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FLUORINE-CONTAINING CARBOCATIONS*.
II. POLYFLUORINATED BENZYL CATIONS

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Summary

When dissolved in SbF_5, polyfluorinated trifluoromethylbenzenes produce polyfluorinated α,α-difluorobenzyl ions. The ^{19}F chemical shifts and spin–spin coupling constants $J(FF)$ have been analysed in terms of the resonance structures which contribute to the overall positive charge distribution. The influence of halogen atoms situated at position 4 on the downfield signal shift of α-fluorines follows the sequence $F > Cl > Br$ which is opposite to that observed for $4\text{-}XC_6H_4CF_2^+$ ions.

Introduction

To date only a small number of polyfluorinated arylcarbonium ions have been described, *i.e.* 2,3,4,5,6-pentafluorobenzyl [1], bis(pentafluorophenyl)methyl [1] and perfluorotriphenylmethyl [1, 2]. Ions of this type are of considerable interest as models for studying the interaction of various substituents with an electron-deficient centre *via* a polyfluorinated aromatic system.

One possible method of generating polyfluorinated α,α-difluorobenzyl ions is the reaction of polyfluorinated trifluoromethylbenzenes with a strong Lewis acid, *e.g.*, antimony pentafluoride. However, by analogy with other work [3], this reaction could also produce the respective cation-radicals as a result of the one-electron oxidation of perfluorinated trifluoromethylbenzenes. With this background, the spectral properties of solutions of some poly fluorinated trifluoromethylbenzenes (I)(a)–(f), (h), (i) and α-*H*-heptafluorotoluene (I)(g) in antimony pentafluoride have been studied.

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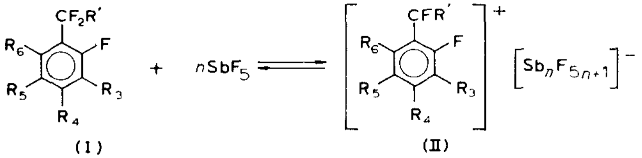
*For Part I, see ref. 10.

Results

It has been shown that freshly prepared solutions contain no paramagnetic species in sufficient quantities for their detection by ESR spectroscopy. At the same time, the NMR spectra of these solutions are sufficiently well resolved to enable the assignment of polyfluorinated benzyl cations (II)(a)–(i).



(a): $R' = R_3 = R_4 = R_5 = R_6 = F$

(b): $R' = R_3 = R_5 = R_6 = F$; $R_4 = Cl$

(c): $R' = R_3 = R_5 = R_6 = F$; $R_4 = Br$

(d): $R' = R_3 = R_5 = R_6 = F$; $R_4 = CH_3$

(e): $R' = R_3 = R_5 = R_6 = F$; $R_4 = H$

(f): $R' = R_3 = R_4 = R_5 = F$; $R_6 = H$

(g): $R_3 = R_4 = R_5 = R_6 = F$; $R' = H$

(h): $R' = R_4 = R_5 = R_6 = F$; $R_3 = CF_3$

(i): $R' = R_4 = R_6 = F$; $R_3 = R_5 = CF_3$

Figures 1 - 4 illustrate the ^{19}F NMR spectra of the ions (II)(a), (d), (f) and (g) as examples. The parameters of the ^{19}F and ^{1}H NMR spectra of the ions generated are listed in Table 1 (δ_F = shift relative to external C_6F_6, $\Delta\delta_F$ = shift relative to the signal of the respective fluorine atom in the spectrum of the precursor solution in CCl_4).

In assigning the signals in the ^{19}F NMR spectra, account was taken of the fact that in the majority of spectra arising from polyfluoroaromatic compounds the signals from fluorine atoms with neighbouring fluorines in the *ortho* position are located upfield relative to the signals from fluorine atoms with non-fluorine substituents [4] as neighbours.

The ^{19}F NMR spectra of all the ions generated are characterised by the presence of downfield signals relating to the α-fluorines. The observed values of δ_F and $\Delta\delta_F$ agree with those for the $C_6H_5CF_2^+$ ion [1]. The signals from all the fluorine atoms in the aromatic nucleus are shifted downfield in going from the precursors to the ions, the absolute values of $\Delta\delta_F$ decreasing in the following sequence: $F = 4 > F = 2(6) > F = 3(5)$* in agreement with the data on the $C_6F_5CH_2^+$ ion [1]. The observed sequences for δ_F and $\Delta\delta_F$ are in agreement with fluorine participation in the delocalisation of the positive charge in the perfluorinated benzyl cation giving rise to the resonance structures (A), (B) and (C), whose relative contributions to the overall structure follows the sequence (A) > (B) > (C).

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*Here and elsewhere the fluorine atoms are designated by the numbers of the respective carbon atoms.

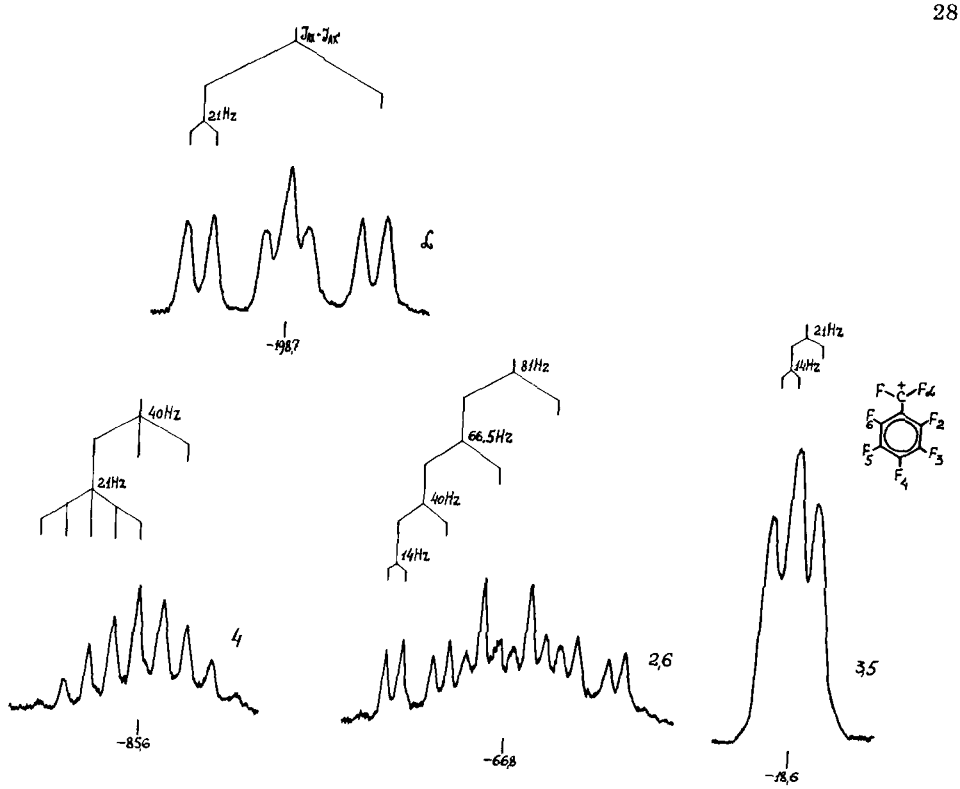


Fig. 1. ^{19}F NMR spectra of a solution of a salt of the ion (II)(a) in SbF_5. (Here and elsewhere the fluorine atoms are designated by the numbers of the respective carbon atoms.)

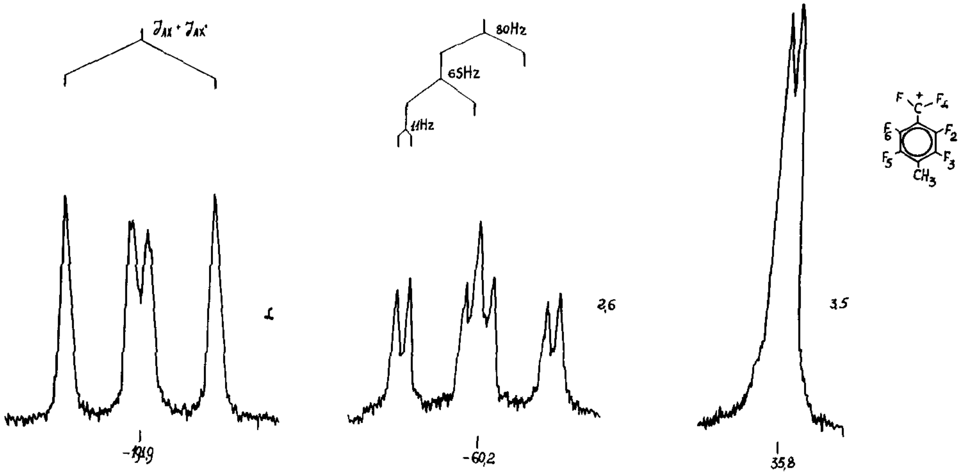


Fig. 2. ^{19}F NMR spectra of a solution of a salt of the ion (II)(d) in SbF_5.

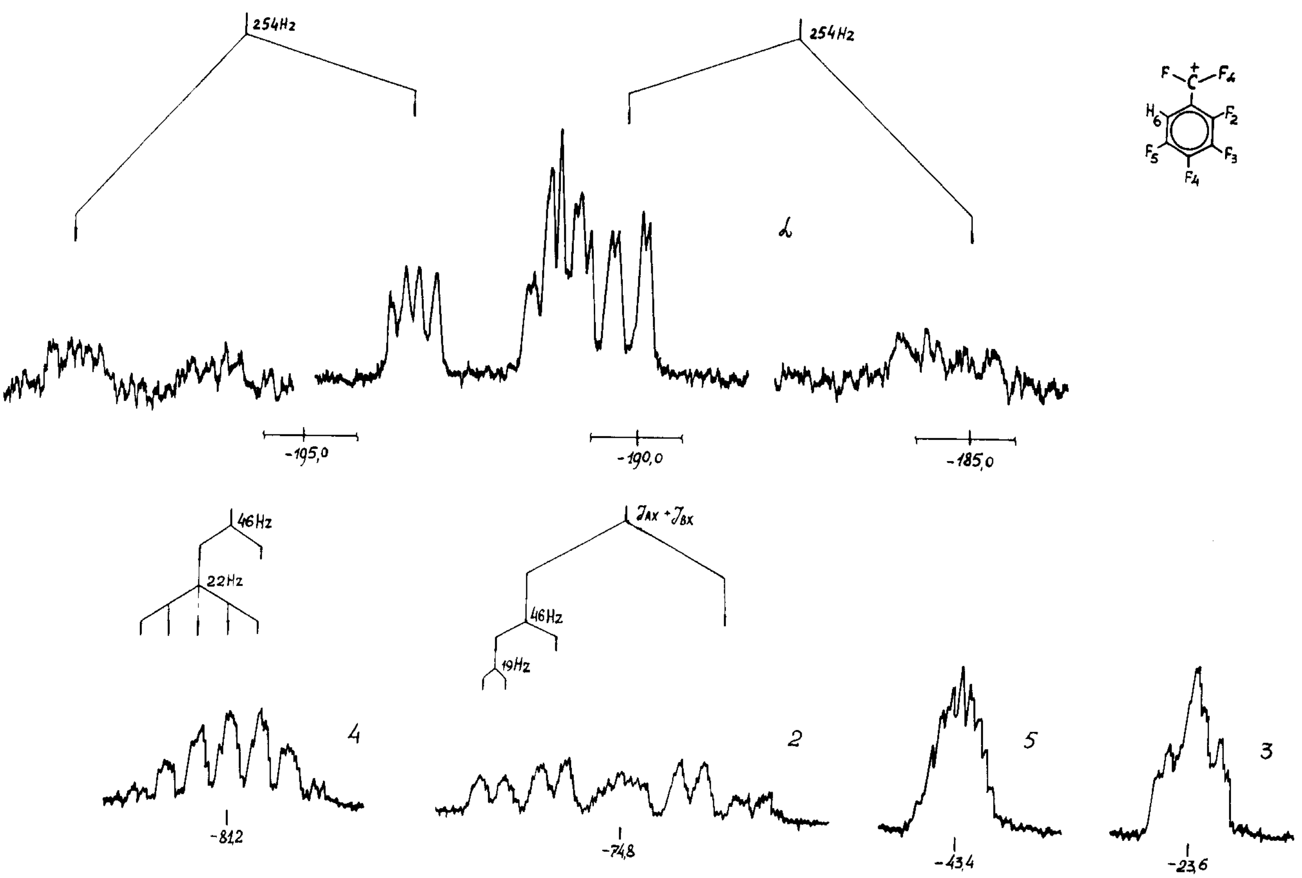


Fig. 3. ^{19}F NMR spectra of a solution of a salt of the ion (II)(f) in SbF_5. (The outer components of the signal attributable to the CF_2 group have been recoded under conditions of larger gain.)

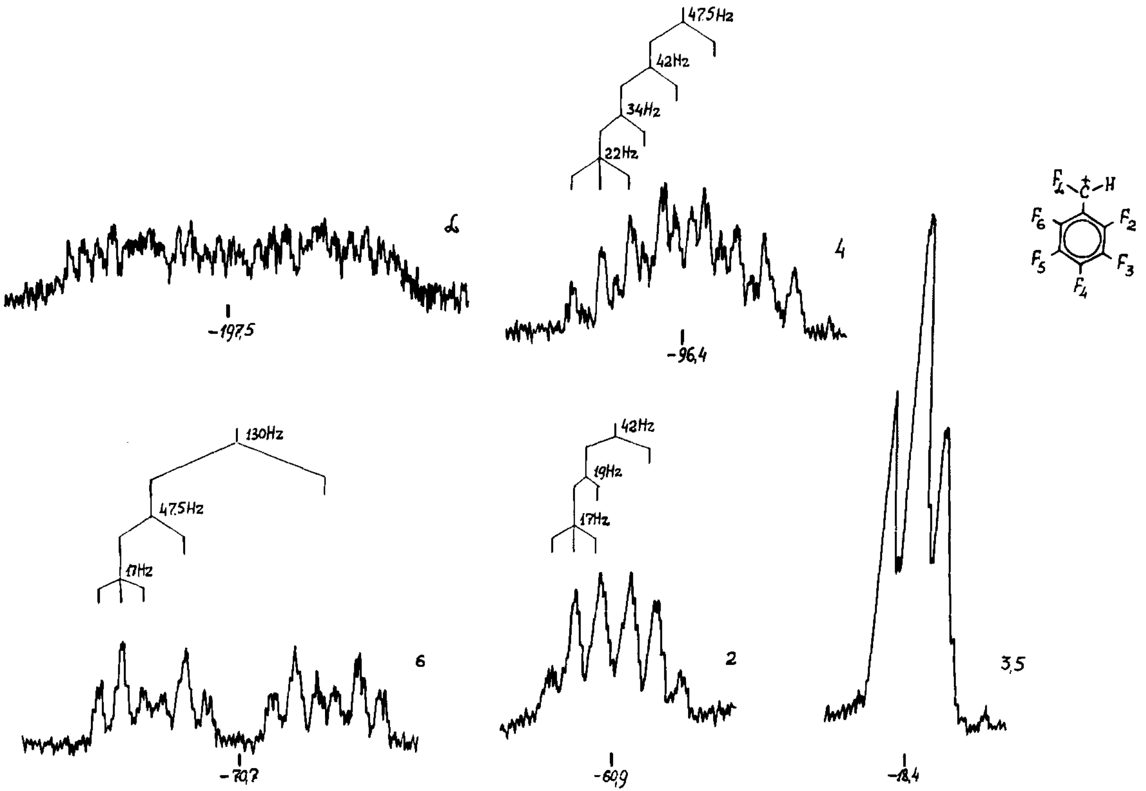


Fig. 4. ^{19}F NMR spectra of a solution of a salt of the ion (II)(g) in SbF_5.

TABLE 1

Characteristics of the ^{19}F and ^{1}H NMR spectra of polyfluorinated benzyl cations

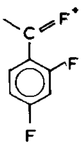
Ion	Downfield chemical shifts from external C_6F_6 and TMS/ppm						Changes in chemical shift in going from precursor* to ion						Absolute values of the spin–spin coupling constants/Hz
	δ_2	δ_3	δ_4	δ_5	δ_6	δ_α	$\Delta\delta_2$	$\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$	$\Delta\delta_6$	$\Delta\delta_\alpha$	
(II)(a)	66.8	18.6	85.6	18.6	66.8	198.7	−43.9	−16.1	−70.5	−16.1	−43.9	−92.8	$J(AX) + J(AX')$** = 147.5; $^{\alpha,4}J(FF) = 21$; $^{3,4(4,5)}J(FF) = 21$; $^{2,4}J(FF) = 40$
(II)(b)	62.0	38.3		38.3	62.0	197.0	−38.2	−14.5		−14.5	−38.2	−91.4	$J(AX) + J(AX') = 147.5$
(II)(c)	60.6	46.2		46.2	60.6	196.1	−37.4	−15.1		−15.1	−37.4	−90.7	$J(AX) + J(AX') = 146.0$
(II)(d)	60.2	35.8	3.12	35.8	60.2	191.9	−39.6	−15.2	−0.74	−15.2	−39.6	−86.2	$J(AX) + J(AX') = 145.0$
(II)(e)	64.7	41.1	9.10	41.1	64.7	204.6	−42.5	−15.3	−2.15	−15.3	−42.5	−99.2	$J(AX) + J(AX') = 155.0$
(II)(f)	74.8	23.6	81.2	43.4	8.75	194.1 190.1	−50.9	−13.6	−67.4	−17.4	−1.40	−92.1 −88.1	$J(AB) = 254$; $J(AX)$*** = 117; $J(BX)$*** = 31; $^{\alpha,4}J(FF) = 22$; $^{2,4}J(FF) = 46$; $^{3,4}J(FFF) = {}^{4,5}J(FF) = 22$.
(II)(g)	60.9	18.4	96.4	18.4	70.7	197.5**** 9.9	−41.2	−16.6	−83.1	−16.6	−51.0	−148.0**** −3.4	$J(HF) = 60$; $^{\alpha,6}J(FF) = 130$; $^{\alpha,2}J(FF) = 19$; $^{2,4}J(FF) = 42$; $^{4,6}J(FF) = 47.5$; $^{\alpha,4}J(FF) = 34$; $^{3,4}J(FF) = {}^{4,5}J(FF) = 22$
(II)(h)	95.2	108.6	105.4	18.1	76.9	200.6	−47.0	−3.2	−69.7	−15.5	−41.2	−95.2	$^{2,3}J[F(CF_3)] = {}^{3,4}J[F(CF_3)] = 25$
(II)(i)	104.2	108.6	127.2	108.6	104.2	203.3	−42.1	−2.6	−65.1	−2.6	−42.1	−97.3	$J(AX) + J(AX') = 163.0$; $^{\alpha,4}J(FF) = 15$; $^{2,3}J[F(CF_3)] = {}^{3,4}J[F(CF_3)] = 25$

*15 mole % solutions in CCl_4.

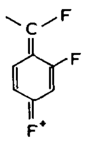
**Measured here and elsewhere for the α-F and *ortho*-F atoms in the AA'XX' sub-system.

***Measured for the α-F and *ortho*-F atoms in the ABX sub-system.

****For the α-F and α-H atoms respectively.



(A)



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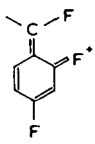

(C)

The observed values of $\Delta\delta_H$ for cations (II)(d), (e), (f), and (g) are close to these for the ions $C_6(CH_3)_5CH_2^+$ [5], $C_6H_5CF_2^+$ [1] and $C_6F_5CH_2^+$ [1].

The values of the spin–spin coupling constants for the ^{19}F NMR spectra of the ions (II)(a)–(i) are characterised by the fact that J(FF) values for fluorine atoms effectively participating in positive charge delocalisation (*i.e.* α-F, F = 2 and F = 4) are considerably greater than the corresponding values for the respective fluorines in the neutral precursors. Thus, $^{\alpha,4}J$(FF) = 1.5 Hz for perfluorotoluene [6] while $^{\alpha,4}J$(FF) = 15 - 34 Hz for the ions (II)(a), (f)–(i) ($^{\alpha,4}J$(FF) = 19.8 Hz for the α,α,4-trifluorobenzyl cation [1]). The coupling constant for F = 2(6) and F = 4 [$^{2(6),4}J$(FF)] has a value of 40 - 47.5 Hz, while ^{meta}J(FF) for polyfluorobenzenes does not usually exceed a value of 10 Hz [7]. A similar sharp increase in the value of $^{2,4}J$(FF) relative to those observed for neutral polyfluoroaromatic compounds has also been observed for the polyfluorinated benzonium ions [8 - 10].

In the case of the ion (II)(g), the value of ^{gem}J(FF) for the coupling between α = H and α = F was found to be equal to 60 Hz, close to the value of 53 Hz observed for the neutral precursor (I)(g) [11]. The values of J(HF) for the ions (II)(d)–(f) have not been determined due to difficulty in resolving the signal.

Two values of $^{\alpha,ortho}J$(FF) for the coupling between *ortho*-F and α-F atoms has been observed for the ions (II)(a)–(e) and (II)(i). In fact, the *ortho*-F and α-F atoms of these ions form an AA′XX′ sub-system. The resonances arising from the CF_2 groups in the spectra of the ions (II)(a)–(e) appear as approximate 1:1:1:1 quartets (additional doublet splitting occurs in the resonance of the CF_2 group in the spectrum of the ion (II)(a) due to coupling with the *para*-F atom). The spacing between the terminal transitions gives the value of J(AX) + J(AX′)*. This result may be a consequence of hindered rotation about the α-C— C-1 bond. This is also supported by the complex pattern of signals arising from the CF_2 groups of the ions (II)(f) and (h) which is attributed to the difference in the δ_F values for the two α-F atoms and to the presence of a large number of non-equivalent nuclei. The two α-F and *ortho*-F atoms of the ion (II)(f) form an ABX sub-system whose analysis gives the two values of 117 and 31 Hz for $^{\alpha,ortho}J$(FF), the interaction of two α-F atoms being characterised by a ^{gem}J(FF) value of 254 Hz. This value is

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*Evaluation of the exact value of J(AX) and J(AX′) was not possible as the spacing between the internal transitions of the AA′ quartet may not be equal to J(AX) — J(AX′) (according to an analysis of the AA′XX′ system performed elsewhere [12]). The effective values of doublet splittings corresponding to the interactions between the α-F and *ortho*-F atoms in the ion (II)(a) have been reported previously [29].

considerably higher than the values for the corresponding neutral species where the fluorine atoms are bound to a sp^2-hybridised carbon atom. Thus, the geminal fluorine atoms attached to the double bond of a fluorinated olefin exhibit a ^{gem}J(FF) value equal to 16 - 87 Hz [13]. For the ion (II)(h), the difference between the δ_F values for the α-F atoms is small and the outer components of the AB system cannot be detected because of their low intensity. The difference between the δ_F values for the *ortho*-F atoms in the ion (II)(g) is also indicative of the hindered rotation of the CFH group about the benzene ring.

When perfluorinated *o*- and *p*-xylenes are dissolved in SbF_5, the respective benzyl cations are produced but not in quantities sufficient to enable their observation by means of an NMR detecting technique. This indicates that the *ortho*- and *para*-CF_3 groups in the polyfluorinated benzyl cation system generate a destabilising effect.

Discussion

An analysis of the values of δ_F, $\Delta\delta_F$ and J(FF) in the systems studied is of considerable interest as these values appear to be closely associated with the character of the π-electron distribution in the ions (II)(a)–(i). A definite relationship is known to exist between the effects of the substituents on δ_F values for the fluorine atoms in a π-system and the participation of these substituents in conjugation, π-electron charge delocalisation [14, 15] and stabilisation [16]. However, interaction between substituents with electron-deficient centres has not been studied in polyfluorinated systems and for this reason a discussion of the observed values of δ_F and $\Delta\delta_F$ for the ions studied here would seem important.

Direct comparison between the values of $\Delta\delta_F$ for α-F atoms, on the one hand, and those in the benzene ring, on the other hand, is not possible because the corresponding fluorines in the precursors are bound to carbon atoms which are in different hybridisation states. However, the large observed δ_F values for α-F atoms seem to indicate that these atoms bear the major portion of the positive charge with participation of the fluorine atoms in charge delocalisation in the phenyl ring decreasing in the following sequence: *para*-F > *ortho*-F > *meta*-F.

The *para* substituents can be arranged in the sequences F > H > CH_3 > Cl > Br and H > F > Cl > Br > CH_3 from a comparison of the values of $\Delta\delta_F$ for *ortho*-F and α-F atoms respectively. In addition to the change in the π-electron charge at a particular fluorine atom, the value of $\Delta\delta_F$ may also be affected by such factors as a change in the electrostatic interaction and van der Waals' forces in passing from the precursor to the corresponding ion [4, 17], but in view of the fact that these factors rapidly decrease with increasing distance it is likely that the values of $\Delta\delta_F$ for α-F provide a more significant indication of the influence of substitution in the 4 position on charge delocalisation in the ion. In this event, the following sequence applies: CH_3 > Br > Cl > F > H.

In addition, it is significant that in both cases *para*-halogen participation in charge delocalisation is still characterised by the sequences Br > Cl > F, and F > H if the corresponding values of $\Delta\delta_{CF_2}$ are compared. However, for the ions $4\text{-}XC_6H_4CF_2^+$ the sequence F > Cl > Br > H has been found [1].

For diphenyloxylcarbonium ions, it is known that the effect of substitution in position 4 on the value of δ_F for the 4′-fluorine atom is linearly related to its effect on the stability of the ion [16], and it has been shown [1] on the basis of the influence of the X substituent on the value of δ_F for $4\text{-}XC_6H_4CF_2^+$ ions that the relative stability in this case follows the sequence F > Cl > Br > H. It is interesting to note in this connection that for ions of the type $4\text{-}XC_6H_4CF_2^+$ a good linear correlation occurs between the values of $\Delta\delta_F$ and σ_R^+ and σ_I [18] for X = H, F, Cl and Br, reflecting the respective resonance and inductive interaction of a substituent with an electron-deficient centre *via* the benzene ring, an interaction which is also governed by the equation $\Delta\delta_{CF_2^+} = -75.62 - 9.3(\sigma_R^+ - 0.08\sigma_I)$ ($r = 0.998, s = 0.25$). However, for the polyfluorinated benzyl cations studied in the present work, no satisfactory correlation was observed between $\Delta\delta_{CF_2^+}$ and either σ_R^+ and σ_I or σ^+ values [19] for the respective substituents in position 4.

The reason for this difference obviously lies in the fact that in going from the ions $4\text{-}XC_6H_4CF_2^+$ [1] to the ions $4\text{-}XC_6F_4CF_2^+$ the absolute values of $\Delta\delta_{CF_2}$ for the corresponding X substituents increase according to the series Br < Cl < F < H (see Table 2) which leads to the above-mentioned reversion in the order of halogen effects and leads to the exclusion of the data for X = Cl, Br from the correlation. It is possible that the electron-donating resonance effect of halogens substituted in position 4 increases in going from non-fluorinated to polyfluorinated benzyl cations because of the increasing "electron demand" of the π-system of the ions, the greatest response to this increase being observed for bromine and the smallest for fluorine (*cf.* refs. 20 and 21). In this connection it is interesting to compare the effect of these substituents on the value of $\Delta\delta_F$ for CF_2 groups in α,α-difluorobenzyl cations with their effect upon the stability of these ions as measured by other methods.

Comparison of the values of $\Delta\delta_F$ for the ions (II)(a) and (II)(h) shows that the substitution of a fluorine atom by a CF_3 group in the *meta* position leads to a decrease in the participation of the isolated *ortho*-F atom and increases the participation of the α-F atoms in charge delocalisation. The signal from the *para*-F atom of the (II)(h) ion is shifted downfield with respect to the corresponding signal in the spectrum of its precursor by about the same amount as occurs for the case of the (II)(a) ion. The signal of the *ortho*-F atom closest to the point of substitution is shifted even further downfield relative to the precursor signal than the corresponding signal for the (II)(a) ion. Account should, however, be taken of the fact that the position of signals arising from fluorine atoms adjacent to the point of substitution of fluorine by a CF_3 group is affected not only by the action of the latter group on the charge distribution in the π-system but also by the change in

TABLE 2

Changes in ^{19}F chemical shifts of the CF_2 group ($\Delta\delta_{CF_2}$) in going from precursors to ions

Ion	Chemical shift ($\Delta\delta_{CF_2}$)/ppm
$F_2\overset{+}{C}C_6F_4X$	
X = H	−99.2
X = F	−92.8
X = Cl	−91.4
X = Br	−90.7
$F_2\overset{+}{C}C_6H_4X$	
X = H	−75.62
X = F	−69.69
X = Cl	−72.10
X = Br	−72.32

the van der Waals' and electrostatic effects [4, 17] of this group in going from the precursor to the ion. The last two factors apparently cause a downfield shift in the signals of fluorine atoms adjacent to a CF_3 group, which in the case of an adjacent *ortho*-F is probably greater than the upfield shift resulting from the diminished contribution of the *ortho*-F atom to the charge delocalisation.

When the adjacent atom is a *para*-F these effects apparently cancel each other out. In going from the (II)(h) ion to the (II)(i) ion, substitution of a second *meta*-F atom by a CF_3 group leads to an additional transfer of positive charge from the ring to the CF_2 group which is apparent from a comparison of the $\Delta\delta_F$ values for the α-F ions (II)(a), (h) and (i). In this case, the decrease in the contributions of the *ortho*-F and *para*-F atoms to the charge delocalisation is now the deciding factor in determining the position of the signals from these atoms and this results in a decrease in the absolute value of $\Delta\delta_F$ for these fluorine atoms relative to those found for the (II)(a) ion. In addition, there is a considerable decrease in the $\Delta\delta_F$ value for the *para*-F atom which is in agreement with the effect of replacing a *meta*-F atom by a CF_3 group on the shielding of neighbouring fluorines, as occurs in the (II)(i) ion.

Substitution of the fluorine atom at position 4 by hydrogen leads to an increase in the extent of α-F participation in charge delocalisation, the contribution from the *ortho*-F atom remaining virtually constant as is demonstrated by a comparison of the values of $\Delta\delta_F$ for the α-F and *ortho*-F atoms of the ions (II)(a) and (II)(e). It is interesting that a similar replacement in position 2 [*cf.* the data for the ions (II)(a) and (f)] leads to an increase in the absolute value of $\Delta\delta_F$ only for F = 6, while signals from F = 4 and α-F even show somewhat smaller downfield shifts relative to those of the precursors. If the changes in values observed for α-F and *ortho*-F atoms could be connected, if only partially, to changes in the degree of coplanarity of the CF_2 group and benzene ring, it would be possible to conclude for F = 4 that its contribution towards delocalisaition of the positive charge is at least not increasing. Finally, substitution of fluorine by hydrogen at the α-carbon atom [*cf.* the data for the ions (II)(a) and (g)] leads to an increase in the absolute values of $\Delta\delta_F$ for the remaining α-F and F = 4 atoms as well as for one of the *ortho*-F atoms. In the case of the F = 4 atom, this is apparently indicative of an increased contribution of this atom towards charge delocalisation. It would be expected that the response of the α-F and *ortho*-F atoms to such a substitution would be similar but this cannot be stated positively since it is not possible to compare the $\Delta\delta_F$ values for these atoms in the ion (II)(g) with similar values for other ions. The change in the mutual effect of the α-F and *ortho*-F atoms on their shielding may be entirely different when a fluorine ion is eliminated from a CF_3 group on the one hand and from a CF_2H group on the other hand; furthermore, in the latter case, due to hindered rotation, one of the *ortho*-F atoms in the (II)(g) ion is nearer to the α-H atom rather than the α-F atom as in the remaining cases studied.

In order to elucidate the relationship between the ^{19}F NMR spectral parameters of polyfluorinated benzyl cations and the nature of their positive charge distribution, an analysis of the observed values of $J(FF)$ is of considerable interest. For polyfluorinated arenonium ions, the large values of $J(FF)$ for fluorine atoms participating effectively in charge delocalisation have been explained qualitatively in terms of the contribution of resonance structures where the fluorine atoms in question are involved directly in conjugation [10]. A similar qualitative explanation may be given for the large values of $J(FF)$ observed for the α-F, *ortho*-F and *para*-F atoms in ions of type (II), which as structures (A), (B) and (C) show, may be associated with the direct participation of these fluorine atoms in charge delocalisation and conjugation. Since the electronic effect of substituents can be interpreted qualitatively in terms of the contributions of the resonance structures (A), (B) and (C), towards the total structure, it is not unreasonable to expect that some relationship should exist between the nature of the substituent and the value of $\Delta\delta_F$ for α-F, *ortho*-F and *para*-F atoms, in addition to the association with $J(FF)$ coupling constants noted above. In particular, it might be expected that an increase in the donor character of the substituent at position 4 would be equivalent to an increase in the contribution of structure (B) towards the overall structure, leading to a decrease in the observed values of $J(FF)$ for the α-F and *ortho*-F atoms due to a decrease in the contributions of structures (A) and (C)*. The data listed in Table 1 show that a weak dependence exists between $J(AX) + J(AX')$ and the nature of the substituent at position 4 in the ions (II)(a)–

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*The observed increase in the values of $^{2,4}J(FF)$ for the neutral compounds C_6F_5X as the electron-withdrawing power of X is increased [14, 22] may be interpreted in a similar manner.

(e). Thus the sum of these coupling constants tends to decrease slightly as the donor character of the substituent at position 4 increases (as measured by its effect on the $\Delta\delta_F$ value for α-F); only in going from the ion (II)(e) to the remaining ions in the series is there any pronounced decrease. Account should be taken however of the following fact. It is difficult to explain the difference in the two values of $^{\alpha,ortho}J$(FF) observed for the same ion if it is assumed that the α-F and *ortho*-F atoms only interact *via* the bonds linking them since the bond distances between the α-F and two *ortho*-F atoms are equal. Furthermore, if coupling does occur through the bonds, the observed values of J(AX) + J(AX′) are too large. Thus, coupling between *ortho*-F and *para*-F atoms separated by the same number of bonds as the α-F and *ortho*-F atoms in the ions studied is characterised by a $^{2,4}J$(FF) value of 40 - 47.5 Hz, whilst it is unlikely that the contribution of coupling through bonds (contribution 1) to the value of $^{\alpha,ortho}J$(FF) is very large when the probable non-coplanarity of the benzene ring and the CF_2 group in the ions (II)(a)–(e) is taken into account. What is more likely is that coupling through space (contribution 2) is significant as far as the value of $^{\alpha,ortho}J$(FF) is concerned, and in fact because of this contribution values of $^{\alpha,ortho}J$(FF) as large as 100 Hz can be attained for neutral polyfluoroaromatic compounds [23, 24].

The relative importance of contributions 1 and 2 towards the magnitude of $^{\alpha,ortho}J$(FF) can be assessed from the results obtained for the ion (II)(g). The smaller of the two values obtained for this ion (~ 19 Hz) is attributable virtually completely to contribution 1, whereas the greater of the two values (130 Hz) is a reflection of the sum of contributions 1 and 2. The two contributions can in fact have the same signs. Thus, the value of $^{\alpha,ortho}J$(FF) has been found to be positive for the neutral compounds [24] while the interaction of *ortho*-F and *para*-F atoms, separated by the same number of bonds as the *ortho*-F and α-F atoms in the ions under investigation, is characterised by positive values of $^{2,4}J$(FF) for compounds of the type C_6F_5X, where X is an electron-withdrawing group [14, 22].

The existence of at least two spin-transfer mechanisms complicates the interpretation of the effect of substituents at position 4 on the value of $^{\alpha,ortho}J$(FF) for the ions (II)(a)–(e). In particular, an increase in the electron-donor character of a substituent should increase contributions 1 and 2 because of the greater coplanarity of the ion; at the same time it should somewhat decrease the magnitude of contribution 1 because the π-electronic character of the ion approaches that of structure (B). It is possible that there is mutual compensation between these two opposing effects and that the resulting moderate size of contribution 1 is mainly responsible for the apparent insensitivity of the values of J(AX) + J(AX′) for the ions (II)(a)–(e) towards the nature of the substituent at position 4. However, if such compensation occurs it is not complete since the changes observed do nevertheless correspond to the respective changes in the electronic effects of the substituent as far as these changes influence the relative importance of structures (A), (B) and (C).

The above considerations provide an adequate explanation for the changes observed in ${}^{\alpha,ortho}J$(FF) values for a series of polyfluorinated α-fluorodiphenylmethyl cations [25]. Increases in the value of ${}^{2,4}J$(FF) in going from the ion (II)(a) to the ions (II)(f) and (II)(g) apparently reflect the increased contribution of *ortho*-F and *para*-F atoms towards charge delocalisation when *ortho*-F or α-F atoms are substituted by hydrogen.

Experimental

Polyfluorinated benzyl cations were prepared using twice distilled SbF_5, b.p. 141 - 142 °C, as a solvent. Solution preparation and ampoule filling for recording the NMR spectra were carried out in a dry box.

The ${}^{19}F$ and ${}^{1}H$ NMR spectra were recorded using a Varian A56/60A spectrometer at 56.4 and 60 MHz, respectively. The concentrations of the solutions employed were 15 - 25 mole % and the temperature was varied from —10 °C to +40 °C in order to obtain the best resolution. The values of δ_F were measured at +10 °C using CF_2ClCF_2Cl as an internal reference and also calculated from the formula $\delta_F = 96.4 + \delta'_F$, where 96.4 ppm is the signal shift for the internal standard relative to that of C_6F_6 (external) and δ'_F is the observed signal shift from that of the internal standard employed. The errors involved in the measurements of the $J(AX) + J(AX')$ values corresponding to the α-F and *ortho*-F atoms in the AA'XX' sub-system were not greater than ±0.5 Hz and not greater than ±1 Hz for the other J values measured. The chemical shifts were accurate to ±0.2 ppm.

The precursors (I)(b)–(e) were prepared using the method of ref. 25, (I)(g) according to the method given in ref. 11 and (I)(h) and (I)(i) as described in ref. 26.

*The preparation of 2-*H*-heptafluorotoluene (I)(f)*

2,3,4,5-Tetrafluorobenzoic acid [27] (2.8 g), HF (0.5 g) and SF_4 (5 g) were heated together in a steel bomb at 165 °C for 22 h. Steam-distillation of the resulting product gave 2.5 g (80%) of 2-*H*-heptafluorotoluene, b.p. 100.5 - 101.5 °C (lit. value [28]: 102 - 105 °C).

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