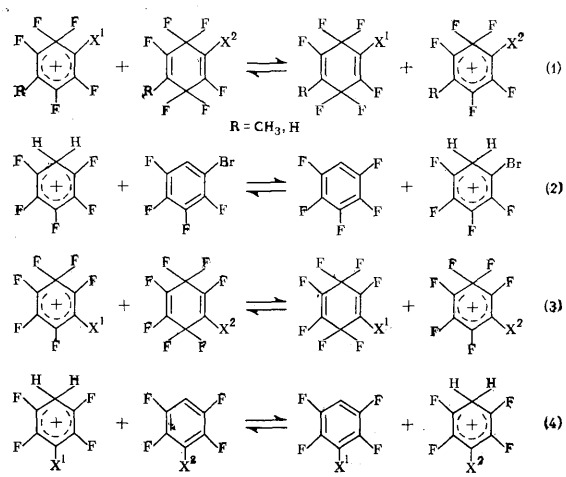
All the results at present available show that the possibility of parallel application of ^{19}F and ^{13}C n.m.r. spectroscopy makes polyfluorinated arenonium ions, and more generally polyfluorinated carbocations of various structural types, extremely interesting subjects for investigation. Detailed study of the dependence of the electronic structure of carbocations on their molecular structure and in particular elucidation of the relations between the electronic effects of substituents become theoretically possible. It may be supposed that, in contrast to the established practice of assessing these relations from the influence of substituents on the relative stability of carbocations or from their rate of formation in solution, such an approach will yield a picture uncomplicated by solvation interactions. The most reliable information can apparently be obtained from a combination of spectral data with results of quantum-chemical calculations.

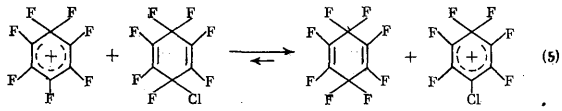
2. Equilibrium Proportions of Polyfluorinated Arenonium Ions and the Stabilising Influence of Substituents

Elucidation of the factors governing the relation between the relative stability of carbocations and their structure is of decisive importance for study of the mechanism of many reactions involving intermediate formation of species of this type. When applied to arenonium ions, this general task becomes the particular problem of establishing a theory of the influence of substituents on the rate and the orientation of reactions of aromatic compounds with electrophilic agents. Polyfluorinated arenonium ions are no exception in this respect, since a considerable volume of data have now accumulated on orientation in electrophilic reactions of aromatic polyfluoro-compounds of two main types—substitution of a hydrogen atom and addition[3,16,51-63].

Although papers on the generation of polyfluorinated arenonium ions contain numerous data on the equilibrium proportions of isomeric ions of this type, they cannot provide information on the relative stabilising effects of substituents at individual positions, since the isomeric ions differ in the nature of substituents at more than one position. In some cases these relations can be assessed from a comparison of the conditions of protonation of the corresponding fluorinated benzenes (Section II). The structure of the resulting benzenonium ions indicates that the *para*-position of a fluorine atom is most favourable to the stability of the ion, whereas the *meta*-position provides the greatest destabilising effect. These results are consistent with quantum-chemical calculations predicting that carbocations with fluorine atoms in resonance positions will be more stable than isomers having a different arrangement of the same substituents[54,55].

Scheme 8





(5)

The traditional approach to elucidating the relative stabilising effects of substituents at individual positions in carbocations is to study the dependence of the equilibrium formation constants of the ions fron neutral precursors on the nature of the substituents[56]. Among polyfluorinated arenonium ions such an approach has been adopted for the equilibrium systems in Scheme 8, formed by the action of a deficiency of a Lewis or a protic acid (depending on the mode of regeneration) on a mixture of equivalent quantities of two precursors[15,20].

The positions of equilibrium in systems (1) and (2) indicate that the stabilising effect of *ortho*-substitutents diminishes the sequence $CH_3 > Br > Cl > H > F$. Similarly, series (3) gives the stability sequence of benzenonium ions with different *meta*-substituents $CH_3 > H > Br > Cl > F$.[15] Relations established in series (4) correspond to variation in the stabilising influence of *para*-substituents in the sequence $CH_3 > F > Br > Cl > H$.[15]

It must be noted that the attempt[20] to assess the relative stabilising effects of *p*-fluorine and *p*-chlorine atoms in corresponding 4-X-hexafluorobenzenonium ions from equilibrium constants in system (5) (with simultaneous generation of the ions by the action of antimony(V) fluoride on a mixture of two cyclohexadienes) gave a relation between chlorine and fluorine opposited to that found for series (4). However, this apparently does not represent the true relation between the stabilising effects of *p*-chlorine and *p*-fluorine atoms in polyfluorinated arenonium ions, since the requirement that structural differences should be remote from the bond undergoing rupture in the precursors is not met[57]. In such a situation differences in the equilibrium position may be due to structural features not so much of the ions as of their precursors, so that the observed relations cannot be interpreted in terms of effects of substituents in the ions themselves. The decisive role may be played by differences in steric stress or in strength of the carbon–fluorine bond in difluoro- and chlorofluoro-methylene groups of the cyclohexadiene precursors (see Refs.58 and 59 for the effect of the accumulation of geminal fluorine atoms on the carbon–fluorine bond strength).

Nevertheless, it must borne in mind that the relative stabilising effects of halogen atoms are apparently very sensitive to other structural characteristics of arenonium ions. Thus in series (1) differences in the relative stability of *o*-bromo- and *o*-fluoro-ions correspond to equilibrium constants of concurrent generation of the ions $K \geq 300$. In the concurrent protonation of 1-bromo-2,3,4,5-tetrafluorobenzene and pentafluorobenzene (system 2) the difference is characterised by the value $K = 1.5$ [15] with preservation of the qualitative relation between the stabilising effects of *o*-bromine and *o*-fluorine atoms.

In view of the correspondence between the influence of substituents on the relative stability of cations and on the shielding of a fluorine atom in a resonance position remote from the substituents in 4-fluorinated di- and tri-phenylmethyl cations and related zwitterions[60,61], considerable interest attaches to a comparison of the above data on the influence of substituents on the ^{19}F n.m.r. spectra and on the relative stability of polyfluorinated arenonium ions. In series (3) the ions exhibit a complete qualitative correspondence between the influence of 3-substituents on $\Delta\delta_F$ for the $F_{(6)}$ atom and on the relative stability of the ion, the relations in both cases being consistent with the generally accepted sequence of variation in inductive effects in the series of substituents[15]. In series (1) and (2) there is similarly a qualitative correspondence between the effects of *o*-halogen or *o*-hydrogen atoms in the benzenonium ion on $\Delta\delta_F$ for a *p*-fluorine atom and on the relative stability of the ion. Such parallelism is characteristic of arenonium ions formed by the protonation of 1-X-2,3,4,5-tetrafluorobenzenes (X = F, Br).[15] If the variation in shielding effect of substituents in this sequence actually represents their relative electron-donor resonance effects (other possible reasons for the observed relationship with halogen atoms have been given in this Section), it may be supposed that these effects are mainly responsible also for the observed variation in stabilising influence.

It is noteworthy that such correspondence does not exist with *p*-substituents and an *o*-fluorine atom acting as indicator: although the shielding sequence of *p*-halogen and *p*-hydrogen atoms for series (4) coincides qualitatively with that of the same substituents located at *ortho*-positions in series (1) and (2), the stabilising effects of halogen atoms in series (4) vary in the different sequence $F > Br > Cl$.[20] The absence of such parallelism may mean that for the given substituents the order of variation in electron-donor resonance effect does not coincide with that in stabilising effect. The main contribution to the relation between the stabilising effects of halogen atoms as substituents bearing considerable fractions of the positive charge may then be made by their solvation interaction with surrounding species[20] (cf. discussion in Ref.62 on the solvation of carbocations). Such solvation effects may also be responsible to some extent for the fact that, as already noted[1,63], halogenated arenonium ions appear more stable in superacid media than could be expected from the effects of halogen atoms in the usual reactions of halogenobenzenes with electrophilic reagents.

In view of the above considerations it is noteworthy that resuits on the shielding and stabilising effects of *p*-halogen atoms in benzyl cations related to arenonium ions indicate that the parallelism between these effects may break down when hydrogen atoms are completely replaced by fluorine atoms[41]. With such modification the shielding effects of halogen atoms are reversed ($F > Cl > Br > H$ for αα-difluoro-*p*-halogenobenzyl cations[64] and $Br > Cl > F > H$ for hexafluoro-*p*-halogenobenzyl cations[41]), while their stabilising effects merely level off. This also may indicate that some factor other than the electronic effect of the substituent may make a significant contribution to the stabilising influence of *p*-halogen atoms, with the qualitative sequence of *p*-substituents apparently maintained with respect to this component of the stabilising effect on passing from αα-difluoro- to hexafluoro-*p*-halogenated benzyl cations[20]. A significant influence of solvation on the relative stabilising effects of halogen atoms may be indicated also by the diminution in stability of benzyl cations in the sequence of *p*-substituents $H > F > Cl$ suggested by the ionisation potentials of the benzyl radicals[65], whereas in antimony(V) fluoride with sulphuryl chloride fluoride *p*-halogen atoms are more strongly stabilising substituents of αα-difluorobenzyl cations than is a hydrogen atom[20].

In series (1), (3), and (4) in Scheme 8 polyfluorinated arenonium ions are considerably more strongly stabilised by a methyl group than by halogen atoms. With *meta*-orientation (series 3) this corresponds to the position occupied by methyl in the shielding sequence of substituents; with *ortho*- or *para*-orientation of this substituent—series (1) and (4)—such correspondence is absent. This apparently indicates that both shielding and stabilising effects of a methyl group differ significantly in nature from the corresponding effects of halogen atoms when these substituents are located in resonance positions.

The relations between the stabilising effects of substituents at individual positions in polyfluorinated arenonium ions revealed in series (1)–(4) provide an approach to an understanding of certain factors predetermining the equilibrium isomeric composition of ions generated by the action of antimony(V) fluoride on polyfluorinated cyclohexadienes (Section II). For example, the formation of *m*-methyl isomers in series (1) in no way means that *meta*-orientation is preferable to *ortho*- or *para*-orientation, but rather is due to a tendency to avoid the destabilising influence of a *m*-halogen atom. An indication of this is that, when a hydrogen atom and a methyl group are present in the same series as substituents other than fluorine atoms, the latter occupies an *ortho*- not a *meta*-position in the corresponding ion. On the other hand, the obvious reason for the strongly marked tendency of a fluorine atom to occupy the *para*-position is that only then is it a stronger stabilising substituent than other halogen atoms.

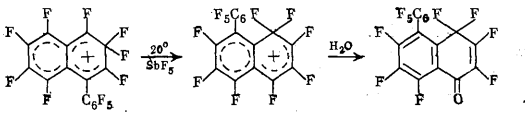
A method of concurrent generation has provided data on the influence of the accumulation of fluorine atoms on the relative stability of 9,9,10-trifluoroanthracenonium ions[66]. Introduction of a fluorine atom at position 2 somewhat stabilises the ion, whereas simultaneous introduction of fluorine atoms at positions 1 and 4 leads to its destabilisation. Further decrease in relative stability occurs on the complete replacement of hydrogen by fluorine atoms, initially in one and then in both benzene rings of the anthracene-9-onium ion. All these changes are consistent with the influence of the structural modifications on the shielding of fluorine atoms, apparently representing a redistribution of π-electron density[23].

3. Isomerisation of Polyfluorinated Arenonium Ions

An urgent task in the investigation of arenonium ions is to study their isomerisation, the importance of which extends far beyond the chemistry of such ions[1,67]. Polyfluorinated arenonium ions undergo several types of isomerisation. In Section II we have already mentioned their reversible isomerisation, involving successive addition and detachment of a fluoride anion with intermediate formation of polyfluorinated dihydro-aromatic compounds. Isomeric polyfluorinated naphthalenonium ions containing the sp^3-hybridised site and the substituent other than fluorine in different rings undergo analogous interconversions. These processes take place under appreciably more severe conditions than does isomerisation in which the positions of the substituent and the sp^3-hybridised site vary within the same ring. The reason is obviously that addition of a fluoride anion to the benzene ring of a naphthalenonium ion entails complete loss of aromaticity[17–19] (Scheme 9).

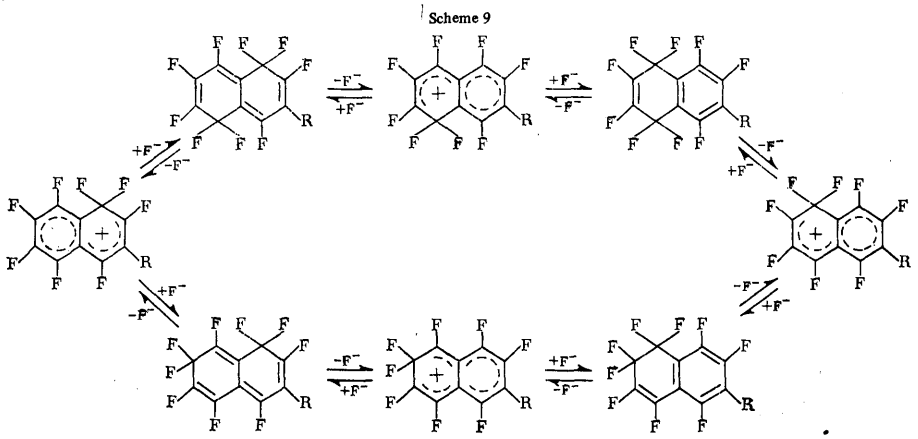
The investigation of such processes broadens significantly our ideas on the thermodynamics of polyfluorinated naphthalenonium ions. Thus 6-X-octafluoronaphthalen-1-onium ions in which X = CH_3, H are completely converted into the corresponding 3-X-isomers[17,18], but with X = C_6F_5 the equilibrium ratio 3-X : 6-X = 2 : 1 is established[19]. When X = Cl, Br, the substituent is also located preferentially at a β-position in the cyclohexadienyl fragment—not in the benzene ring—of the polyfluorinated naphthalene-1-onium ion[17]. In all these cases transfer of the substituent X from the benzene to the cyclohexadienyl ring is accompanied by the reverse migration of the fluorine atom, which, situated *ortho* or *meta* in the cyclohexadienyl fragment, is the most destabilising of the substituents examined (see data in subsection 2 on relative stabilising effects of substituents at individual positions in polyfluorinated benzenonium ions). Therefore the thermodynamic relations displaced in these examples can obviously be linked with the greater effect, on the relative stability of the ion, of substituents present in the cyclohexadienyl fragment than of those located in the benzene ring.

Somewhat different relations hold when a substituent other than fluoro occupies an α-position in a polyfluorinated naphthalenonium ion. For example, the perfluoro-4-phenylnaphthalen-2-onium ion passes into the perfluoro-8-phenylnaphthalen-1-onium ion, as is indicated by the isolation of dodecafluoro-1,4-dihydro-5-phenylnaphthalen-1-one from the products of hydrolysis of the reaction mixture[21]:



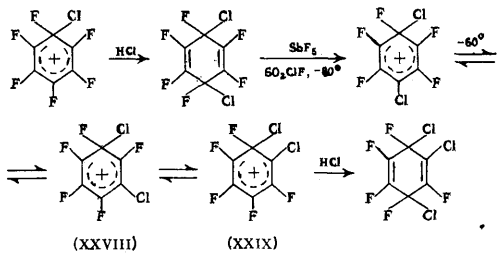
The first example of migration of a geminal substitutent in polyfluorinated arenonium ions was observed in those formed by addition of a proton to an unsubstituted carbon atom in fluorobenzene, *o*- and *p*-difluorobenzenes, and also 1,2,3,4-tetrafluorobenzene. These processes involve those isomers between which transition can be achieved only by 1,2-migration of a hydrogen atom from one unsubstituted ring position to another. The temperature conditions under which changes due to these intramolecular processes are detected in the n.m.r. spectra indicate that 4-mono- and 3,4-di-fluorobenzenonium ions are considerably more stable than their isomers[7]. Such a substantial difference in ease of occurrence of individual stages in 1,2-migration of a hydrogen atom as occurs with protonated fluorobenzenes is not observed with toluene and *o*-oxylene. This is because differences in energy between isomeric benzenonium ions distinguished by the position of a methyl group in the unsaturated part of the ion are not so large as with isomers differing in the position of a fluorine atom[7].

Scheme 9



Recent years have seen the discovery of isomeric changes in arenonium ions involving migration of various electronegative heteroatomic groups corresponding to active attacking species in electrophilic reactions of aromatic compounds[1,68]. A series of polyfluorinated arenonium ions have undergone isomerisation as a result of migration of a chlorine atom, which, unlike the proton in the above examples, is able to pass from one to another geminal position relative to a fluorine atom. Thus the 1,4-dichloropentafluorobezenonium ion, generated as in Scheme 10, is converted with rise in temperature of the solution from −80 to −60 °C into a mixture of 1,4-, 1,3-, and 1,2-dichloropentafluorobenzenonium ions (5%, 62%, and 33% respectively). Treatment of this mixture with hydrogen chloride yields 1,3,6-trichloropentafluorocyclohexa-1,4-diene[69] (Scheme 10).

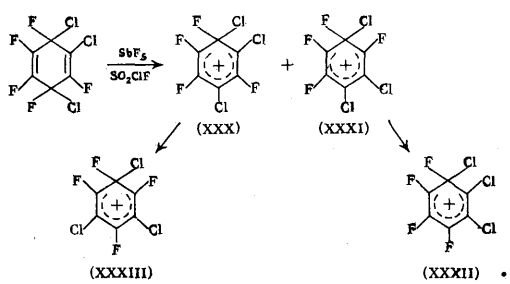
Scheme 10



(XXVIII) (XXIX)

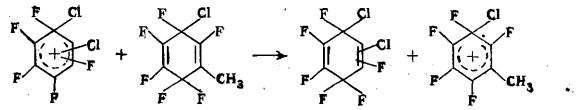
Reaction of this diene with antimony(V) fluoride in sulphuryl chloride fluoride at −90 °C yields not only the primary products of detachment of a fluoride anion—1,2,4- and 1,3,4-trichlorotetrafluorobenzenonium ions (XXX) and (XXXI)—but also two other ions, the 1,2,3- and 1,3,5-trichlorotetrafluorobenzenonium ions (XXXII) and (XXXII), having a different relative arrangement of chlorine atoms than in the original diene (Scheme 11). With rise in temperature to −70 °C the signals of the initially formed ions (XXX) and (XXXI) disappear from the ^{19}F n.m.r. spectrum of the solution, and only those of their isomerisation products (XXXII) and (XXXIII) in the proportions 1 : 1.3 remain. It is interesting that these two ions are extremely stable: right up to −30 °C they are not converted into isomers having two fluorine atoms at the sp^3-hybridised site[36], in contrast to other polyfluorinated benzenonium ions containing chlorofluoromethylene as geminal group (Section II). This may be due to improvement in the stability of polyfluorinated arenonium ions relative to their cyclohexadiene precursors as fluorine atoms in the unsaturated part of the ion are replaced by chlorine atoms, with a consequent raising of the energy barrier to addition of a fluoride anion at resonance positions in the arenonium ion.

Scheme 11



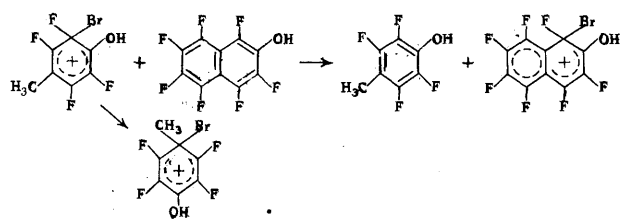
(XXXIII) (XXXII)

In the above cases isomerisation apparently occurs by intramolecular migration of a chlorine atom. This is indicated by absence of transfer of chlorine to pentafluorotoluene or pentafluorobenzene added to the reaction medium under conditions for isomerisation of the dichloropentafluoro- and trichlorotetrafluoro-benzenonium ions, although both additives are chlorinated by a mixture of molecular chlorine and antimony(V) fluoride in sulphuryl chloride fluoride, with formation respectively of the 1-chloro-3-methylpentafluorobenzenonium ion[14] and chloropentafluorobenzene[35]. The absence of such transfer to added pentafluorotoluene cannot be attributed to displacement of the equilibrium towards the ions (XXVIII)–(XXXIII), since addition of 3-chloro-1-methylhexafluorocyclohexa-1,4-diene to a solution containing the ions (XXVIII) and (XXIX) shifts the equilibrium towards an ion that is a chlorination product of pentafluorotoluene[69]:

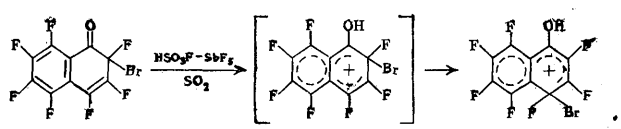


This result was to be expected from the relations elucidated[15] between the stabilising effects of halogen atoms and the methyl group as substituents in polyfluorinated arenonium ions.

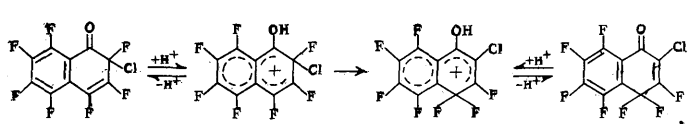
In contrast to this, conversion of the 1-bromo-1,3,4,6-tetrafluoro-2-hydroxy-5-methylbenzenonium ion into the 1-bromo-4-hydroxy-1-methyl isomer occurs most probably by intermolecular migration of the bromine atom, since addition of heptafluoro-2-naphthol yields the 1-bromoheptafluoro-2-hydroxynaphthalen-1-onium ion and tetrafluoro-*p*-cresol[27]:



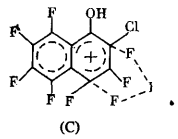
In an attempt to protonate 2-bromoheptafluoro-1,2-dihydronaphthanlen -1-one in the $HSO_3F–SbF_5–SO_2ClF$ system between −70 and −40 °C formation of the corresponding 1-hydroxynaphthalen-2-onium ion could not be observed at all. Its isomer—the 1-bromoheptafluoro-4-hydroxynaphthalen-1-onium ion—was detected, undoubtedly as a consequence both of the greater stability of the naphthalen-1-onium than of the naphthalen-2-onium ion and of the ease of migration of the bromine atom[27]:



It is interesting that the 2-chloroheptafluoro-1-hydroxynaphthalen-2-onium ion, corresponding to protonation of 2-chloroheptafluoro-1,2-dihydronaphthanlen-1-one, could be detected. This also isomerises into the more stable 4-hydroxynaphthalen-1-onium ion, not by migration of the chlorine atom, as might have been expected from the relative tendencies of chloro- and fluoro-aromatic compounds to undergo isomerisation[67], but formally by transfer of a fluorine atom[27]:



This process is due to isomerisation either of the ion or of the precursor in equilibrium with it, apparently by a specific mechanism[70] involving hydrogen fluoride and a cyclic transition state of the type



(C)

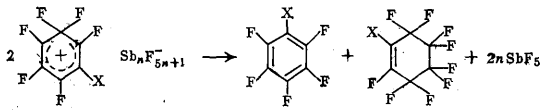
Thus known processes involving the isomerisation of polyfluorinated arenonium ions are at present limited to the transfer of hydrogen, chlorine, and bromine atoms. Apparently only in the case of the chlorine atom does intramolecular migraton occur from one position occupied by a fluorine atom to another. Determination of the relative tendencies of various groups to migrate for arenonium ions in the broad sense is important for interpreting the factors responsible for the orientation observed in reactions of aromatic compounds with electrophilic agents.

The most thoroughly studied reactions of this type in polyfluoro-aromatic compounds are those with nitrating agents, during which attack by the nitronium cation can be directed either at an unsaturated position in the aromatic ring or at those occupied by various substituents, including fluoro[3]. In this connection special interest attaches to the ability of a nitro-group to migrate "around the framework of the polyfluorinated molecule", a problem whose solution is prevented by the lack of methods for generating stable arenonium ions containing geminal fluorine atom and nitro-group at the sp^3-hybridised site. The only known fluorine-containing arenonium ion corresponding to addition of a nitronium cation to the aromatic ring—the 2,4,6,-trifluoro-1,3,5-trimethyl-1-nitrobenzenonium ion—exhibits no tendency to undergo rearrangement, whereas its completely methylated analogue—the hexamethyl-1-nitrobenzenonium ion—readily automerises as a result of intramolecular migration of the nitro-group[30]. The absence of rearrangement in the former case is apparently due to the significantly lower stability of the isomer corresponding to addition of the nitronium cation to trifluoromesitylene at a position occupied by a fluorine atom: this results in a considerably lower activation barrier to movement of the nitro-group from a position occupied by a methyl group to a neighbouring position.

4. Transformations of Polyfluorinated Arenonium Ions in the presence of or in Antimony(V) Fluoride

Progress made during recent years in the development of methods for generating arenonium ions under "long life" conditions not only has extended the possibility of solving various theoretical problems associated with the properties of these species but has also enabled their synthetic utilisation to be envisaged. In this category we can include results obtained in studying the reactions of polyfluorinated arenonium ions in the presence of or in antimony(V) fluoride.

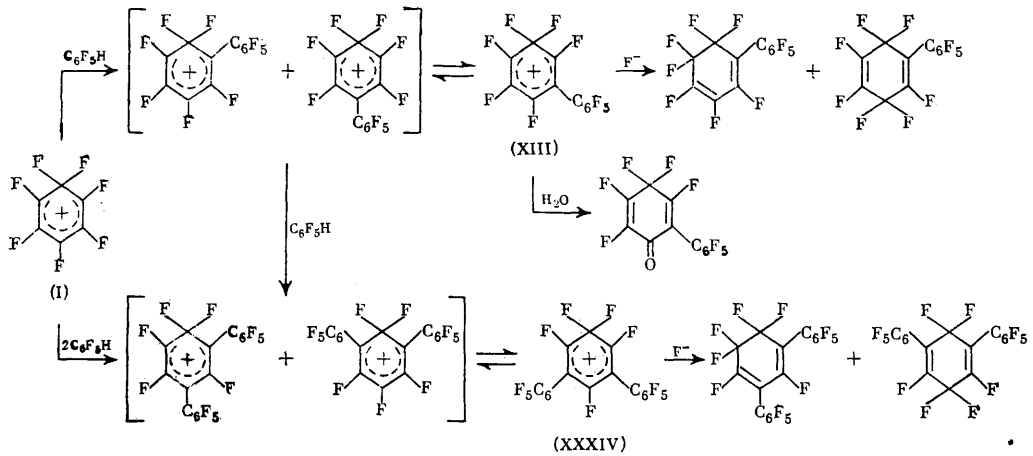
Perhaps the most interesting feature of these reactions is the capacity of polyfluorinated arenonium ions in many cases to undergo aromatisation by formal removal of a fluorine cation from the sp^3-hybridised site. Thus heptafluorobenzenonium hexafluoroantimonate disproportionates in solution to form equal quantities of hexafluorobenzene and decafluorocyclohexene[71]. Perfluoro-3-phenylbenzenonium hexafluoroantimonate undergoes an analogous transformation, but in this case the reaction is apparently complicated by fluorination by antimony(V) fluoride of phenylcyclohexadiene present in equilibrium with the benzenonium ion, so that perfluorophenylcyclohexene predominates over perfluorobiphenyl among the reaction products[19]:



X = F, C_6F_5

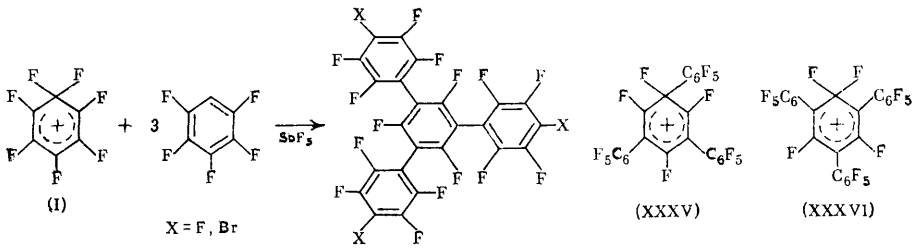
Aromatisation of polyfluorinated arenonium ions has been observed also when they react with partly fluorinated aromatic compounds in antimony(V) fluoride. Reaction of the ion (I) with one equivalent of pentafluorobenzene yields the perfluoro-3-phenylbenzenonium ion (XIII) [Scheme 12]. A mechanism has been suggested involving electrophilic attack on pentafluorobenzene by the most electrophilic centre in the heptafluorobenzenonium ion—the *p*-carbon atom—followed by a series of interconversions of polyfluorinated phenylated cyclohexadienes and benzenonium ions[19]. Addition of a second equivalent of pentafluorobenzene to (XIII) or interaction of (I) with two equivalents of pentafluorobenzene yields the perfluoro-3,5-diphenylbenzenonium ion (XXXIV).

Scheme 12



(XXXIV)

Scheme 13



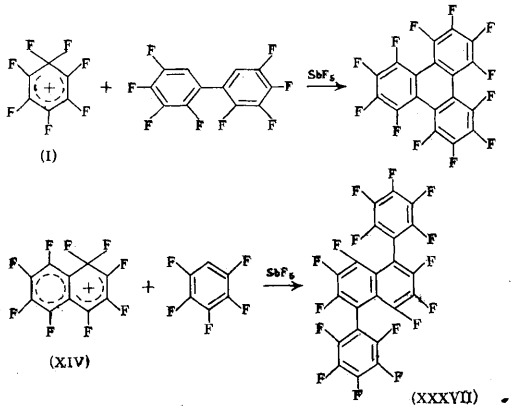
The structure of the latter indicates that the second equivalent probably interacts not with (XIII) but with the perfluoro-2-phenylbenzenonium ion, present in low concentration in equilibrium with (XIII), after which the reaction proceeds by a mechanism similar to that suggested to explain formation of the ion (XIII). Hydrolysis of solutions of salts of arenonium ions generated in this way or their dilution with sulphur dioxide yields polyfluorinated phenylated cyclohexadienones or cyclohexadienes respectively[72].

When the ion (I) is treated with three or more equivalents of pentafluorobenzene in antimony(V) fluoride, formation neither of any arenonium ions containing three or more pentafluorophenyl groups nor of compounds corresponding to hydrolysis of these species or their capture by a fluoride anion can be detected. Furthermore, perfluoro-1,3,5-triphenylbenzene is obtained in yields up to 70%. This apparently means that entry of a third pentafluorophenyl group is immediately followed by rapid aromatisation of the cyclohexadienyl fragment of one of the perfluorophenylbenzenonium ions (XXXV) and (XXXVI), a process distinct from the above disproportionation of the hexafluoroantimonates of the ions (I) and (XIII).

The ion (I) reacts similarly with 1-bromo-2,3,5,6-tetrafluorobenzene. Of the two most probable precursors of a polyfluorinated 1,3,5-triphenylbenzene—ions of types (XXXV) and (XXXVI) (Scheme 13)—the former is prefered, since its structure corresponds to the tendency of the pentafluorophenyl group to occupy a *meta*-position in the unsaturated part of the ion. Furthermore, no aromatisation processes other than the above disproportionation have been observed for benzenonium ions containing two fluorine atoms attached to the sp^3-hybridised carbon atom, which include ions of type (XXXVI).[72]

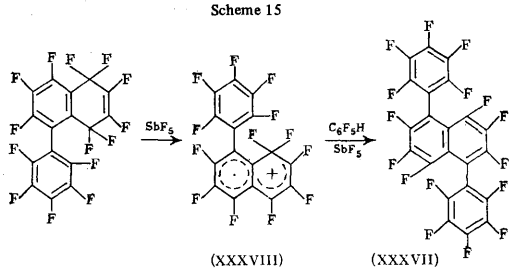
Reactions of this type are obviously of interest as routes for the synthesis of difficultly accessible polyfluorinates polycyclic aromatic compounds. This is illustrated by the syntheses of perfluorotriphenylene from (I) and 2,2',3,3'4,4',5,5'-octafluorobiphenyl[72] and of perfluoro-1,5-diphenylnaphthalene (XXXVII) from the perfluoronaphthalen-1-onium ion (XIV) and pentafluorobenzene[21,73] [Scheme 14].

Scheme 14

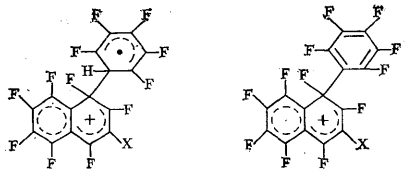


The second reaction apparently involves electrophilic attack on pentafluorobenzene by the 4-carbon atom in (XIV), followed by a series of isomeric conversions of polyfluorinated phenylnaphthalenonium ions yielding the perfluoro-8-phenylnaphthalene-1-onium ion (XXXVIII). This reacts with a second equivalent of pentafluorobenzene to form the compound (XXXVII). The reality of this transformation is confirmed by the formation of (XXXVII) by the action of pentafluorobenzene on the precursor of the ion (XXXVIII)—perfluoro-1,4-dihydro-5-phenylnaphthalene (Section II)—in the presence of antimony(V) fluoride[21] (Scheme 15).

Scheme 15



Those of the isomeric ions in which a fluorine atom and a pentafluorophenyl group are geminal substituents are probably responsible for aromatisation of the cyclohexadienyl fragment in polyfluorinated arenonium ions during the above reactions. This hypothesis has found some support in the formation of polyfluorinated 1-mono- and 1,5-di-phenylnaphthalenes also in the reactions of stable radical-cations of 2-X-heptafluoronaphthalenes (X = F, H, CH_3) with pentafluorobenzene[21] and with tetrafluorobenzenes[74] in antimony(V) fluoride. In terms of the schemes usually employed to describe the oxidative condensation of aromatic compounds involving radical-cations these reactions suggest, in view of the orientation for X = H, CH_3 (cf. data in Section II on relative stabilities of isomeric polyfluorinated arenonium ions containing these substituents), intermediate formation of species of type (XXXIX) and/or (XL), with the former perhaps being converted into the latter[21].



Examples of the reactions of polyfluorinated arenonium ions given in the present Review form only a small fraction of the results illustrating the opening of a new chapter in organic synthesis with the development of methods for generating and studying the properties of stable carbocations. The ensuing possibilities are difficult to overestimate, and at the present time we are witnessing the initial stage of their realisation.

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