Journal of Fluorine Chemistry, 4 (1974) 297 - 316

FLUORINE-CONTAINING CARBOCATIONS*. III. ALKYLATION OF POLYFLUOROBENZENES WITH POLYFLUORINATED α,α-DIFLUOROBENZYL CATIONS AND GENERATION OF POLYFLUORINATED α-FLUORODIPHENYLMETHYL CATIONS

Yu. V. POZDNYAKOVICH and V. D. SHTEINGARTS

Institute of Organic Chemistry, Siberian Division of the Academy of Sciences,
90 Novosibirsk (U.S.S.R.)

(Received July 25, 1973)

Summary

Alkylation of incompletely fluorinated benzenes with polyfluorinated α,α-difluorobenzyl cations in an SbF_5 medium results in the formation of polyfluorinated α-fluorodiphenylmethyl cations whose precursors are the primary products of alkylation, *i.e.* the corresponding polyfluorinated α,α-difluorodiphenylmethanes. The influence of substituents on the ^{19}F chemical shifts and spin–spin coupling constants $J(FF)$ has been analysed in terms of their effects on contributions of the resonance structures controlling the positive charge distribution and on the coplanarity of the phenyl rings and the plane of the α-carbon bonds.

Introduction

In the previous communication it was reported that dissolving polyfluorinated trifluoromethylbenzenes in SbF_5 resulted in the formation of polyfluorinated α,α-difluorobenzyl cations [1]. The possibility of using these ions in alkylation reactions is of interest, especially leading to the generation of polyfluorinated α-fluorodiphenylmethyl cations whose ^{19}F NMR spectra should provide information regarding substituent effects in polyfluorinated carbocations.

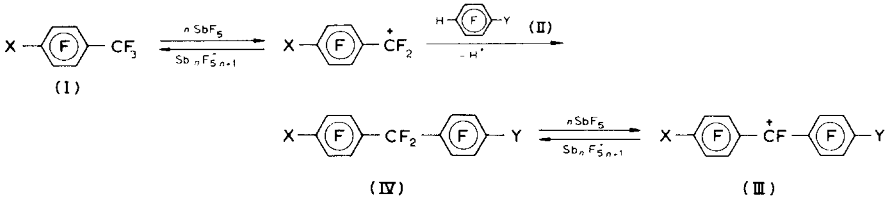
Results and discussion

Addition of one equivalent of a polyfluorinated benzene (II) to a solution of a polyfluorinated benzyl cation (I) in SbF_5 results in the formation of the corresponding polyfluorinated α-fluorodiphenylmethyl cation (III).

---

*For part II, see ref. 1.

The latter is apparently produced *via* the primary alkylation product, *i.e.* a polyfluorinated α,α-dufluorodiphenylmethane (IV). Use of excess of (II) does not result in its alkylation by the ion (III).



where X = H, F, Cl, Br, CH_3 and CF_3 respectively in (I) and Y = H, F, Cl, Br and CH_3 respectively in (II).

The ions (III)(X = F; Y = CF_3) and (III)(X = CH_3; Y = CF_3) may be generated by adding pentafluorobenzene and 2,3,5,6-tetrafluorotoluene respectively to a solution of perfluoro-*p*-xylene in SbF_5. This solution has been shown [1] to contain the cation $4\text{-}CF_3C_6F_4CF_2^+$ in amounts insufficient to enable its ^{19}F NMR spectrum to be recorded. Alkylation of compounds (II)(Y = F, CH_3) also probably points to the formation of small quantities of this cation.

The parameters of the ^{19}F and ^1H NMR spectra of the ions (III) are given in Table 1, where δ_F corresponds to a shift relative to C_6F_6 as an internal standard and $\Delta\delta_F$ corresponds to a shift relative to the signal of the respective fluorine atom in the spectrum of polyfluorinated α,α-difluorodiphenylmethane (IV), produced by pouring a solution of the salt of the ion (III) into HF [2]. In order to measure the values of δ_F (Table 1) solutions of the salts of the ions in SbF_5 were diluted 8 to 10-fold with SO_2. Figures 1 - 6 illustrate typical ^{19}F NMR spectra for solutions of the salts of the ions (III) (X = Y = F), (III)(X = F; Y = CH_3), (III)(X = F; Y = CF_3), (III)(X = Y = Cl), (III)(X = CH_3; Y = H) and (III)(X = CH_3; Y = CF_3).

The ^{19}F and ^1H NMR spectra of the ions (III) generated by the action of SbF_5 on the precursors (IV) are identical to those observed for the same ions produced by the alkylation of compounds (II) with the cations (I). The use of more than 2.5 mol of SbF_5 per mole of (IV) for producing (III) followed by subsequent dilution of the salt solution 8 to 10-fold with SO_2 produced only signals corresponding to the ions (III) in the ^{19}F NMR spectrum. If the amount of SbF_5 did not exceed 0.8 - 1.5 mol, the resulting spectrum of the solution diluted with SO_2 exhibited signals from the ion (III) as well as those from the corresponding precursor (IV) for which the values of $\Delta\delta_F$ were measured. For the ions (III)(X = F; Y = CF_3) and (III)(X = CH_3; Y = CF_3), the use of 2.5 mol of SbF_5 per mole of diphenyldifluoromethane led to the retention of considerable quantities of the precursors (IV)(X = F; Y = CF_3) and (IV)(X = CH_3; Y = CF_3) respectively.

In assigning the signals in the ^{19}F NMR spectra of the ions (III), account was taken of the regularities previously noted in the analysis of the ^{19}F NMR spectra of polyfluorinated α,α-difluorobenzyl cations [1].

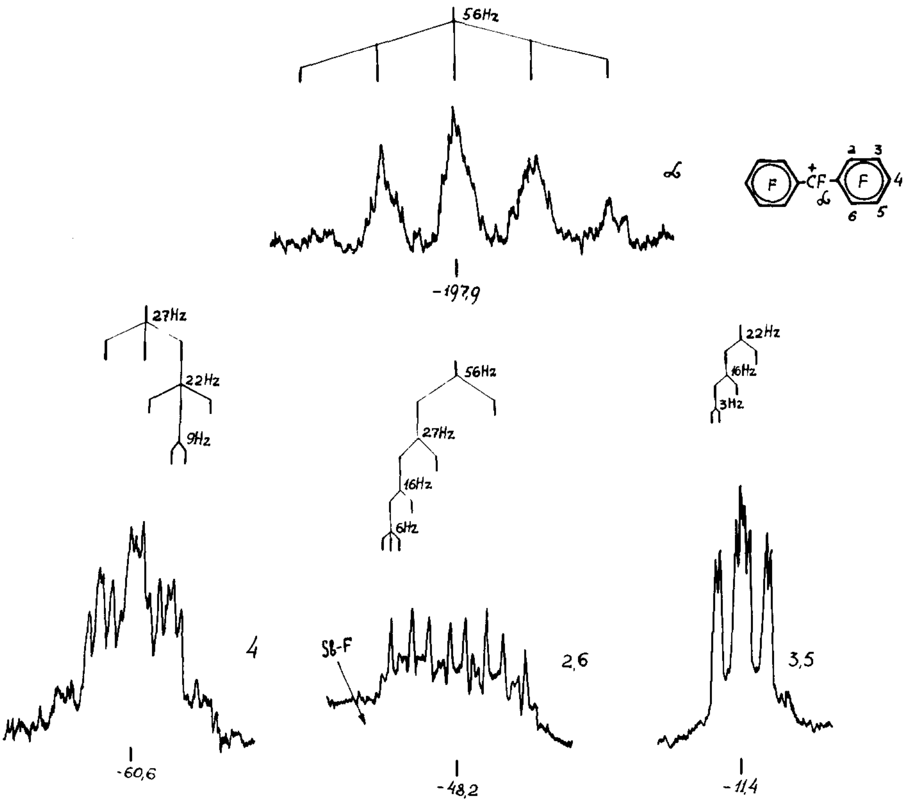


Fig. 1. ^{19}F NMR spectra of the solution of the salt of the ion (III)(X = Y = F) in a SbF_5—SO_2 solvent system. (Here and elsewhere the fluorine atoms are designated by the numbers of the respective carbon atoms.) The signals of the *para*-F and α-F atoms were recorded with increased gain relative to that employed for the *meta*-F and *ortho*-F atom signals.

The downfield signal shift for the ions (III) changes in the sequence α-F > F = 4 > F = 2(2′) > F = 3(3′)* which probably corresponds to the relative extent of the contributions of the resonance structures (A), (B) and (C) to the π-electron distribution in the overall structure of the ion. In the spectra of the symmetrical ions (III)(X; X) at —20 °C, all the four *ortho*-F atoms exhibit one signal resulting in one value for $^{\alpha,ortho}J(FF)$ for coupling between the α-F and *ortho*-F atoms. For this reason, signals from the α-atoms in the spectra of these ions are quintets (to a first approximation). This demon

---

*Here and elsewhere fluorine substituents are numbered in accordance with the corresponding carbon atoms. Non-primed numbers correspond to fluorine atoms in the ring containing the substituent first listed in the designation of the ion [*i.e.* (III)(X; Y), for example], while fluorine atoms in the other ring correspond to the primed numbers. The term "*ortho*" refers to the positions 2,2′,6,6′, "*meta*" to the positions 3,3′,5,5′ and "*para*" to the positions 4,4′.

TABLE 1

Characteristics of the ^{19}F and ^{1}H NMR spectra of polyfluorinated di- and tri-phenylmethyl ions[a]

Ion	Downfield chemical shifts from internal 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	$\delta_{2'}$	$\delta_{3'}$	$\delta_{4'}$	δ_α	$\Delta\delta_2$	$\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_{2'}$	$\Delta\delta_{3'}$	$\Delta\delta_{4'}$	$\Delta\delta_\alpha$	$^{\alpha,2}J(FF)$	$^{2,4}J(FF)$	$^{4,3}J(FF)$	$^{\alpha,4}J(FF)$	$^{\alpha,2}J(FF)$
(III)																			
(X = Y = F)	48.2	11.4	60.6	48.2	11.4	60.6	197.9	−26.4	−9.2	−46.8	−26.4	−9.2	−46.8	−119.2	56	27	22	9	56
(X = F;Y = Cl)	48.2	11.4	60.5	44.8	31.2		197.0	−25.8	−9.3	−46.7	−22.4	−8.8		−118.8	56	27	22	9	55
(X = F;Y = Br)	48.0	11.3	59.9	44.4	39.2		196.4	−26.0	−9.0	−46.0	−22.4	−8.2		−118.4	53	26	22	9	54
(X = F;Y = CH_3)	44.7	9.6	53.2	45.4	29.3	2.74	194.0	−23.0	−7.8	−39.9	−26.0 (−25.0)	−8.9 (−9.9)[f]		−115.4	45	22	21	6	~61
(X = F;Y = H)	50.2	11.7	63.5	44.6	33.3	8.34	202.3	−28.7	−9.7	−50.1	−23.1	−7.8		−124.3	60	30	22	12	52
(X = F;Y = CF_3)	45-70[b]	13.8	76.8	41.9	29.8	104.6	205.0		−11.5	−62.6	−18.5	−5.4		−128.0	120				39
	60.4[c]	17.3	81.0	45.6	33.9	108.0	208.0	−37.8	−14.7	−66.5	−21.4	−9.7		−130.2	70	36	20	20	38
(X = Y = Cl)	44.7	31.2		44.7	31.2		196.0	−22.0	−8.5		−22.0	−8.5		−118.3	55				55
(X = Cl;Y = Br)	44.2	30.9		44.2	38.8		195.5	−21.8	−8.5		−21.8	−7.9		−118.3	54				54
(X = Cl;Y= CH_3)	41.6	29.4		45.3	29.4	2.74	192.8	−19.1	−6.9		−26.0 (−24.7)	−8.8 (−10.1)		−114.8	46				62
(X = Cl;Y = H)	46.3	31.5		44.4	33.1	8.40	201.2	−24.3	−9.5		−22.4	−7.7		−124.0	59				51
(X = Y = Br)	43.8	38.7		43.8	38.7		194.6	−21.2	−7.9		−21.2	−7.9		−117.4	54				54
(X = Br;Y = CH_3)	41.3	37.6		45.3	29.3	2.75	192.5	−18.8	−7.1		−25.9 (−24.6)	−8.6 (−9.9)		−114.5	46				60
(X = Br;Y = H)	45.9	39.4		44.0	33.2	8.36	201.0	−23.3 (−24.6)	−8.6		−22.7 (−21.4)	−7.7		−123.4	60				52
(X = Y = CH_3)	42.1	28.2	2.67	42.1	28.2	2.67	191.0	−22.7 (−21.8)	−7.9 (−8.8)		−22.7 (−21.8)	−7.9 (−8.8)		−112.0	53				53
(X = CH_3;Y = H)	47.0	29.6	2.78	41.0	31.7	8.26	196.5	−27.7 (−26.3)	−8.9 (−10.2)		−20.3	−6.5		−118.4	64				44

(X = CH_3;Y = CF_3)																			
	55.4[b]	31.8	2.82	39.3	28.9	106.0	197.0	−36.1	−10.8		−16.0	−5.6		−120.0	130				
	49.2							−29.9											
	57.0[c]	35.3		42.4	32.5	108.0	201.0	−36.3	−14.6		−18.4	−8.5		−123.6	76				30
(X = Y = H)	46.2	32.7		46.2	32.7		207.0	−25.1	−7.3		−25.1	−7.3		−129.4	57				57
(V)[d]	60.2	17.2	76.8	60.2	17.2	76.8	104.6	−35.0	−14.7	−63.0	−35.0	−14.7	−63.0	−19.8		36	22		
(VI)	38.4	10.4	52.4	38.4	10.4	52.4										21	23		
(VIII)[e]	45-70[b]	14.0	74.4	43.2	36.4		204.0		−11.8	−60.2	−19.1	−8.3		−125.3		~35	~20	~16	40
	59.7[c]	17.2	80.0	45.3	39.6		207.0	−35.6	−15.0	−65.8	−21.2	−11.7		−128.3					

[a] Proton chemical shifts measured relative to tetramethylammonium perchlorate as an internal standard (δ = 3.2 ppm) [15].

[b] This row presents spectral data for a solution of the salt of an ion in a SbF_5—SO_2 solvent system where hindered rotation of the phenyl ring may occur; $\delta_{4'}$ = chemical shift of fluorine atoms of CF_3 group.

[c] This row presents spectral data for a solution of the salt of an ion in SbF_5 where free rotation of both phenyl rings may occur; $\delta_{4'}$ = chemical shift of fluorine atoms of CF_3 group. For ion (III)(Y = F; X = CF_3) a J(FF) value of 23 Hz is observed for the interaction of F = 3′(5′) and the CF_3 group in the signal from the CF_3 group.

[d] Spectral data presented for a solution of the salt of an ion in SbF_5 where free rotation of both phenyl rings may occur; δ_α and $\Delta\delta_\alpha$ = values of fluorine chemical shifts for α-CF_3 group. A J(FF) value of 20 Hz is observed for the interaction of F = 2(6) and an α-CF_3 group.

[e] Non-primed numbers designate positions in pentafluorophenyl rings.

[f] The values in parentheses arise from signal uncertainties in the spectra of the precursors.

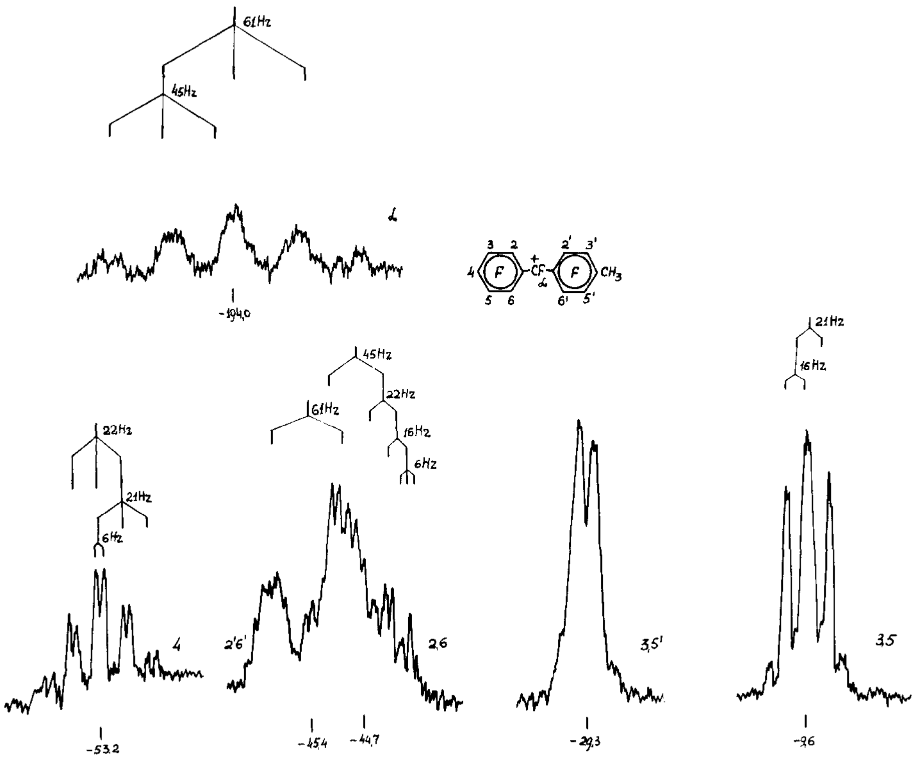
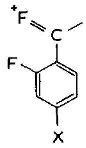
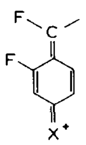
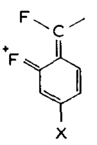


Fig. 2. ^{19}F NMR spectra of the solution of the salt of the ion (III)(X = F; Y = CH_3) in a SbF_5—SO_2 solvent system.


(A)


(B)


(C)

strates that free rotation about the α-C–C-1 bond exists in these ions, and hence ions of type (III) are essentially different from polyfluorinated benzyl cations [1]. This difference in the energy barriers to rotation about the α-C–C-1 bond for the two types of ions is probably best explained by the fact that in the latter case the resulting α-C—C-1 bond order is lower because of the participation of two phenyl rings in the delocalisation of the positive charge. A similar difference has also been observed with the non-fluorinated species [3]. The signals arising from the *ortho*-F atoms in the spectra of the ions (III) (X; X), where X = Cl, Br, CH_3 and H, are doublets to a first approximation due to coupling with α-F. For the ion (III)(X = Y = F), the *ortho*-F

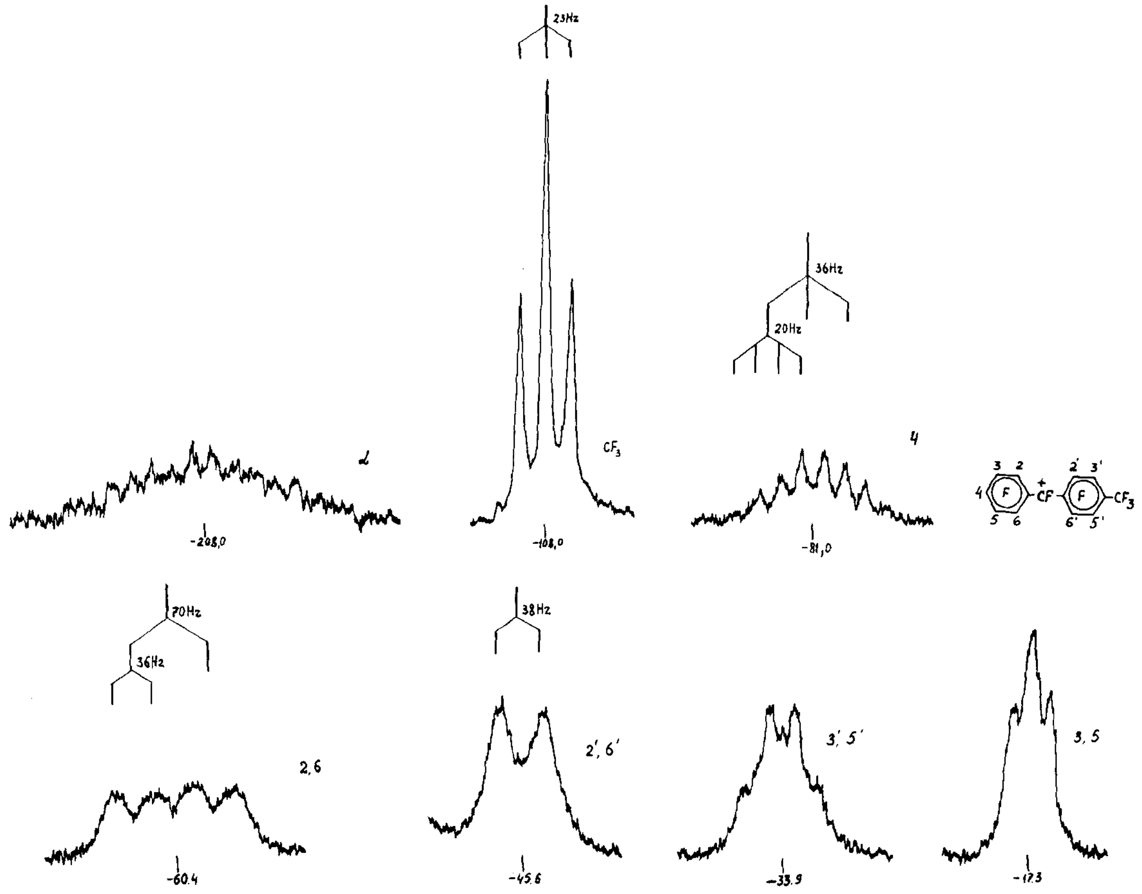


Fig. 3. ^{19}F NMR spectra of the solution of the salt of the ion (III)(X = F; Y = CF_3) in SbF_5 under conditions where free rotation of the phenyl rings may occur.

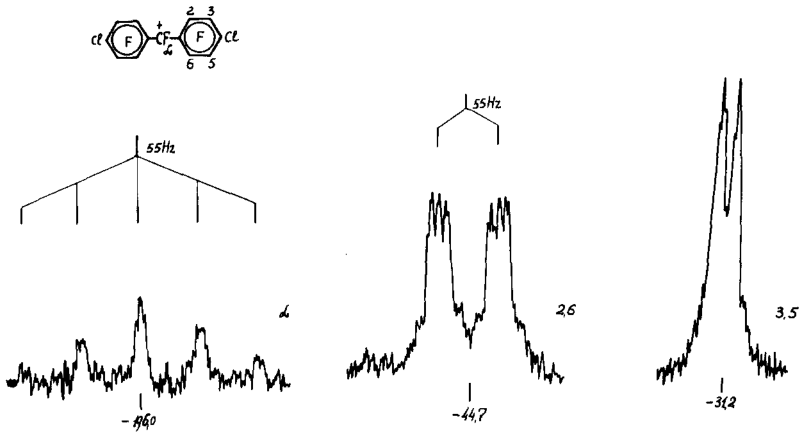


Fig. 4. ^{19}F NMR spectra of the solution of the salt of the ion (III)(X = Y = Cl) in a SbF_5—SO_2 solvent system.

signal is more complicated as the $^{2,4}J(FF)$ coupling constant of the *ortho*-F and *para*-F atoms has a considerable value.

Two signals arise from both the *ortho*-F and *meta*-F atoms in the spectra of the asymmetric ions (III)(X; Y); this can be explained in terms of the different nature of the substituents at the 4 and 4′ positions. The assignment of the *meta*-F signals in the spectra of the asymmetric ions is based on a comparison with the spectra of respective symmetric ions (III)(X; X) and (III)(Y; Y) containing the same substituents. To enable such a comparison, it has been assumed that the δ_F values for the *meta*-F atoms in the symmetric and asymmetric ions are approximately identical when the same substituent is present at the adjacent *para* position. The non-equivalent pairs of *ortho*-F atoms observed for asymmetric ions belong to different rings, since, as it was noted above, no similar non-equivalence is observed for symmetric ions. This conclusion is also supported by the fact that only one doublet splitting in each *ortho*-F signal which is observed in the spectra of asymmetric ions corresponds to coupling with α-F. Signal assignment for *ortho*-F atoms in the spectra of the ions (III)(F; Y), where Y = Cl, Br, CH_3 and H, is facilitated by the fact that the signal corresponding to F = 2 is complicated by F = 2–F = 4 coupling. The δ_F values for F = 2(6) in these ions are virtually independent of the nature of the halogen substituent at position 4′. If it is assumed that this behaviour is typical of all ions of type (III), it is possible to assign the signals at δ_F = —45.3 ppm in the spectra of the ions (III)(X = Cl; Y = CH_3) and (III)(X = Br; Y = CH_3) to F = 2′(6′) [*cf.* the value of δ_F for F = 2(6) in the ion (III)(X = F; Y = CH_3)]. In a similar manner, the signals at δ_F = —44.4 and —44.0 ppm respectively in the spectra of the ions (III)(X = Cl; Y = H) and (III)(X = Br; Y = H) have been assigned to F = 2′(6′) [from a comparison with the data for the ion (III)(X = F; Y = H)]. Comparison of the δ_F values for the ions (III)(X = F; Y = H) and (III)(X = F; Y = CH_3) shows

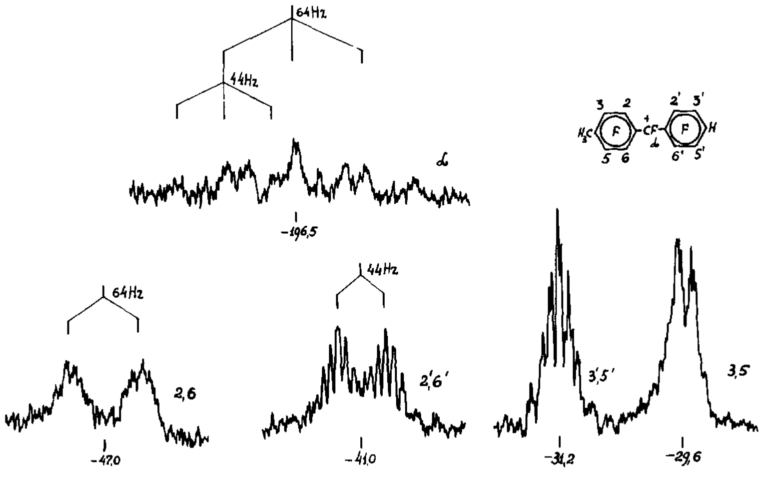


Fig. 5. ^{19}F NMR spectra of the solution of the salt of the ion (III)(X = CH_3; Y = H) in a SbF_5—SO_2 solvent system.

that replacement of a hydrogen by a CH_3 group causes an upfield shift of the F = 2(6) signals. Arising from this, it is possible to assign the signals in the spectrum of the ion (III)(X = CH_3; Y = H) [*cf.* data on the ions (III)(X = Y = H) and (III)(X = Y = CH_3)].

The values of the $^{2,4}J$(FF) constants for ions containing a pentafluorophenyl ring can be obtained from the signals arising from F = 4 and F = 2(6), while the doublet splitting ascribed above to coupling with α-F atoms can be extracted only from F = 4 signals. The interpretation of the α-F signals is made difficult however due to their complex structure which results from coupling between these atoms and the phenyl ring fluorines, and probably also from coupling with hydrogen nuclei in the case of the ions (III)(X = F; Y = H) and (III)(X = F; Y = CH_3). The doublet splitting in the spectrum of the ions (III) (X = F; Y), which has a value of J(FF) = 2 - 3 Hz, is specific to the F = 3(5) signals, apparently due to F = 3(5)—α-F coupling (this is demonstrated by the absence of similar splitting in the signals of the F = 3(5) atom in the spectra of the ions (V) and (VI) generated as described below). Triplet splitting with J(FF) = 6 Hz in the signals of F = 2(6) may be attributed to F = 2(6) –F = 2′(6′) coupling averaged over all conformations. It was found difficult to obtain similar values from the F = 2′(6′) signals of the ions (III)(X = F; Y) and from the F = 2(6) and F = 2′(6′) signals of other ions of type (III).

The ^{19}F NMR spectral pattern of the ions (III)(X = F; Y = CF_3) and (III)(X = CH_3; Y = CF_3) reveals that hindered rotation of the rings from which CF_3 groups are absent occurs (signal assignment in the spectra of these ions being similar to that employed for the other ions (III)(X = F; Y) and (III)(X = CH_3; Y), respectively). The spectra of the ions (III)(X = CH_3; Y = CF_3) at 80 °C and (III)(X = F; Y = CF_3) at 40 °C (in SbF_5 solution), as well as other ions at —20 °C, exhibit equivalent δ_F values for the *ortho*-F

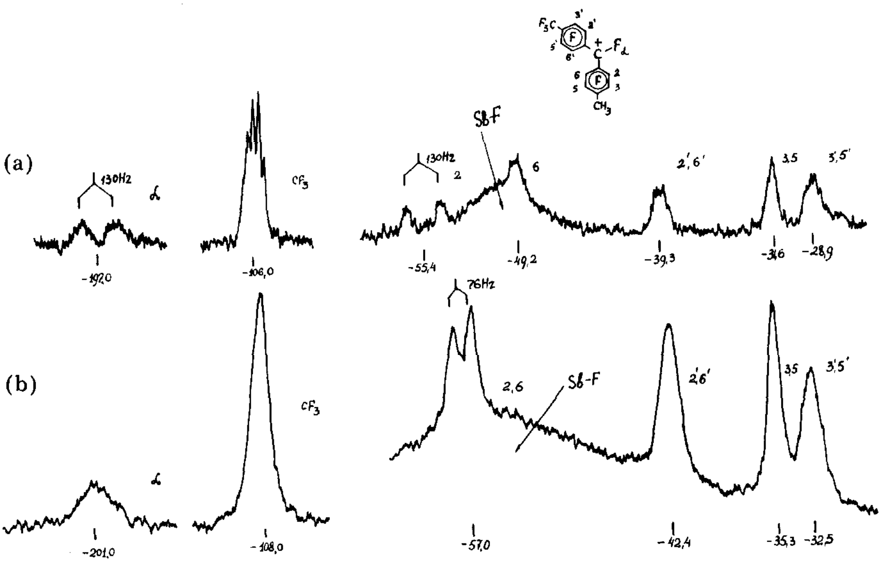


Fig. 6. (a) ^{19}F NMR spectra of the solution of the salt of the ion (III)(X = CH_3; Y = CF_3) in a SbF_5—SO_2 solvent system under conditions where hindered rotation of the phenyl ring containing the CH_3 group occurs.
(b) ^{19}F NMR spectra of the solution of the salt of the ion (III)(X = CH_3; Y = CF_3) in SbF_5 under conditions where free rotation of the phenyl rings may occur.

atom in the same ring, indicating rapid rotation of the phenyl rings about the C = 1(1′)—α = C bonds. However at —20 °C the signals arising from F = 2 and F = 6 are different in the spectrum of the ion (III)(X = CH_3; Y = CF_3) indicating hindered rotation involving the ring containing a CH_3 group. Coupling between an α-F atom and a less shielded *ortho*-F atom (two non-equivalent *ortho*-fluorines exist) is characterised by the larger of the values of $^{\alpha,ortho}J$(FF)(= 130 Hz) while coupling with the more shielded fluorine atom leads to a value of $^{\alpha,ortho}J$(FF) not greater than 30 Hz. The ion (III)(X = F; Y = CF_3) exhibits a spectrum at —20 °C in which only the F = 2(6) signal is broadened (but still not split into two signals) pointing to the decreased rotation at this temperature. If the temperature is further decreased, it is still difficult to identify the signals arising from F = 2 and F = 6 in the range —70 to —50 ppm because of overlap with signals from $Sb_2F_{11}^-$ and $SbF_5 \cdot SO_2$ [4] (the intensity of these signals is low at —20 °C but increases with decreasing temperature). However, hindered rotation of a pentafluorophenyl ring at —40 °C is evident from the nature of the α-F signal at this temperature which differs considerably from that observed when rapid rotation occurs. Thus, at the lower temperature, this signal exists as a doublet with J(FF) = 120 Hz similar to the splitting with $^{\alpha,ortho}J$(FF) = 130 Hz which occurs for the ion (III)(X = CH_3; Y = CF_3). In all of these cases F = 2′ and F = 6′ remain equivalent due to rapid rotation of the ring containing the CF_3 group. Thus, in the ions (III)(X = CH_3; Y = CF_3) and (III)(X = F; Y =

CF_3) the energy barrier for rotation of the rings from which the CF_3 groups are absent exceed the values for all the other ions studied, the barrier for the first ion being greater than that for the second. This may be explained in terms of the decreased ring participation in charge delocalisation on introducing a CF_3 group in the *para* position. In this case, resonance participation of the other ring and the degree of double bonding with the α-carbon atom increase and approach the values in the benzyl ions 4-$CH_3C_6F_4CF_2^+$ and $C_6F_5CF_2^+$, respectively, as is evident from the $\Delta\delta_F$ values for these latter ions (*cf.* ref [1]). Participation of the ring containing a CH_3 group in charge delocalisation in the case of the ion (III)(X = CH_3; Y = CF_3) is more efficient than the pentafluorophenyl ring of the ion (III)(X = F; Y = CF_3). This is probably the result of the high electron-donating ability of the CH_3 group in comparison with that of the *para*-F atoms in ions of type (III), in agreement with observations for the non-fluorinated analogues [5].

The effect of substituents on the values of $\Delta\delta_F$ in the 4-X-α,α-difluorobenzyl cation [3] and their polyfluorinated analogues [1] has been explained in terms of substituent participation in positive charge delocalisation. In the case of the ions (III), additional information on the participation of substituents X(Y) is provided by an analysis of the $\Delta\delta_F$ values for the *ortho*-F and *para*-F atoms in the other ring. The changes in the $\Delta\delta_F$ values for α-F and for *ortho*-F and *para*-F atoms in the second ring in the series (III)(X = F; Y), (III)(X = Cl; Y), (III)(X = Br; Y), (III)(X = CH_3; Y) and (III)(X = H; Y) indicate that differences in the effects of F, Cl and Br substituents on the $\Delta\delta_F$ values under consideration are small, with the differences in these effects on $\Delta\delta_{\alpha\text{-F}}$ values for ions of type (III) being smaller than for ions of type 4-X-$C_6F_4CF_2^+$ [1]. The sensitivity of $\Delta\delta_F$ values to changes in the nature of the substituent at position 4′ is illustrated by the sequence α-F > F = 4 > F = 2, which appears to correspond to the contributions of these substituents towards charge delocalisation. However, the influence of substituents at position 4′ on the corresponding values of $\Delta\delta_F$ for α-F, F = 2 and F = 4 are not completely consistent, especially for Cl and Br substituents. In general, though, the information available appears to indicate the following sequence for *para*-substituent participation in positive charge delocalisation in ions of type (III): $CH_3 > Br \gtrsim Cl > F > H$.

Table 2 lists the increments i_X^Y which characterise the effects of substituents X at position 4 in the ions (III) on the $\Delta\delta_F$ values for α-F atoms relative to X = H for a series of ions in which the substituent Y at position 4′ remains constant. The values obtained indicate that ions with no CH_3 groups have values of i_X^Y for X = F, Cl and Br which are approximately constant. This enables an accurate estimation of the $\Delta\delta_F$ values for these ions from the mean increments for the substituents X using an additive scheme (*cf.* Table 3). The presence of the methyl group causes the "saturation" of the substituent effects; thus the $i_X^{CH_3}$ values for X = F, Cl and Br are considerably less than those of the same substituents in the series Y = H, F, Cl and Br. Furthermore, the $i_{CH_3}^Y$ increments decrease in the series $i_{CH_3}^H > i_{CH_3}^F \approx i_{CH_3}^{Cl} > i_{CH_3}^{Br} >$

TABLE 2

The increments i_X^Y as a measure of the effect of *para* substitution in ions of type (III) upon the $\Delta\delta_F$ values of the α-F atom

Substituent X	Increments i_X^Y (substituent Y determining the series)					Mean values (i_X^{mean}) for Y = F, Cl, Br, H	Substituent increments for ions $4\text{-}XC_6F_4CF_2^+$ [1]
	i_X^H	i_X^F	i_X^{Cl}	i_X^{Br}	$i_X^{CH_3}$		
F	+5.1	+5.1	+5.2	+5.0	+3.0	+5.1	+6.4
Cl	+5.4	+5.5	+5.7	+5.1	+3.6	+5.4	+7.8
Br	+6.0	+5.9	+5.7	+6.0	+3.9	+5.9	+8.5
CH_3	+11.0	+8.9	+9.2	+8.9	+6.4		+13.0

$i_{CH_3}^{CH_3}$, *i.e.* with increasing donor effect of the substituent Y (and according to its influence on $\Delta\delta_F$). The reason for such "saturation" is probably related partly to the compensation of a partial increase in the coplanarity of the ring with α-carbon plane with increasing donor capacity of the *para* substituent by a partial decrease in the coplanarity of the second ring with α-carbon plane. This suggestion is supported by an analysis of the observed values of $^{\alpha,ortho}J(FF)$ (see below). For ions which contain no CH_3 groups the effects appear to be small and approximately constant, making the substituent effects practically additive. For ions which contain the CH_3 group, which is the strongest electron donator of the substituents under consideration, the changes in ring coplanarity are evidently much more pronounced and result in the breakdown of the additive nature of substituent effects on the $\Delta\delta_F$ values for α-atoms.

In a similar manner to polyfluorinated benzyl cations [1], $\Delta\delta_F$ values for ions of type (III) do not correlate satisfactorily either with σ^+ values or with linear combinations of σ_R^+ and σ_I constants (*cf.* refs. 6 and 7).

The ^1H chemical shifts for ions (III)(X; Y = H) and (III)(X; Y = CH_3) (Table 1) are in agreement with similar parameters for their non-fluorinated analogues [3, 8].

The values of $J(FF)$ which characterise the spin–spin coupling of α-F, *ortho*-F and *para*-F atoms which are effectively participating in the positive charge delocalisation are considerably greater than the corresponding values for the neutral precursors. This may be explained in terms of the contributions made to the charge delocalisation by the structures (A), (B) and (C) in which the atoms concerned are linked *via* direct conjugation.

The values of $^{\alpha,ortho}J(FF)$ when averaged by phenyl ring rotation about the α-carbon atom are quite considerable and it is possible to assume that coupling through space is of considerable importance in determining these values (*cf.* ref. 1). For all symmetric ions (III)(X; X), the $^{\alpha,ortho}J(FF)$ values lie in the range 53 - 57 Hz and are little affected by the nature of X. Comparison of rotation-averaged values of $^{\alpha,ortho}J(FF)$ for the *para* substituents of symmetric ions leads to the following sequence: H $>$ F $\gtrsim$ Cl $\gtrsim$ Br $>$ CH_3. For

TABLE 3

The $\Delta\delta_F$ values for α-F atoms in ions of the type (III)(X; Y) estimated by using the i_X^{mean} values (see Table 2) from the formula $\Delta\delta_F = -129.4^* + i_X^{mean}$

Ion	$\Delta\delta_F$ (calc.)	$\Delta\delta_F$ (calc.) — $\Delta\delta_F$ (obs.)
(III)(X = H; Y = F)	−124.3	0.0
(III)(X = H; Y = Cl)	−124.0	0.0
(III)(X = H; Y = Br)	−123.5	0.1
(III)(X = Y = F)	−119.2	0.0
(III)(X = F; Y = Cl)	−118.9	−0.1
(III)(X = F; Y = Br)	−118.4	0.0
(III)(X = Y = Cl)	−118.6	−0.3
(III)(X = Cl; Y = Br)	−118.1	0.2
(III)(X = Y = Br)	−117.6	−0.2

*The $\Delta\delta_F$ value for the α-F atom of the ion (III)(X = Y = H).

asymmetric ions (III)(X; Y), the values of J(FF) for coupling of α-F with *ortho*-F, *ortho*-F with *para*-F, and α-F with *para*-F are strongly dependent on the nature of the substituents. The largest value of ${}^{\alpha,ortho}J$(FF) is always observed for the ring containing the strongest electron-donating *para* substituent in the sense of the series of substituent effects on $\Delta\delta_F$ given above. The further apart the two substituents X and Y in this series, the greater the difference between the respective values of ${}^{\alpha,ortho}J$(FF). In the series of ions (III)(X; Y) with Y constant, an increase of the donor effect of X is always accompanied by an increase in the average value of ${}^{\alpha,ortho}J$(FF) for the ring containing the substituent X, and by a decrease in this value for the ring containing substituent Y. For substituents X = F, Cl and Br, the corresponding effects on ${}^{\alpha,ortho}J$(FF) are practically identical. For a given ion, the sum of the two averaged values of ${}^{\alpha,ortho}J$(FF) varies in the range 106 - 114 Hz in all cases investigated, with the value tending to increase on passing from ions with stronger electron-donating groups to those with weaker donor substituents.

The dependence of the averaged value of ${}^{\alpha,ortho}J$(FF) on the nature of X and Y for the asymmetric ions (III)(X; Y) is opposite to the similar dependence of J(AX) + J(AX′) which characterises the interaction of α-F and *ortho*-F atoms in polyfluorinated α,α-difluorobenzyl cations [1]. In contrast, the dependence of the sum of the two averaged ${}^{\alpha,ortho}J$(FF) values for the asymmetric ions (III)(X; Y) corresponds closely to the effect of substituents on the J(AX) + J(AX′) values for 4-$XC_6F_4CF_2^+$ ions.

In our opinion, the influence of *para* substituents upon ${}^{\alpha,ortho}J$(FF) values in ions of type (III) may be interpreted in terms of the complex character of spin coupling between *ortho*-F and α-F atoms and of the dependence in an averaged ion state of the coplanarity of the two phenyl rings and the α-carbon plane on the X and Y substituent combination. It has been suggested for polyfluorinated α,α-difluorobenzyl cations [1] that the value of ${}^{\alpha,ortho}J$(FF) is related to the sum of the contributions from coupling through bonds (contribution 1) and through space (contribution 2) with contribution 1 being dependent on the relative importance of resonance structures (A) and (C) in which α-F and *ortho*-F atoms are linked directly *via* conjugation.

In each symmetric ion (III)(X; X) the coplanarities of both rings with the α-carbon plane are the same and probably close to those for other ions of this type. Under these circumstances an increase in the donor effect of X should lead initially to a greater contribution of structure (B) and a lower average value of ${}^{\alpha,ortho}J$(FF) due to the decreased importance of structures (A) and (C), as is actually found to be the case. However, the differences are probably small because this trend is partly compensated by the increase in contribution 2 because of the slight increase in coplanarity. This behaviour of the ${}^{\alpha,ortho}J$(FF) values for the ions (III)(X; X) is similar to that of the J(AX) + J(AX′) values for ions of the type 4-$XC_6F_4CF_2^+$ mentioned above.

For asymmetric ions (III)(X; Y), the relative coplanarities of the two rings towards the α-carbon plane are different, with an increase in the coplanarity of one ring with the α-carbon plane being only attained at the expense of the coplanarity of the other ring. An increase in coplanarity should result in an increase in the value of ${}^{\alpha,ortho}J$(FF) for coupling between *ortho*-F and α-F atoms due to an increase in contribution 2, and also possible due to an increase in contribution 1 because of the better conditions for conjugation. The combined effects should result in an increase in the averaged ${}^{\alpha,ortho}J$(FF) value for the ring containing the stronger electron-donating *para* substituent and to the reverse effect for the ring containing the weaker substituent.

Since the conformational changes, and consequently the changes in contributions 1 and 2, for the two rings cancel each other out, the sum of the averaged ${}^{\alpha,ortho}J$(FF) values changes principally because of the change in the relative importance of the canonical structure (B) which is dependent on the electron-donating power of the *para* substituent, with a consequent change in the relative importance of the contributions of structures (A) and (C). In fact, the greater the electron-donating power of the two *para* substituents, the smaller the sum of the averaged ${}^{\alpha,ortho}J$(FF) values and *vice versa.* In our opinion, a combination of these factors provides a reasonable explanation for the dependence of the averaged ${}^{\alpha,ortho}J$(FF) values for ions of the type (III)(X; Y) on the nature of the X, Y substituent pairs present.

The above assumptions are confirmed by the observed values of ${}^{\alpha,ortho}J$(FF) for the ions (III)(Y = CH_3; X = CF_3) and (III)(Y = F; X = CF_3). Because of the unfavourable electronic effect of the CF_3 group, its participation in the ring charge delocalisation is reduced which apparently leads to considerable non-coplanarity with the α-carbon plane and the lowest averaged value of ${}^{\alpha,ortho}J$(FF). The corresponding higher coplanarity of the second ring in the structure probably accounts for the high value of 120 - 130 Hz for ${}^{\alpha,ortho}J$(FF) for coupling between an adjacent α-F atom and an *ortho*-F atom under such conditions of restricted ring rotation. The observed value of

$^{\alpha,ortho}J(FF)$ (*ca.* 30 Hz) for the coupling between an α-F atom and a remote *ortho*-F atom in the ring containing a CH_3 group in the ion (III)(X = CH_3; Y = CF_3) appears to be approaching the value which is attributable virtually completely to contribution 1.

Since the values of $^{2,4}J(FF)$ and $^{\alpha,4}J(FF)$ for the ions (III)(X = F; Y) are evidently determined only by coupling through bonds, it is to be expected that the influence of the nature of Y on these values will correspond to the corresponding effects of these substituents on the participation of the pentafluorophenyl ring in charge delocalisation. This effect may be related to an increase or decrease in the contribution of structures (B) and (C) for the pentafluorophenyl ring as the electron-donating ability of Y decreases or increases respectively. Indeed, the observed sequence corresponding to the influence of the change of the electron-donating effect of Y on the values of $^{2,4}J(FF)$ or $^{\alpha,4}J(FF)$ for the ions (III)(X = F; Y) is as follows: $CH_3 > Br \gtrsim Cl \sim F > H > CF_3$. (For Y = CF_3, the $J(FF)$ values concerned were observed under conditions where free rotation of the pentafluorophenyl ring occurred.)

A similar change in the values of $\Delta\delta_F$ for α-F, *ortho*-F and *para*-F atoms and the values of $^{2,4}J(FF)$ and $^{\alpha,4}J(FF)$ for ions of type (III) suggests that a linear correlation exists between the δ_F values and the $J(FF)$ values, as observed for the δ_F values of *para*-F atoms and $^{2,4}J(FF)$ values in neutral compounds of the type C_6F_5X [9]. A least-squares treatment of the data listed in Table 1 actually leads to such dependencies with quite good correlation parameters [*cf.* Table 4, equations (1) - (6)]. The correlation parameters are improved when the $J(FF)$ values are correlated with linear combinations of *ortho*-F and *para*-F chemical shift values for the pentafluorophenyl rings or with those of the α-F and *para*-F atoms of the ions (III)(X = F; Y). In addition, a common correlation is observed between the $^4\delta_F$ and $^{2,4}J(FF)$ values for a wide range of compounds of the type C_6F_5X including the six ions (III)(X = F; Y), Y = H, F, Cl, Br, CH_3 and CF_3, the ions $(C_6F_5)_2C^+CF_3$ (V), $(C_6F_5)_3C^+$ (VI), $C_6F_5CF_2^+$ [1] and $C_6F_5CFH^+$ [1], and neutral compounds for which a similar correlation was established elsewhere [9] [Table 4, equation (7)]. All these correlations, as well as that between δ_F for *para*-F atoms and $^{2,4}J(FF)$ values on the one hand and the σ_R° and σ_I constants for the X substituents on the other hand found for the neutral compounds C_6F_5X [9], indicate that a direct relationship exists between the effects of substituents on δ_F and $J(FF)$ as given in equations (1) - (7) of Table 4 and the effects of the same substituents on the π-electron distribution. Analogously to the assumption made for the polyfluorinated benzenonium ions [10], benzyl cations [1] and neutral compounds [1, 10], the existence of such a relationship for ions of type (III) may be taken as a qualitative representation of the effects of substituents on the relative contributions of the canonical structures (A), (B) and (C) to the overall π-electron distribution in these ions. These contributions in turn define the values of the chemical shifts and spin–spin coupling constants for the fluorine atoms participa-

TABLE 4

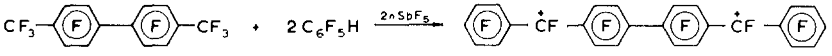
Relationships connecting values of $^{2,4}J(FF)$ and $^{\alpha,4}J(FF)$ with $^{6}\phi_F$ values for *para*-F, *ortho*-F in pentafluorophenyl rings and α-F atoms for polyfluorinated phenylmethyl cations and connecting the values of $^{2,4}J(FF)$ with chemical shift values $(\phi_F)^b$ for C_6F_5X compounds [9]

Equation	r^a	s^a	Number of points
(1) $^{2,4}J(FF) = -0.52\ ^{4}\phi_F + 80.1$	0.985	1.6	11
(2) $^{2,4}J(FF) = -0.34\ ^{2,6}\phi_F - 0.33\ ^{4}\phi_F + 98.8$	0.992	1.1	11
(3) $^{\alpha,4}J(FF) = -0.60\ ^{4}\phi_F + 70.6$	0.978	2.1	8
(4) $^{\alpha,4}J(FF) = -0.52\ ^{4}\phi_F + 62.3$	0.993	0.6	6^c
(5) $^{\alpha,4}J(FF) = -0.94\ ^{\alpha}\phi_F - 23.3$	0.979	1.1	6^c
(6) $^{\alpha,4}J(FF) = -0.37\ ^{4}\phi_F - 0.30\ ^{\alpha}\phi_F + 37.0$	0.995	0.3	6^c
(7) $^{2,4}J(FF) = -0.482\ ^{4}\phi_F + 76.34$	0.997	0.92	72^d

[a] r = correlation coefficient and s = mean-square deviation.
[b] $\delta_F = 163.0 - \phi_F$ [9].
[c] $J(FF)$ and ϕ_F values are included only for polyfluorinated diphenylmethyl ions.
[d] $^{2,4}J(FF)$ and ϕ_F values for 61 neutral compounds of type C_6F_5X [9] are included together with similar values for the corresponding ions. The relation connecting the values of $^{2,4}J(FF)$ and $^{4}\phi_F$ for these compounds was represented by the equation $^{2,4}J(FF) = -0.453\ \phi_p + 71.98$.

ting effectively in charge delocalisation and interacting with each other *via* direct conjugation in the structures (A), (B) and (C). This latter fact provides a qualitative explanation for the large values of $J(FF)$ for these fluorine couplings.

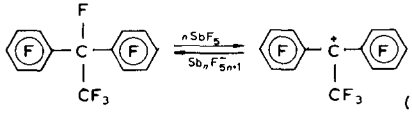
It has been shown that perfluoro-4,4'-dimethyldiphenyl (VII) when dissolved in SbF_5 fails to produce either a mono- or di-cation in amounts sufficient to enable their ^{19}F NMR spectra to be detected. The authors obtained a chemical proof for the formation of at least a monocation, *i.e.* 4,4'-$CF_3C_6F_4C_6F_4CF_2^+$, in such a solution. When two equivalents of pentafluorobenzene were added to a solution of (VII) in SbF_5, the resulting solution exhibited a ^{19}F NMR spectrum both before and after addition of SO_2 (Table 1) corresponding to the formation of the dication (VIII) indicating alkylation of pentafluorobenzene.



(VII) (VIII)

Formation of the dication (VIII) is also confirmed by its subsequent transformations during addition of the solution of its salt [produced by addition of pentafluorobenzene to the SbF_5 solution of (VII)] to water or HF [2]. The ^{19}F NMR spectrum of the dication (VIII) as recorded for the solution of its salt in the system SbF_5—SO_2 is reminiscent of the spectra of the cations (III)(X = F; Y). From the ^{19}F NMR spectra obtained it appears that the 4-$C_6F_4CF^+C_6F_5$ group in the ion (VIII) is either slightly weaker or of the same electron acceptor strength as the CF_3 group in the ion (III)(X = F; Y = CF_3). The signal of the *ortho*-F atom in the pentafluorophenyl ring is broadened at —20 °C due to the hindered rotation of this ring. Observations of this signal, especially at lower temperatures, are complicated by its overlap with signals from $SbF_5 \cdot SO_2$ and $Sb_2F_{11}^-$ [4]. However, the signal of the α-F atom at —207.0 ppm observed at —60 °C is split into a doublet with $^{\alpha,ortho}J(FF) \approx 120$ Hz, which corresponds to that of the ions (III)(X; Y = CF_3) when hindered rotation of the ring from which the CF_3 group is absent occurs. The signal of the *ortho*-F atoms of the pentafluorophenyl rings of the dication (VIII) can be observed in the spectrum of the freshly prepared solution of its salt in SbF_5 at 40 °C. The comparatively weak effect of the positive charge on one part of dication (VIII) on that on the other is best explained by the considerable non-coplanarity of the rings in this ion (*cf.* the data on decafluorobiphenyl [11]).

The facts revealed by the analysis of the ^{19}F NMR spectra of the ions (III) make an investigation of the effect of substituents at the α-carbon atom upon the values of $\Delta\delta_F$ and $J(FF)$ of considerable interest. As an initial step towards such a study, the generation of the perfluoro-1,1-diphenylethyl cation (V) was achieved by dissolving perfluoro-1,1-diphenylethane in SbF_5.



(V)

The parameters of the ^{19}F NMR spectrum of the solution of the salt of this ion dissolved in SbF_5 and measured at 40 °C are listed in Table 1. Under these conditions free rotation of the pentafluorophenyl groups occurs, and it can be readily seen that replacement of the α-F atom by a CF_3 group, as occurs in going from the ion (III)(X = Y = F) to the ion (V), leads, as might be expected, to a considerable increase in the participation of the pentafluorophenyl groups in charge delocalisation. In the ion (V), the extent of this participation is probably similar to that occurring in the ion (III)(X = F; Y = CF_3) as is demonstrated by a comparison of the $\Delta\delta_F$ and $^{2,4}J(FF)$ values for the two ions.

On analysis of the parameters of the ^{19}F NMR spectra of polyfluorinated benzyl and diphenylmethyl cations [3], it was found that surprisingly no large values of $J(FF)$ for the coupling of *ortho*-F and *para*-F atoms were involved in the interpretation of the ^{19}F NMR spectra of mono-, bis- and tris-pentafluorophenylmethyl cations. The considerable width of the signals of these fluorine atoms in the spectra of the ions $C_6F_5CH_2^+$ and $(C_6F_5)CH^+$ was explained [3] in terms of their coupling with α-hydrogen atoms. However, the present data suggest that a more reasonable explanation for such broadening would be coupling between *ortho*-F and *para*-F atoms. Furthermore, the signal from *para*-F atoms in the ^{19}F NMR spectrum of the ion $(C_6F_5)_3C^+$ (VI) has been represented in the work [3] as a triplet as a result

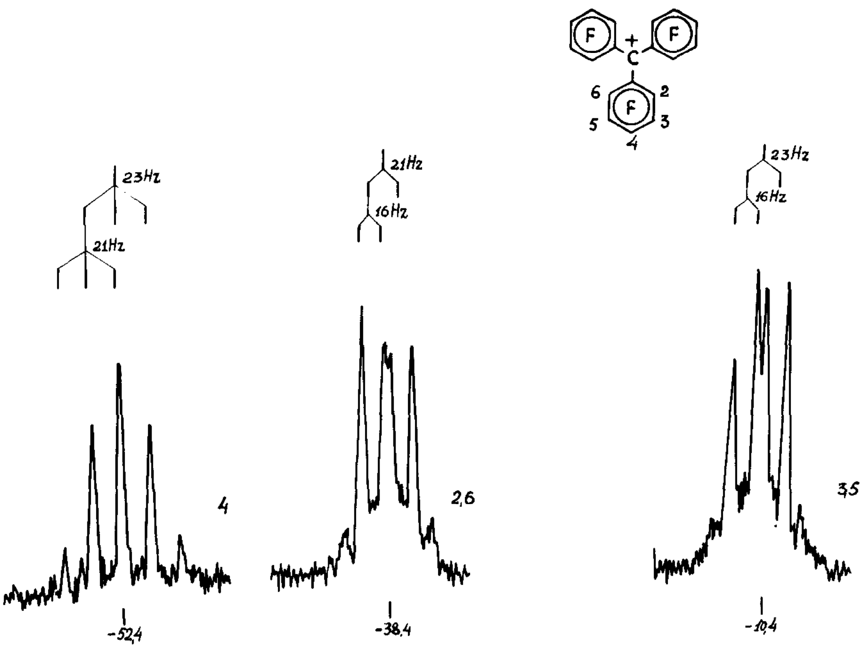


Fig. 7. ^{19}F NMR spectra of the solution of the salt of the ion (VI) in a SbF_5—SO_2 solvent system.

of coupling between the *meta*-F and *para*-F atoms. Ion (VI) was generated in this work by dissolving perfluorotriphenylmethane* in a SbF_5—SO_2 solvent system.

$$(C_6F_5)_3CF \xrightarrow{SbF_5-SO_2} \underset{(VI)}{(C_6F_5)_3C^+}$$

In general, the ^{19}F NMR spectrum of this ion (Fig. 7 and Table 1) agrees with earlier data. Minor differences in the $\Delta\delta_F$ values may be due to differences in the standards employed. However, the *para*-F signal was not a triplet as suggested earlier [3] but a quintet with a component ratio close to 1:4:6:4:1 and a component separation of about 21.5 Hz. This signal pattern may be explained by the closeness in the values of J(FF) for coupling between the *para*-F atom and *meta*-F and *ortho*-F atoms. Because of this, signals from the *ortho*-F and *meta*-F atoms exist as doublet splitting with the spacings between the lines being equal to 21 and 23 Hz, respectively. The former value was used in deriving equation (7) listed in Table 4.

The electronic spectra of solutions of the salts of ions of type (III) are listed in Table 5 and are in good agreement with the spectra of the non-flu-

---

*The authors wish to thank Dr. T. M. Gerasimova for kindly supplying the sample of perfluorotriphenylmethane [12].

TABLE 5

Positions of the absorption bands in the electronic spectra of solutions of the salts of some polyfluorinated diphenylmethyl ions in SbF_5

Ion	$\lambda_{max.}/m\mu$	$\epsilon \times 10^{-3}$
(III)(X = Y = F)	313 420	7.7 35.6
(III)(X = F; Y = Br)	336 453	7.3 50.0
(III)(X = F; Y = CH_3)	319 429	7.2 41.0
(III)(X = F; Y = H)	312 417	7.0 47.0
(III)(X = Y = Br)	364 480	9.2 54.0
(III)(X = Br; Y = H)	334 446	6.7 62.5
(III)(X = Y = CH_3)	325 438	5.7 36.6
(III)(X = Y = H)	312 412	8.1 81.6

orinated species [13]. It should be noted that α-fluorodiphenylmethyl cations (III) having a halogen or methyl group in the 4(4′) position absorb at a longer wavelength than the ion (III)(X = Y = H).

Experimental

The preparation of compounds (I), (II), (IV) and (VII) used for the generation of the ions has been described in ref. 2. Perfluoro-1,1-diphenylethane was prepared by the method of ref. 14. Solutions of diphenylmethyl ions were prepared using doubly-distilled SbF_5, b.p. 141 - 142 °C, as a solvent. All operations involving solution preparation and filling of the NMR sample tubes and spectroscopic cells were carried out in a dry box.

Solutions of diphenylmethyl cations used for recording the ^{19}F and ^{1}H NMR spectra were prepared by two methods:

(i) SO_2 (0.3 - 0.5 cm^3) was condensed in an NMR sample tube containing a solution consisting of equimolar amounts of polyfluorinated benzene (0.04 - 0.08 g) and trifluoromethylbenzene (0.06 - 0.10 g) in SbF_5 (0.15 - 0.50 g), and the mixture was shaken until a homogeneous solution was obtained.

(ii) Precursor (IV) was added to 0.06 - 0.15 g of SbF_5 (molar ratio SbF_5:(IV) = 0.8 - 2.0) in an NMR sample tube, 0.3 - 0.5 cm^3 of SO_2 was condensed on top of this mixture and the contents of the tube were shaken until a homogeneous solution was obtained.

Solutions for the measurement of electronic absorption spectra were prepared by dissolving a weighed sample of diphenyldifluoromethane (IV) at 50 - 60 °C in SbF_5 with continuous shaking for 2.5 - 3 h.

The ^{19}F and ^{1}H NMR spectra were recorded using a Varian A56/60A spectrometer at 56.4 and 60 MHz respectively. The spectra of solutions of the salts of the ions in SbF_5 (15 - 25 mole %) were recorded at temperatures within the range 40 - 100 °C while spectra of solutions in SbF_5—SO_2 were recorded at —60 °C to —20 °C. The electronic spectra of solutions of the salts of the ions in SbF_5 (0.2×10^{-3} mol l^{-1}) were recorded using a Unicam SP-700C spectrometer at 25 - 28 °C. The errors involved in the measurement of the spin–spin coupling constants were not greater than ± 1 Hz and not greater than ± 0.2 ppm for the measurement of the chemical shifts.

References

1 Yu. V. Pozdnyakovich and V. D. Shteingarts, J. Fluorine Chem., 4 (1974) 283.
2 Yu. V. Pozdnyakovich and V. D. Shteingarts, J. Fluorine Chem., 4 (1974) 317.
3 G. A. Olah and M. B. Comisarow, J. Amer. Chem. Soc., 91 (1969) 2955.
4 J. Bacon, P. A. W. Dean and R. J. Gillespie, Can. J. Chem., 47 (1969) 1655.
5 N. C. Deno, J. J. Jaruzelski and A. Schriesheim, J. Amer. Chem. Soc., 77 (1955) 3044; N. C. Deno and W. L. Evans, J. Amer. Chem. Soc., 79 (1957) 5804.
6 L. M. Stock and H. C. Brown, Adv. Phys. Org. Chem., 1 (1963) 35.
7 O. Exner, Collect. Czech. Chem. Commun., 25 (1960) 642.
8 H. Kwart and S. Alekman, J. Amer. Chem. Soc., 90 (1968) 4482.
9 M. G. Hogben and W. A. G. Graham, J. Amer. Chem. Soc., 91 (1969) 283.
10 V. D. Shteingarts and Yu. V. Pozdnyakovich, Zh. Org. Khim., 7 (1971) 734.
11 N. N. Neronova, Zh. Struct. Khim., 9 (1968) 147; N. Boden, J. W. Emsley, J. Feeney and L. H. Sutcliffe, Mol. Phys., 8 (1964) 467.
12 T. N. Gerasimova, A. G. Badashkeeva, E. G. Lubenets, V. A. Barkhash and N. N. Vorozhtsov, Zh. Org. Khim., 5 (1969) 2199.
13 G. A. Olah, C. V. Pittman, J. R. Waack and M. Doran, J. Amer. Chem. Soc., 88 (1966) 1488.
14 V. V. Brovko, V. A. Sokolenko and G. G. Yakobson, Abstr. All-Union Conf. Fluoroorg. Chem., Naukova Dumka, Kiev, 1973, p. 26.
15 D. M. Brouwer, Rec. Trav. Chim., 86 (1967) 879.