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NMR Spectroscopy of Polyfluorinated Allyl Cations

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The results of the NMR study of the hydrocarbon allyl cations are briefly surveyed. The ^{13}C and ^{19}F NMR spectra of polyfluorinated cyclic and acyclic allyl cations are considered and the spectral features of their formation in solutions are discussed. The influence of substituents and of the positive charge on the chemical shifts and the spin-spin coupling constants $^1J(^{13}C-^{19}F)$ and $^4J(^{19}F-^{19}F)$ of polyfluorinated allyl cations are considered. NMR data are presented on the relative stabilities of polyfluorinated allyl cations.
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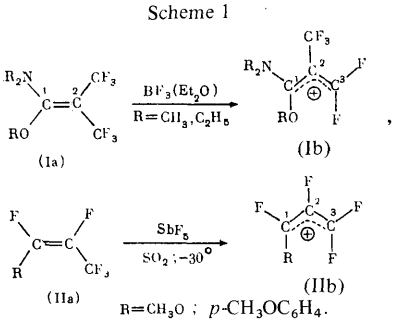
I. INTRODUCTION

The study of the structures, thermodynamic stabilities, and reactivities of carbenium ions remains one of the most rapidly developing fields in modern organic chemistry of current interest. Since the publication of the first studies by Olah (see, for example, Ref.1), already regarded as classical, which have laid the foundations of this field and have made an appreciable contribution to its development, an enormous amount of data has accumulated in the world literature on carbonium ions with the most varied structures and on their properties, spectroscopic characteristics, and reactivities.[2] The ^1H and ^{13}C NMR spectroscopy has played a decisive role in the establishment and development of the chemistry of carbenium ions. The results obtained by this method have in essence led to the formulation of new fundamental concepts in the theory of the chemical bond. On the other hand, the experimental difficulties in the detection and investigation of charged organic species have exerted a certain influence on the improvement of the NMR experimental technique and on the search for increasingly new features relating the spectroscopic and structural characteristics of organic molecules.[3,4]

Studies on cations of the allyl type have made a major contribution to the formulation of the fundamental ideas in the chemistry of carbenium ions. The ^1H NMR spectra of allyl and 2-methylallyl cations, published in 1964,[5] induced an avalanche-like development of this field, which is indicated by hundreds of publications devoted to the investigation of the structures of positively charged allyl system (see, for example, Refs.6-11). However, until very recently there was virtually no information in the world literature about the polyfluorinated allyl cations, which have been merely postulated as intermediate species in electrophilic alkenylation reactions of fluoroolefins in the presence of Lewis acids.[12-14]

The theoretical interest in polyfluorinated allyl cations can be accounted for also by the following factors. The direct observation of α-fluoro-αα-diphenyl- and αα-difluoro-α-phenyl-methyl cations by ^{19}F NMR[8,11] has made it possible to put forward the concept of the ability of the fluorene atom to stabilise the positive charge localised on a neighbouring carbon atom. However, this concept, which has been convincingly justified experimentally in relation to cations of the alkyl type, for a long time clearly conflicted with the unsuccessful attempts to obtain perfluorinated allyl cations by treating perfluoropropene[8,14] and perfluorocyclobutene[14,15] with antimony pentafluoride. The perchlorinated allyl cation has been isolated in the form of the solid salt $C_3Cl_5AlCl_4$,[16] which in fact suggested that fluorine exerts an influence which is the opposite of that of chlorine, namely a destabilising influence in the case of allyl systems.[17] At the same time, the introduction of markedly electron-donating groups in the 1-position in perfluoroisobutene and perfluoropropene makes it possible to obtain smoothly the corresponding cations:[14,18]

Scheme 1



The present review, which is based on the literature of the last five years, is in fact devoted to the resolution of the uncertainties which have thus arisen.

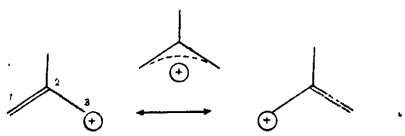
The main method for the investigation of carbonium ions and carbanions is known to be NMR spectroscopy, which makes it possible not only to detect the appearance of a charged centre in the molecule but also to investigate in detail the structural features of the species formed. This is based on the comparatively simple relations found at the present time between the spectroscopic and structural parameters of organic molecules.[3,4] On the other hand, in the case of the ^{19}F and ^{13}C NMR of organofluorine compounds,[19,20] the problem of spectroscopic-structural relations is still far from being resolved. The present review therefore also has a methodological purpose—to survey the characteristic features of the NMR spectra of polyfluorinated allyl cations.

II. NMR SPECTRA AND CHARGE DISTRIBUTION IN HYDROCARBON ALLYL CATIONS

Before discussing polyfluorinated allyl cations, it is useful to consider briefly data on the hydrocarbon allyl cations, demonstrating the possibilities of NMR spectroscopy in the study of the structures of such species in solutions.

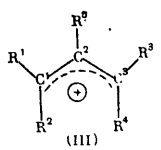
According to the current classification,[11] allyl cations can be regarded as cations of the classical type with the localisation of the positive charge on the terminal carbon atoms,[21,22] as shown in Scheme 2, from which the difference between the terminal and central atoms evidently follows:

Scheme 2



Accordingly, the analysis of the ^{13}C NMR spectra of a large number of acyclic cations having the general formula (III), presented in Scheme 3,[23,24,26–28] shows that the transition from the precursors (olefins) to cations is accompanied by appreciable downfield shifts (up to 100 p.p.m.) of the ^{13}C signals in the 1- and 3- positions so that the C(1, 3) chemical shifts δ are always significantly greater than the shifts δ for the C(2) nuclei in the same cation:

Scheme 3



(III)

R^{1-5}=H [5]; R^{1-4}=H, R^5=CH_3 [5];
$R^{1,3,5}$ = H, $R^{2,4}$ = CH_3 [23, 24]; $R^{1,3,5}$ = CH_3, $R^{2,4}$ = H [24]
$R^{1,3,5}$ = H, $R^{2,4}$ = cyclopropyl [23]
$R^{1,2}$ = CH_3, R^{3-5} = H [23]; R^{1-3} = CH_3, $R^{4,5}$ = H [27]
$R^{1,3}$ = Ph, $R^{2,4,5}$ = H [23]
R^{1-4} = CH_3, R^5 = H [24]; R^{1-5} = CH_3 [24]
R^{1-3} = CH_3, $R^{2,4}$ = H, R^5 = Ph [24]
$R^{1,2}$ = CH_3, $R^{4,5}$ = H, R^3 = CH=C $(CH_3)_2$ [25]
R^1 = CH_3, R^{2-5} = H [26]; $R^{1,2,5}$ = CH_3, $R^{3,4}$ = H [27]
$R^{1-3,5}$ = CH_3, R^4 = H [27]

[Here and henceforth the numerals in square brackets denote references (Translator)].

Thus the relative positions of the C(1 – 3) signals in the ^{13}C NMR spectra correspond satisfactorily to the structure of the allyl cation, agree with the *ab initio* calculations of the π-electron density on the atoms of the allyl triad, and hence can be used successfully for the identification of systems of this kind in solutions. As regards the ^1H NMR spectra, in this case there is no unambiguous correspondence with the charge distribution scheme (Scheme 2).[5,25] Indeed, despite the fact that, on passing from the precursors to the cations downfield shifts of the signals are indeed observed in the ^1H NMR spectrum, there are nevertheless by no means infrequent cases where $\delta(^1H)$ for C(2) is greater than for the C(1, 3) atoms bearing a positive charge. This effect has been observed for example, for the simplest allyl cation (II) with R^{1-5} = H where $\delta(^1H)$ for C(2) is 9.64 p.p.m., whereas $\delta(^1H)$ for the terminal carbon atoms are smaller (δ = 9.0 p.p.m.).[5] Fig.1 indicates the ranges of the $\delta(^1H)$ and $\delta(^{13}C)$ for allyl cations (Scheme 3) which partly illustrates what has been said above.

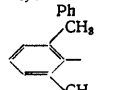
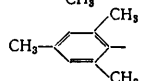
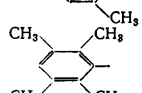
The change in the nature of the substituents in allyl cations naturally leads to a redistribution of their charge density, which is also reflected in the ^{13}C NMR spectra. Thus the successive introduction of methyl groups into the allyl cation (III) has a significant influence on the positions of the signals in the ^{13}C NMR spectra in such a way that a linear relation is observed between the observed values of $\delta(^{13}C)$ and the π-charge density calculated by the *ab initio* method:[22]

$$\delta^{13}C = (433 \pm 11) - (449.5 \pm 22.2)\, q^{\pi},\ r = 0.97 \qquad (1)$$

Relations of this kind make it possible to investigate the distribution of charge density in the allyl cations[23] presented in Table 1. Evidently the shifts δ for the terminal carbon atoms are comparatively close in the case of the 1,3-disubstituted cations. On the other hand, for the 1,1-disubstituted allyl cations the difference δ[C(1)] – δ[C(3)] is large and can reach 120 p.p.m., which in fact permits the conclusion that there is a non-uniform charge distribution between the 1- and 3-atoms, namely that the charge is localised predominantly at C(1). The degree of charge localisation is then determined by the nature of the substituent and, on the basis of the values of $\delta[^{13}C(3)]$, decreases in the following sequence: cyclopropyl ≳ Ph > CH_3.[23] Indeed, in this series $\delta[^{13}C(3)]$ increases by 25 p.p.m. [we may note that in situations of this kind it is correct to compare the values of δ not for C(1) but for C(3) to which the substituent being varied is linked directly].

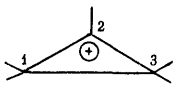
Table 1. The ^{13}C chemical shift of the allyl cations.

$R^1R^2C^1 = \overset{2}{C}H - \overset{3}{C}HR^3$ (⊕)

R^1	R^2	R^3	$\delta(^{13}C)$, p.p.m. C(1) C(2) C(3)	Refs.
cyclo-Pr	H	CH_3	227.0 139.4 194.7	[23]
Ph	H	CH_3	196.9 136.5 205.1	[23]
	H	CH_3	199.9 138.1 188.9	[28]
	H	CH_3	193.2 137.1 184.8	[28]
	H	CH_3	197.5 139.5 189.8	[28]
cyclo-Pr	H	Ph	218.1 132.0 181.2	[23]
cyclo-Pr	CH_3	H	249.6 141.8 150.3	[23]
cyclo-Pr	cyclo-Pr	H	276.4 132.7 148.5	[23]
Ph	Ph	H	227.0 136.2 149.5	[23]
cyclo-Pr	Ph	H	234.6 133.8 157.7	[23]

The principal mechanism of the stabilisation of the positive charge in acyclic allyl cation is *p*, π conjugation, which leads to the localisation of the charge on the ends of the allyl triad. However, when the distance between the terminal carbon atoms is shortened, direct overlap of their orbitals with increase in the resonance contribution of the structure (IV), ensuring the appearance of a positive charge on the central carbon atom (the so called 1,3-interaction[29]), becomes

possible in principle.



(IV)

From the standpoint of NMR, this method of charge stabilisation, together with the classical method, should correspond to the equalisation of the values of δ[C(1−3)] and δ(H) for the given atoms.

For this reason, 1,3-interaction as a method of charge stabilisation was initially invoked to account for the similarity of the values of $\delta(^1H)$ and δ[C(1−3)] for the simplest allyl cation,[5] which, however, was not confirmed by quantum-chemical calculations.[30] On the basis of purely geometrical considerations, 1,3-interaction may be expected for the four-membered cyclic cations (V) (Scheme 4), exhaustive information about which has been published.[31,32] Some of these data are presented in Table 2, from which it follows that a shift of the ^{13}C and ^1H signals of the C(2)−H fragment an even weaker field, compared with the signals of the C(1, 3)−H fragment,

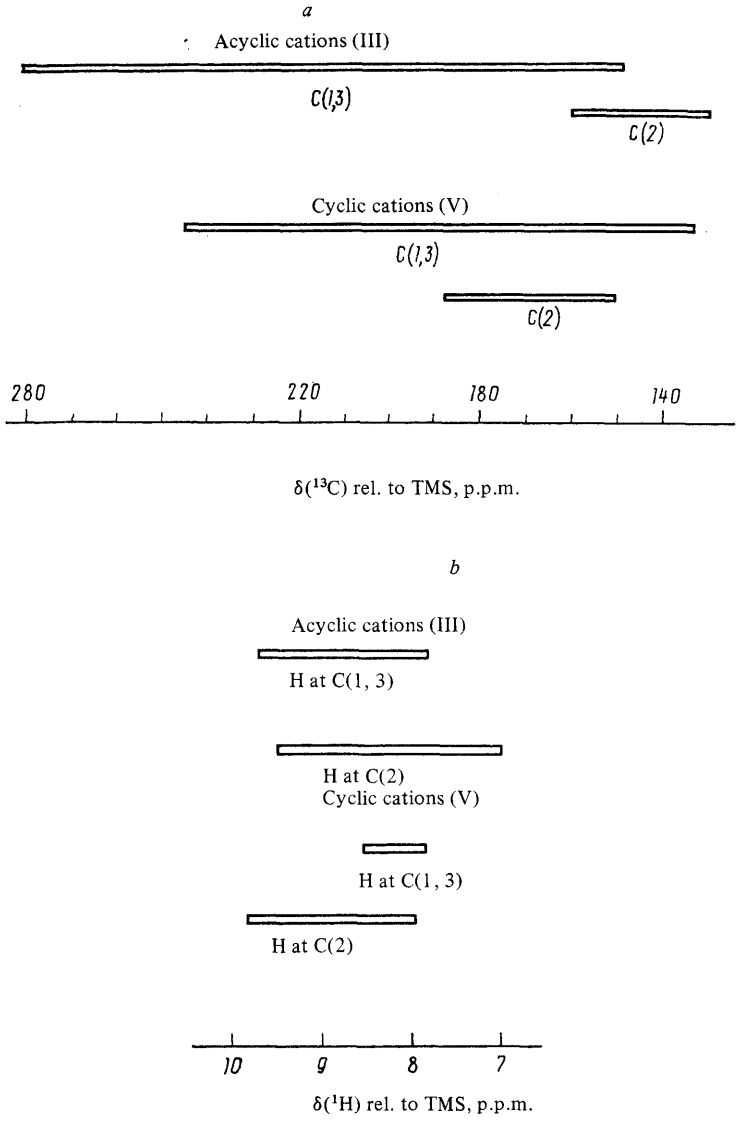
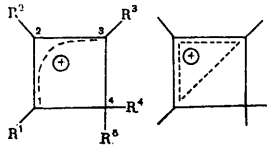


Figure 1. The scales of the ^{13}C (a) and ^1H (b) chemical shifts of hydrocarbon allyl cations.

is characteristic of the compounds considered, with the exception of the last.

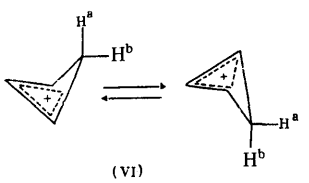
Scheme 4



(V)

$R^{1-5} = H$; $R^{1-4} = H$, $R^5 = Cl$; $R^{1-4} = H$, $R^5 = F$; $R^{2,4,5} = H$, $R^{1,3} = CH_3$;
$R^{1-4} = CH_3$, $R^5 = H$; $R^{1-4} = CH_3$, $R^5 = Cl$; $R^{1-4} = CH_3$, $R^5 = F$;
$R^{1,4} = H$, $R^{2,3} = CH_3$, $R^5 = Cl$; $R^{1,4} = H$, $R^{2,3} = CH_3$, $R^5 = F$;
$R^{1,3} = Ph$, $R^{2,4,5} = H$; $R^{1,3} = Ph$, $R^{2,4} = CH_3$, $R^5 = H$;
$R^{1-4} = Ph$, $R^5 = H$; $R^{1-4} = Ph$, $R^5 = Br$; $R^{1,4,5} = F$, $R^{2,3} = Ph$.

Thus NMR data for the first three cations suggest a distribution of their positive charge throughout the allyl system, as shown in Scheme 4. On the other hand, the introduction of methyl groups into the 1- and 3-positions in the cyclobutenyl cations alters the situation and, as can be seen from Table 2, shifts the C(1, 3) and C(2) resonance downfield and upfield respectively, thus making their spectral parameters closer to the parameters of acyclic allyl cations (Table 1). Consequently, according to NMR data, the probability of the 1,3-overlap depends on the nature of the substituents in the 1- and 3-positions and diminishes with increase in their ability to stabilise the positive charge on the α-carbon atom. Indeed, substituents such as Ph and F exhibit an analogous "spectral" activity.[31,32] Here it is essential to note that all the considerations put forward by the above workers[31,32] and described above are based on a "chemical shift–atomic charge" relation of type (I), which holds in the series of cations considered. However, the chemical shifts of the ^{13}C nucleus occupying the α-position relative to the carbon atom with sp^2 hybridisation in four-membered rings are known to be anomalously high;[33] this is due to the unique nature of the structural and orbital properties of the four-membered ring, which leads to an additional increase in the paramagnetic component of the ^{13}C shielding constant. In other words, the similarity of the values of δ for the C(1, 2, 3) nuclei or the observation of the C(2) signal in an even weaker field than for the C(1, 3) signals may be induced also by this cause and not by the uniqueness of the distribution of charge density. However, the magnetic non-equivalence of the H^a and H^b protons of the cyclobutenyl cation (VI), which is manifested in the NMR spectrum at a low temperature[31] and indicates a non-planar structure of the ring, suggests that the above conclusions[31,32] are correct.

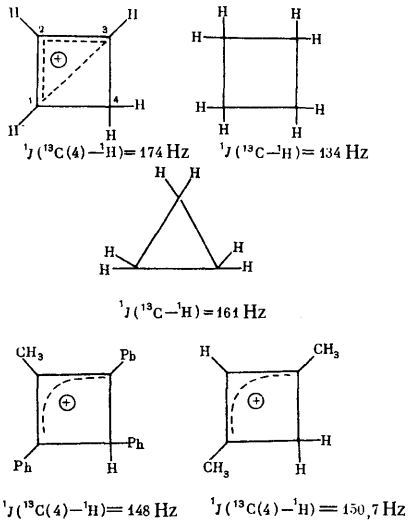


(VI)

This is also indicated by the study of the dependence of $\delta(^{13}C)$ for the allyl triad in cyclic cations on the ring size,[35] which has shown that the 1,3-interaction is pronounced only in the cyclobutenyl cation and is not manifested in the ^{13}C NMR spectra of five- and six-membered structures.

In discussing the question of the 1,3-interaction, it is of interest to consider how such overlap is reflected in the spin–spin coupling constants $J(^{13}C-^{1}H)$, which in the case of cycloalkanes are extremely sensitive to angular deformations and increase with decrease in the ring size.[34] It is known that the constants $^{1}J(^{13}C-^{1}H)$ increase when a positive charge appears on the carbon atom, the increase being mainly due to the Fermi-contact contribution.[4] We shall therefore consider the values of the direct constants $J(^{13}C-^{1}H)$ characterising the unchanged carbon atom in the 4-position in cyclobutenyl cations and carrying information about the geometrical structure of the ring. As can be seen from Scheme 5, $^{1}J[^{13}C(4)-^{1}H] = 174$ Hz for the cyclobutenyl cation and exceeds greatly the analogous constant for cyclobutane and only slightly that for cyclopropane (Scheme 5).

Scheme 5



On the other hand, the substitution of the hydrogen atoms in the 1- and 3-positions by methyl and phenyl groups increases the direct constants $J[^{13}C(4)-^{1}H]$, which corresponds to a decrease in the degree of 1,3-interaction.

Table 2. The ^{1}H and ^{13}C chemical shifts of substituted cyclobuteyl cations (V).[31,32]

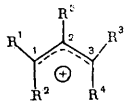
R^1	R^2	R^3	R^4	R^5	δ(^{1}H), p.p.m.				δ(^{13}C), p.p.m.			
					H (1)	H (2)	H (3)	H (4)	C (1)	C (2)	C (3)	C (4)
H	H	H	H	H	7.95	9.72	7.95	4.53	133.5	187.6	133.5	54.0
H	H	H	Cl	H	8.38	9.80	8.38	6.62	141.6	176.7	141.6	63.7
H	H	H	F	H	8.58	9.90	8.58	6.92	136.7	173.8	136.7	86.8
CH_3	H	CH_3	H	H	2.93	8.03	2.93	3.90	197.6	163.1	197.6	51.4

Thus, in conclusion of this Section of the review, one may state that NMR spectroscopy (and in the first place ^{13}C NMR) makes it possible to obtain unique and reliable information about the structure of allyl cations in solutions.

III. ^{13}C AND ^{19}F NMR SPECTROSCOPY OF POLYFLUORINATED ALLYL CATIONS

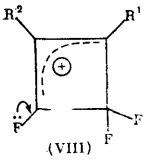
As stated above, the first attempts to obtain polyfluorinated allyl cations by treating perfluoropropene and perfluorocyclobutene with SbF_5 in SO_2 and SO_2FCl were unsuccessful[8,14,15] despite the fact that certain fluorinated cyclic and acyclic allyl cations containing electron-donating groups in the 1-position had been obtained under similar conditions and characterised by ^{19}F NMR.[13,15,18,36] However, in recent years the appliation of this methodological procedure (treatment of fluoro-olefins with SbF_5 in SO_2FCl or in the SbF_5 bulk phase) permitted the synthesis of a whole series of polyfluorinated allyl cations, including the perfluoroallyl and perfluoromethylallyl cations (the references are given in Scheme 6). Some of them proved to be stable and long-lived species even at room temperature. The negative results of the studies quoted above[8,14,15] are therefore incomprehensible. This is presumably due to the inadequate degree of purification of SbF_5 and SO_2FCl.

Scheme 6



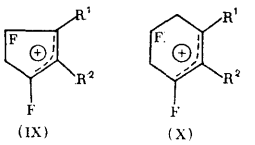
(VII)

$R^1 = Alk_2N$, $R^2 = AlkO$, $R^{3,4} = F$, $R^5 = CF_3$ [18];
$R^1 = n\text{-}CH_3OC_6H_4$, $R^{2-5} = F$ [14]; $R^{1,2,5} = Cl$, $R^{3,4} = F$ [37];
$R^{1,2} = Cl$, $R^{3,4} = F$, $R^5 = CF_3$ [37];
$R^{1,2,5} = Cl$, $R^3 = F$, $R^4 = C_2F_5$ [37]; $R^{1-4} = F$, $R^5 = CF_3$ [38];
$R^{1-4} = F$, $R^5 = H$, Cl, Br, F [39];
$R^{1,3,4} = F$, $R^5 = CF_3$, $R^2 = I$, Br, Cl, OCH_3 [40];
$R^{1,2,4,5} = F$, $R^5 = CF{=}CF_2$ [41]; $R^{1-3,5} = F$, $R^4 = H$, Cl, Br .



(VIII)

$R^1 = OCH_3$, $R^2 = F$, Cl, OCH_3, SCH_3 [15, 36];
$R^1 = OCH_3$, $R^2 = C_2F_5$, F, OCH_3 [42].



(IX) (X)

$R^1 = OCH_3$, $R^2 = CF_3$ [42] $R^1 = OCH_3$, $R^2 = C_2F_5$ [42] .

Scheme 6 presents the polyfluorinated allyl cations known at the present time and Fig.2 indicates the $\delta(^{13}C)$ and $\delta(^{19}F)$ scales characterising these species. Analysis of the spectral chraracteristics of the acyclic cations (VII) permits the following generalisations. On passing from the precursor fluoro-olefin to allyl cations, downfield shifts of the C(1) signals ($\Delta\delta$ = 20–80 p.p.m.) and C(3) signals ($\Delta\delta$ = 50–65 p.p.m.) are recorded in the ^{13}C NMR spectra with the virtual retention of the position of the C(2) signal (small changes in δ for this signal, both downfield and upfield, are observed as a function of the nature of the olefin and the cation), which indicates the localisation of the charge on the terminal fragments of the allyl system. This is also demonstrated by the very fact of the observation of the C(1, 3) signals in a weaker field than the C(2) signal (Fig.2). Analogous effects are characteristic also of the ^{19}F NMR spectra. The ^{19}F NMR spectra of the cations illustrated in Scheme 1 are an exception. For example, on passing from the olefins (IIa) to the corresponding cations (IIb), extremely small downfield shifts

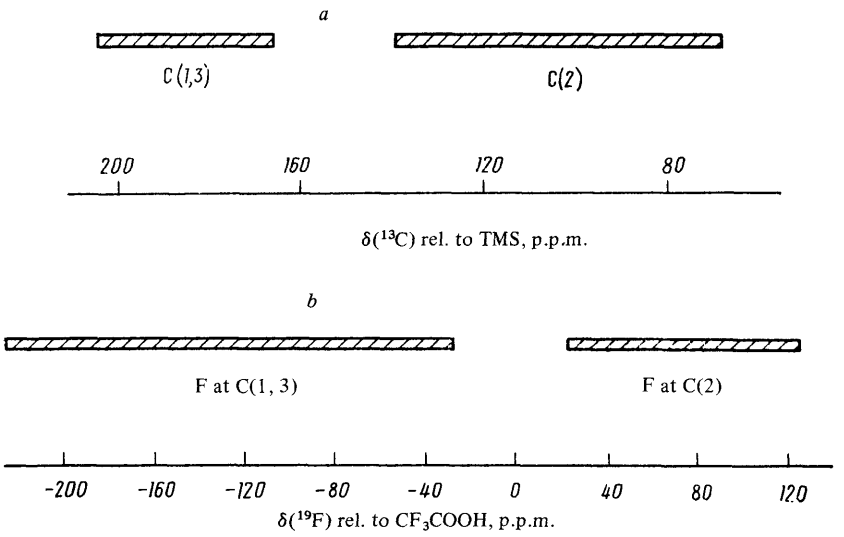
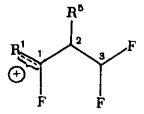


Figure 2. The scales of the ^{13}C (a) and ^{19}F (b) chemical shifts of polyfluorinated allyl cations.

are characteristic of the ^{19}F nuclei in the 3-position, while the downfield shift of the signal of the ^{19}F nuclei at C(1) is by more than 90 p.p.m., which corresponds to the localisation of the charge on the C(1) atom in the structure (XI).[14]



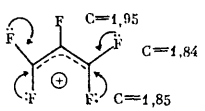
(XI)

$R^1 = p\text{-}CH_3OC_6H_4$
$R^5 = F$,
$R^1 = CH_3O$, $R^5 = CF_3$

An analogous conclusion that the positive charge is localised preferentially in the 1-position has been reached for the cation (VII), with $R^{1,3,4} = F$, $R^5 = CF_3$, and $R^1 = OCH_3$, on the basis of ^{19}F and ^{13}C NMR data.[40] In this case, on passing from the precursor to the cation, a downfield shift of the signal due to the OCH_3 group ($\Delta\delta$ = 15 p.p.m.) is observed in the ^{13}C NMR spectrum. Furthermore, this cation is characterised by a rapid rotation about the C(1)=C(2) bond, which can be retarded only at -70 °C on the ^{19}F NMR time scale (188.3 MHz).

Examination of the generalised spectral parameters presented in Figs.1 and 2 permits the conclusion that in the case of polyfluorinated allyl cations the signals of the C(1) and C(3) atoms, carrying a positive charge, are recorded in a weaker field compared with their hydrocarbon and chlorine-containing analogues.[37,39] On the other hand, the signals of the ^{19}F nuclei at the C(1, 3) atoms in fluorinated allyl cations are observed in extremely weak fields and their chemical shifts reach values down to -200 p.p.m. relative to CF_3COOH. These features of the NMR spectra of the cations (VII) have been explained by the involvement of the fluorine atoms in the delocalisation of the positive charge via the reverse suply of the *p*-electron density (Scheme 7) which has been confirmed by calculations of the charge distribution by the INDO[43] and MNDO[41,44] methods.

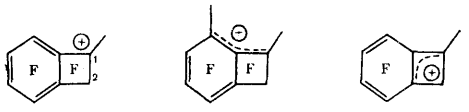
Scheme 7



We may note that, according to the *ab initio* calculation, the introduction of a fluorine atom in the 1-position in the simplest allyl cation increases its stability by 2.8 kcal mol^{-1}.[45]

Virtually analogous changes in the ^{19}F and ^{13}C NMR spectra have been observed on passing from the initial cyclic olefins to the corresponding cations (VIII)–(X).[15,36,42] In describing the delocalisation of the positive charge in the cyclobutenyl cation (VIII) with $R^1 = OCH_3$ and $R^2 = F$,[15] 1,3-interaction was postulated on the basis of the downfield shift of the signal of the ^{19}F nucleus in the 2-position, observed on passing from the precursor to the cation. However, the study of the ^{13}C NMR spectra of the series of cyclic allyl cations (VIII)–(X), containing four-, five-, and six-membered fragments, did not confirm this hypothesis. It was shown that the C(2) signal for such cations is located at stronger fields compared with the C(1, 3) signals and that the difference between their chemical shifts $\delta[C(1, 3)] - \delta[C(2)]$ is 36–63 p.p.m.[42]

Thus experimental and theoretical data have accumulated in recent years which has made it possible not only to provide a firm answer to the previously controversial question of the existence of polyfluorinated allyl cations as kinetically independent species but also to represent the distribution of their positive charge. Unfortunately, there is as yet no information in the literature about the perfluorocyclobutenyl cation.[14,15] Its only and purely speculative analogue is the perfluorobenzocyclobutenyl cation (XII), which has been detected by ^{19}F NMR[46] and to which the authors have attributed the structure of the carbenium ion (XIIa) on the basis of the large shift of the ^{19}F resonance at C(1), observed on passing from the precursor to the cation ($\Delta\delta$ = 145 p.p.m.).



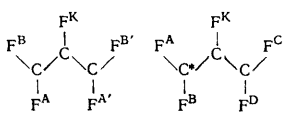
(a) (b)

(XIII)

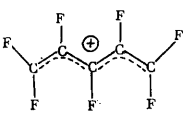
1. Characteristic Features of the ^{19}F and ^{13}C NMR Spectra of Polyfluorinated Acyclic Allyl Cations

The ^{19}F NMR spectra of organofluorine compounds are characterised by high values of *J*, which reach hundreds of Hz units.[19,47] Precisely for this reason, situations frequently arise where the differences between the chemical shifts $\Delta\nu$ become comparable to the spin–spin coupling constants ($J/\Delta\nu \geqslant 0.1$), which leads to the appearance of the NMR spectra of strongly bound spin systems,[48] in which the differences of the absorption frequencies of the spectral lines do not correspond to the real values of *J*. Hence it follows that, in order to obtain the true values of δ and *J* and hence in order to identify the structure, the complete quantum-mechanical calculation of such structures is necessary.[49] We shall explain this in relation to several examples. It has been noted[37] that, after the addition of SbF_5 to perfluoropropene, complex multiplets appear in the ^{19}F NMR spectrum in the -89 – -100 and +117 p.p.m. regions (relative to CF_3COOH), which were later identified[39] as the spectrum of a five-spin system of the type AA'BB'K (Scheme 8), which in fact makes it now possible to make the unambiguous claim that the perfluoroallyl cation is formed in the given mixture.

Scheme 8



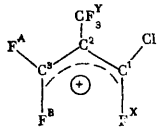
Similarly the agreement between the theoretical spectrum of the seven-spin system, containing more than 140 bands, with the experimental spectrum demonstrates the formation of the perfluoropentadienyl cation which exists in solution in the form of the *s-trans*, *s-trans*-isomer (XIII):



(XII)

This is also confirmed by quantum-chemical calculations by the MNDO method,[41] according to which the *s-trans*, *s-trans*-structure is

energetically more favourable. The ^{19}F NMR spectrum of the *cis-isomer* of the 1-chloro-2-trifluoromethylallyl cation (XIV) is of interest as regards the complexity of the interpretation.



(XIV)

Thus, in the −144 p.p.m. region, it is possible to observe six signals in the above spectrum (Fig.3), each of which is split into a quartet with a non-equidistant disposition of lines. Calculation of the spectrum[40] permitted the classification of the given multiplet as the X-component of the $ABXY_3$ system and made it possible to obtain the true spin−spin coupling constants and hence to identify the cation investigated. Thus the principal feature of the ^{19}F NMR spectra of acyclic fluorinated allyl cations is their complex character. The ^{13}C NMR spectra of these cations are also complex, especially in the case of the symmetrical 2-substituted structures (VII) with R^{1-4} = F.[38,39] We shall illustrate this in relation to the perfluoroallyl cation as an example (Scheme 8). It was stated above that the ^{19}F NMR spectrum of this cation corresponds to the AA'BB'K spin system and is therefore rigorously symmetrical. On the other hand, on passing to ^{13}C NMR, the spectrum loses symmetry and is calculated as the X-component of another spin system, namely ABCDKX (Scheme 8).[39] Such a change in the type of spin system formed by the ^{19}F nuclei, is due to the specific features of the recording of the ^{13}C spectra, namely the isotopic shift on passing from ^{12}C to ^{13}C [50–52] and the associated loss of symmetry by the molecule. The isotopic shift of the signals due to the fluorine nuclei in all the 2-substituted analogues of the perfluoroallyl cation is 0.11 p.p.m.[39] In conclusion, we may note yet again that, despite the by no means simple procedure used to calculate the ^{13}C and ^{19}F NMR spectra of fluorinated allyl cations, requiring a certain amount of time, this approach is absolutely essential both for the establishment of the fact of their formation in solutions and in order to obtain accurate values of their spectral characteristics, including the signs of the constants J, whose knowledge permits the investigation of the relations between the spectral and structural parameters. Some of these relations are described below.

2. The "^{13}C Chemical Shift−Atomic Charge" Relation for Polyfluorinated Allyl Cations and Olefins as an Example

One of the central questions in NMR spectroscopy is the relation between the values of δ and the electron distribution in the molecules. According to Saika and Sliehter,[53] the shielding constants of the magnetically active nucleus can be represented by the sum of three terms [Eqn.(2)]:

$$\sigma=\sigma_d+\sigma_p+\sigma_a \ , \qquad (2)$$

where σ_d is the diamagnetic contribution, σ_p the paramagnetic contribution, and σ_a represeents the sum of the shielding constants due to the magnetic anisotropy of the bond, the influence of the solvent, etc. The ideas concerning the shielding constant of the ^{13}C nuclei[54–56] permit the assumption that in this case the paramagnetic contribution plays a decisive role. It is expressed by the simplified equation[56]

$$\sigma_p=(-e^2h/2m^2c^2\Delta E)\langle r^{-3}\rangle(Q_{AA}+\Sigma Q_{AB}) \ , \qquad (3)$$

where e, h, m, and c are known constants, ΔE is the average excitation energy, r is the distance between the nucleus and the $2p$ electrons, and Q_{AA} and Q_{AB} are elements of the "charge density/bond order" matrix. The first report of the observation of a correlation between the experimental values of $\delta(^{13}C)$ and the charge q' [Eqn.(4)] appeared after the comparison of the ^{13}C NMR spectra of aromatic molecules with the π-charge density calculated by the Hückel

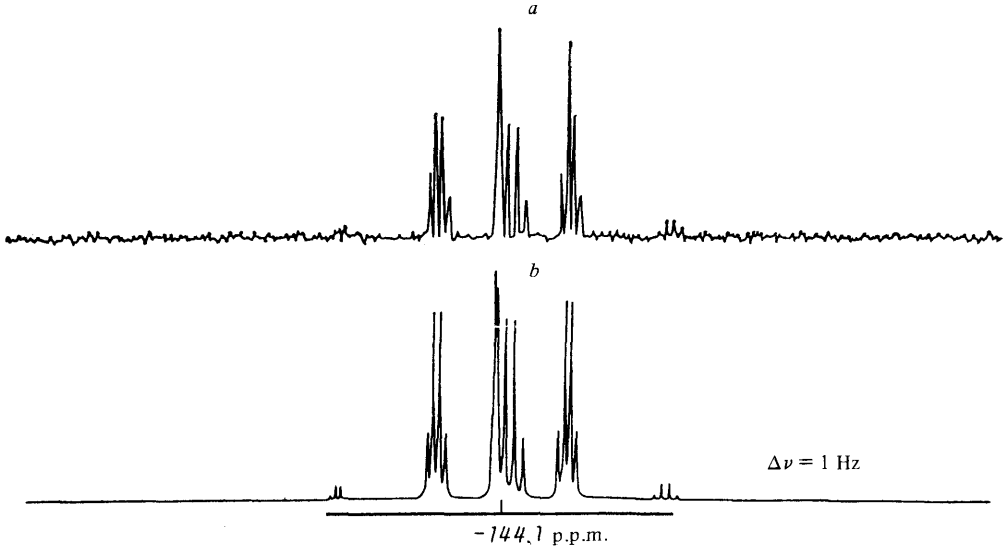


Figure 3. The experimental (a) and theoretical (b) spectra of the X-component of the type $ABXY_3$ spin system of the cation (XIV).[40]

method:[57]

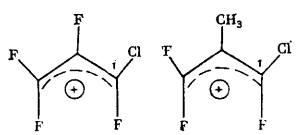
$$\delta^{13}C = A q^t + B$$
$$A = 160 \text{ p.p.m./electron.} \quad (4)$$

The above linear relation can be explained by the fact that the main charge-dependent term in Eqn.(3) is $\langle r^{-3} \rangle$ (ΔE and Q remain constant on passing from one compound to another); this is confirmed by calculations of the atomic charges and the parameter r for a large number of organic compounds.[58,59] Among studies published later, devoted to the investigation of the "^{13}C chemical shifts – atomic charge" relation (see, for example, Refs.59–63), the study of Baumann and Olsen[59] in which this relation was analysed for 20 organic compounds (50 values of δ), including aromatic cations and anions, is of special interest in our view. The results obtained showed that (1) the coefficient A in Eqn.(4) depends on the LCAO-MO method used for the calculation, (2) that the change in the character of the chemical bond and in geomtetry on passing from one compound to another precludes the description of the "δ(^{13}C) – charge" relation by simple linear equations of the type of Eqn.(4) as a consequence of the change in Eqn.(3) of not only r but also of other parameters, and (3) in the analysis of the relation of the "δ(^{13}C) – charge" type it is essential to take into account also the diamagnetic component of the shielding constant. Summarising the foregoing, one may conclude that it is completely obscure in what way the simplified but nevertheless still complex Eqn.(3) frequently reduces in practice to simple equations of type (4). Nevertheless, this has been established for many classes of organic compounds and it has even been suggested that relations of this type be used for the computer analysis of ^{13}C NMR spectra.[64]

In the study quoted above,[59] a deviation of fluorine-containing compounds from the so called "δ(^{13}C) – charge" correlations was reported. This concerns, for example, δ[C(1)] for the 1-fluorobenzocyclopropyl cation. On the other hand, it has been shown that, on passing from fluorinated olefins to the corresponding allyl cations (VII), downfield shifts of the C(1, 3) resonance are observed in the ^{13}C NMR spectra[38,39] and, conversely, on formation of carbanions from fluorinated cycloalkenes, upfield shifts, reaching 70 p.p.m., are characteristic of the carbon atom carrying the negative charge.[65] Thus there are grounds for seeking correlations of type (IV) also in the case of organofluorine compounds. The geometries and charge density distributions in polyfluorinated olefins and acyclic allyl cations have been calculated[41,44,66] by the LCAO-MO MNDO method. This made it possible to analyse[67] 27 values of δ(^{13}C) as a function of the overall atomic charge of the sp^2-hybridised carbon atom q^t and to observe the linear relation

$$\delta_{^{13}C} = (84.2 \pm 7.5) q^t + (124.4 \pm 3.8), \; r = 0.93 \; , \quad (5)$$

which can be used to estimate the atomic charges from ^{13}C NMR spectra. The values of δ for the ^{13}C(1) nuclei in the cations (XV), i.e. for the atoms which are linked directly to the substituent, in the given instance to the Cl atom, deviate from the given correlation to the greatest extent.



cis-, trans- *cis-, trans-*

(XV)

Indeed, on passing from perfluorinated analogues to the cations (XV), the positive charge on the G(1) atom fails as a consequence of the polarisation of the C–Cl bond along the σ-skeleton,[44] while δ(^{13}C) increases significantly (by 20 p.p.m.). Such increase in δ[C(1)] on substitution of fluorine by a "heavy" halogen is in general characteristic of 1-halogeno-derivatives of the perfluoroallyl and perfluoromethylallyl cations (Table 3), the effect being thus opposite in sign to the "heavy" atom effect usually observed in ^{13}C NMR spectroscopy (see, for example, Levy and Nelson[4]), which is illustrated here in relation to fluoro-olefins in Table 3. In order to elucidate the cause of the deviation of the δ(^{13}C) for the C(1) atoms in compound (XV) from the relation (5), the diamagnetic contributions to the shielding constant were estimated[67] by the method of Flygar and Goodisman[69] and then, after introducing the diamagnetic correction ($\delta^{exp} - \delta^d = \delta^p$), the values obtained were again compared with the overall charge q^t. It was found that the application of this correction improves the situation, but again with the exception of the δ[C(1)] points for the cation (XV). Thus one can only assume that, on passing to 1-halogeno-substituted polyfluorinated allyl cations, δ[C(1)] is determined not so much by the change in the charge (or in other words in the parameter $\langle r^{-3} \rangle$) as by the change in the orbital properties of the C(1) atom replaced by the halogen atom.[67]

Table 3. The ^{13}C chemical shifts of the C(1) atoms of allyl cations and their precursors (p.p.m. relative to TMS_{ext}).

$F_2\overset{3}{C}\overset{2}{=}\overset{1}{C}(X)\overset{+}{\cdots}\overset{+}{\cdots}CFY$; $\overset{3}{CF_3}-\overset{2}{C}(X)=\overset{1}{C}FY$

Cation		δ(^{13}C)	Olefin		δ(^{13}C)	Refs.
X	Y		X	Y		
F	F	170.2	F	F	153.2	[39]
F	Cl*	187.6; 191.0	F	Cl*	140.8; 142.5	[68]
F	Br*	187.6; 193.4	F	Br*	130.3; 133.7	[68]
CF_3	F	176.1	CF_3	F	157.0	[38]
CF_3	Cl*	202.2; 201.0	CF_3	Cl	159.6	[40]
CF_3	Br*	205.0; 202.7	CF_3	Br	150.0	[40]
CF_3	I*	197.5; 194.6	CF_3	I	121.6	[40]
CF_3	Cl**	214.3				[37]

*The two values are quoted for the *cis-* and *trans-*isomers respectively.

**The 1-dichloroperfluoromethylallyl cation.

3. The ^{19}F – ^{19}F Spin – Spin Coupling Constants of Polyfluorinated Allyl Cations

The spin – spin coupling constants play a major role in the determination of the structures of organic compounds and in the study of their electronic structures by NMR.[3] For this reason, it is legitimate to analyse the constants $J(^{19}F - ^{19}F)$ for polyfluorinated allyl cations in order to discover to what extent they are characteristic of the given class of compounds. It follows from the analysis of the ^{19}F NMR spectra[14,18,37–41,68] that the geminal $J(^{19}F - ^{19}F)$ constant (J^{gem}) increases sharply on passing from fluorinated olefins (10–60 Hz) to the corresponding cations (VII) (160–245 Hz), which can be used as the spectroscopic sign of the formation of the given cations. We may note that the constants J^{gem} for allyl cations and fluoroalkanes have similar values. This may be caused by the fact that the F–C(1, 3)–F angle in acyclic fluoroallyl cations is close to the tetrahedral angle and, according to a MNDO calculation carried out with complete optimisation of the geometry, amounts to

110–112°.[41,44] In contrast to the constants J^{gem}, the vicinal (spanning three bonds) $J(^{19}F-^{19}F)$ constants of polyfluorinated allyl cations are not characteristic. Indeed, they are approximately equal for the initial olefins ($^3J^{cis}$ = 6–40 Hz, $^3J^{trans}$ = 117–143 Hz) and for the acyclic cations (VII) ($^3J^{cis}$ = 8–30 Hz, $^3J^{trans}$ = 90 to 124 Hz).

Table 4. The constants $^4J(^{19}F-^{19}F)$ for the allyl cations (VII) (Scheme 6) (R^1 = R^2 = R^4 = F[73]).

R^3	R^5	J, Hz				r, Å
		«U»	«W»	«S»	J^{np}	
H	F	−122.4	−92.4	−22.2	−100.2	2.975
F	F	−140.3	−104.5	−30.9	−109.4	2.907
OCH_3	F	−157.6	−101.3	−35.6	−122.0	2.860
Cl	F	−149.6	−92.0	−29.3	−120.3	2.850
Br	F	−150.7	−87.7	−29.4	−121.3	2.821
F	Br	−156.0	—	−42.0	−114.0	2.821
CF_3	F	−146.7	−83.8	−23.2	−123.5	2.775
CF_3	Cl	−175.3	—	−31.5	−143.8	2.644
CF_3	Br	−173.4	—	−36.9	−136.5	2.634

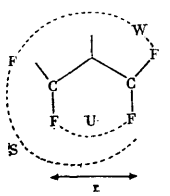
The appearance in the ^{19}F NMR spectra of large long-range (spanning four bonds) spin–spin $^{19}F-^{19}F$ coupling constants (Table 4), which, for the *cis–cis* disposition of the interacting nuclei, exceed by a factor greater than two the ^4J ($^{19}F-^{19}F$) constant for the isostructural but uncharged 1,8-difluoronaphthalene (XVI) fragment, must be regarded as an invariable sign of the formation of fluorinated acyclic allyl cations.[70]



(XVI)

We may note that $J(^{19}F-^{19}F)$ constants spanning six bonds and amounting to 10–12 Hz have been observed for the perfluoropentadienyl cation (XIII).[71] The constants J spanning three and more bonds are known to depend markedly on the mutual orientation of the chemical bonds along the interaction pathway.[19,49,72] Table 4 illustrates this situation for polyfluorinated allyl cations. It follows from the data presented that the constants $^4J(^{10}F-^{19}F)$ decrease in absolute magnitude in the sequence "U" > "W" > "S" (Scheme 9) without change in their sign.[73]

Scheme 9



The deviation from the W-rule, well known for the proton–proton spin–spin coupling constants,[49] can be explained by the spin–spin coupling "through space" in the case of the *cis–cis* orientation. (Examples, mechanisms, and semiempirical theories of the transfer of spin information by-passing chemical bonds can be found in several communications[72,74–80]). Indeed, it has been shown that [73] the "spatial" contribution (J^{sp} = J^U – J^s) to $^4J(^{19}F-^{19}F)$ constants for the *cis–cis* orientation (Table 4), which has been differentiated by Bakhmutov et al.,[71] diminishes with increase in the internuclear distant r (Scheme 9) determined by the LCAO-MO MNDO method.[44,73] The experimental dependence is then best fitted, taking into account the sign, by Eqn.(6), whose physical significance can be interpreted in terms of direct overlap of the *p*-electron clouds of the fluorine atoms in close proximity in space:

$$J^{sp} = -431(\pm 50)\exp(-0.16\cdot r^2) + 1.2 \qquad (6)$$

It is noteworthy that the variation of the overlap integral for the fluorine molecule for distances between the atoms exceeding the sum of the van der Waals radii is a function of an analogous type.[73] In the calculation of the constant $J(^1H - ^1H)$ spanning five chemical bonds on the basis of the Fermi-contact mechanism for the *s-cis*-conformation of butadiene, a dependence of $^5J(H-C)$ on the internuclear distance of the Gaussian type was also obtained.[81] Thus, there are grounds for the assumption that the nuclei interacting through space can be regarded as "magnetic probes" for "sensing" the form of the overlapping part of the electron clouds.

4. The $^{13}C-^{19}F$ Spin–Spin Coupling Constants of Polyfluorinated Allyl Cations

The accumulation of extensive data concerning the influence of various factors on the constants for the direct spin–spin coupling (via one chemical bond) with participation of ^{13}C nuclei constitutes the basis of their use for the determination of the structures of organic compounds by NMR.[3] The spectroscopic data on polyfluorinated olefins and allyl cations (VII) permit certain generalisations also for the $^1J(^{13}C-^{19}F)$ constants characterising the sp^2-hybridised carbon atoms and atoms with a hybridisation close to sp^2. A significant (up to 100 Hz) increase in $^1J(^{13}C-^{19}F)$ on passing from fluoro-olefins to the corresponding allyl cations has been noted[37–40,42] (this concerns carbon atoms carrying a positive charge). The constants of the acyclic and cyclic cations (VII)–(X) are themselves in the range from 310 to 410 Hz. We may note that these values greatly exceed the direct $J(^{13}C-^{19}F)$ constants observed in the NMR spectra of related polyfluorinated arenonium ions.[82,83] The foregoing refers to the increase in the spin–spin coupling constants in absolute magnitude, since $^1J(^{13}C-^{19}F)$ is negative.[3,83] More than 30 values of the direct constants $J(^{13}C-^{19}F)$ of fluorinated olefins and allyl cations have been analysed and on this basis it has been established that there is a tendency towards their increase with increase in the positive charge on the sp^2-hybridised carbon atom and with decrease in the negative charge on the neighbouring fluorine atom, which is expressed in the two-parameter correlation[7]

$$^1J(^{13}C-^{19}F) = 92q^C + 501q^F + 325,\ r = 0.89 \qquad (7)$$

However, the one-parameter Eqn.(8), which makes it possible to estimate the atomic charge on the carbon atom using available spectroscopic data, is apparently of greater practical value:

$$^1J(^{13}C-^{19}F) = 122q^C + 277;\quad r = 0.84. \qquad (8)$$

The increase in $^1J(^{13}C-^{19}F)$ following the appearance of a positive charge on C(1, 3) corresponds, in principle, to the increase in the amount of *s* character of the given atom as a result of the splitting off of the fluorine atom from the initial olefin and the subsequent

delocalisation of the *p*-electron density, i.e. is treated within the framework of the Fermi-contact mechanism.[19] However, within the framework of this mechanism, it is difficult to explain the fact that $^1J(^{13}C^1-^{19}F)$ for the cation (XV) is greater than $^1J(^{13}C^3-^{19}F)$ despite the smaller positive charge localised on the C(1) atom (Table 5). Moreover, an increase in the direct constant J with decrease in the electronegativity of the heteroatom of the substituent is characteristic of 1-substituted fluorinated olefins and allyl cations (Table 6). However, in each specific case, the direct $J(^{13}C-^{19}F)$ constant for the cation is significantly greater compared with the olefin. Such complex character of the variation of J under the influence of the substituent and on passing from olefins to cations can apparently be explained by non-concerted changes in the Fermi-contact and spin–orbital contributions,[68] which have been shown by quantum-chemical calculations[83] to be virtually equal for interaction through one chemical bond. Despite this, the constants J discussed should be recognised as characteristic in relation to polyfluorinated allyl cations.

Table 5. The spin–spin coupling constants (SSCC) $^1J(^{13}C-^{19}F)$ and the overall atomic charges (LCAO-MO MNDO) of polyfluorinated allyl cations.[68]

Structure	Isomer	SSCC, Hz	q^C, electronic charge units
$F_2\overset{3}{C}=\overset{2}{C}(F)-\overset{1}{C}FCl$ ⊕	*cis*	−375.9 C (1) −254.0 C (2) −354.7 C (3)	+0.469 −0.047 +0.669
	trans	−375.7 C (1) −274.0 C (2) −357.9 C (3)	+0.455 −0.042 +0.666
$F_2\overset{3}{C}=\overset{2}{C}(CF_3)=\overset{1}{C}FCl$ ⊕	*cis*	−386.2 C (1) −360.7 C (3)	+0.514 +0.716
	trans	−384.0 C (1) −356.2 C (3)	+0.530 +0.724

Table 6. The direct spin–spin coupling constants $^1J(^{13}C-^{19}F)$ for the C(1)–F fragment in the fluoro-olefins $FYC^1=C^2X-CF_3$ and the allyl cations

$$FY\overset{1}{C}=\!=\!=C^2X=\!=\!=CF_2 \quad (\oplus)$$

and the electronegativites E of the substitutent Y.[68]

X	Y	$^1J_{olefin}$, Hz	$^1J_{cation}$, Hz	E
F	F	−272.8	−354.0	4.0
F	H	−291.1*	−364.5*	2.1
F	Cl	−304.0*	−375.9*	3.2
F	Br	−323.0*	−397.5*	3.0
CF_3	F	−306.3	−360.0	4.0
CF_3	OCH_3	−306.7*	−363.2**	3.4
CF_3	Cl	−322.0	−385.1**	3.2
CF_3	Br	−342.6*	−400.4**	3.0
CF_3	I	−351.2*	−408.8**	2.7

**trans*-Disposition of F–C–C–X or CF_3–C–C–X.
**Averaged value for the *cis*- and *trans*-isomers.

Information about the values and signs of the constants $^2J(^{13}C-^{19}F)$ and $^3J(^{13}C-^{19}F)$ of polyfluorinated olefins and cations can be found in a number of communications.[37–41] Here we shall note that the values of J spanning three bonds for the *trans*-disposition of the interacting nuclei vary from −9 to −34 Hz. On the other hand, in the case of the *cis*-disposition they change sign and do not exceed 4 Hz in absolute magnitude.

Table 7. Thermodynamic parameters of the formation of polyfluorinated allyl cations.

$$F_2\overset{3}{C}=\!=\!=\overset{2}{C}(X)=\!=\!=\overset{1}{C}FY \quad (\oplus) \quad [84, 85]$$

X	Y	ΔH, kcal mol^{-1}	ΔS, e.u.	ΔG^{298}, kcal mol^{-1}
F	H	−4.16±0.2	−22.5±0.8	2.6
F	F	−5.6±0.5	−26.1±1.8	1.8
CF_3	F	−4.6±0.1	−23.9±0.8	2.5
CF_3	Br	−6.4±0.8	−28.5±3.0	2.1
CF_3	Cl*	−7.0±0.2	−28.5±0.4	1.5

*The 1,1-dichloroperfluoromethylally cation.

5. ^{19}F NMR Spectra and Relative Stabilities of Polyfluorinated Allyl Cations

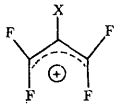
The spectral characteristics of polyfluorinated allyl cations described in the preceding Sections and their characteristic features permit a reliable solution of the problem of the identification of such species in solutions by NMR. Another important problem, namely the problem of the influence of the substituents on the relative stabilities of polyfluorinated allyl cations, can also be solved successfully by NMR. For this purpose, one can use three approaches: (1) the study of the thermodynamics of the equilibrium (9) on the basis of the measurement of the relative integral intensities of the signals of the olefins and cations in ^{19}F NMR spectra at different temperatures:[68,84]

$$CF_2=\overset{R^1}{\underset{|}{C}}=CFR^2 + SbF_5 \overset{Kp}{\rightleftharpoons} F_2C=\overset{R^1}{\underset{|}{C}}=CFR^2 \quad (\oplus) + SbF_6^- ; \qquad (9)$$

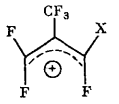
(2) analysis of the ^{19}F NMR spectra of a mixture of two polyfluoro-olefins in the presence of a deficiency of a Lewis acid, i.e. under the conditions of a competing reaction;[85] (3) the study of the kinetic characteristics of the reaction involving the addition of counterions to the corresponding allyl cation[84] on the basis of the analysis of the temperature dependent evolution of the line form in the ^{19}F NMR spectrum containing the olefin and cation signals. The qualitative and quantitative data obtained in this way are compiled in Tables 7

and 8 and in Scheme 10.

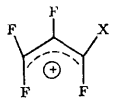
Scheme 10



$CF_3 < F < Br < Cl < H$ (a)



$F < Cl < Br < I < OCH_3$ (b)



$H < F < Cl < Br$ (c)

$F_2C{=}C(CF_3){-}CF_2 < F_2C{=}C(CF_3){-}CFCl < F_2C{=}C(CF_3){-}CCl_2$

As can be seen, the formation of polyfluorinated allyl cations from the corresponding fluoro-olefins in solutions is an energetically favourable process, since the enthalpy of formation ($\Delta H = H^{cat} - H^{ol}$) is always negative. On the other hand, the negative values of ΔS, which are almost identical in all cases, correspond satisfactorily to an increase in order in the system following the appearance of a charge centre in the latter. Comparison of the data in Tables 7 and 8 shows that the kinetically less favourable addition of the counter-ion to the cation corresponds to its high thermodynamic stability.

Table 8. Kinetic parameters of the addition of the fluoride ion to the polyfluorinated allyl cations [84,85]

$F_2\overset{3}{C}{=}\overset{2}{C}(X){=}\overset{1}{C}FY$ ⊕

X	Y	E_a, kcal mol^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	$\Delta G^{298\neq}$, kcal mol^{-1}
F	F	6.2±0.3	6.9±0.3	−8.4±0.4	9.4
Cl	F	21.6±1.3	22.2±1.3	−12.1±1.5	25 5
Br	F	13.7±0.9	14.2±0.9	−15.0±1.0	18.7
CF_3	Cl*	9.5±0.9	8.9±0.9	−16.8±3.2	13.9
Cl	Cl**	11.8±1.1	12.4±1.1	−12.1±2.5	16.0

*The 1,1-dichloroperfluoromethylallyl cation.
**The 1,1,2-trichloroperfluoroallyl cation.

The influence of substituents on the relative stabilities of polyfluorinated allyl cations is expressed by the series presented in Scheme 10. As can be seen, in the case of 2-substituted perfluoroallyl cations (10a) this influence cannot be treated in terms of a change in only the electronic properties of the substituents. It is apparently necessary to invoke also steric factors. The increase in the stability of 1-substituted analogues of the perfluoromethylallyl cation (10b) corresponds to a decrease in the $-I$ effect of the substituent and to an increase in its polarisability. An increase in the number of "heavy" halogens at one of the ends of the allyl system also increases the stability of the given species (10d). The decrease in stability on passing from the perfluoroallyl cation to its 1-hydro-derivative (10c) must be specially emphasised. The observed effect then amounts to 1.5 kcal mol^{-1} (Table 7)[68] and agrees well with the results of a theoretical calculation by the *ab initio* method.[45] It follows from the NMR spectra that the F atom participates in the stabilisation of the positive charge localised on a neighbouring carbon atom via the reverse supply of *p*-electron density. Apparently this ability of the fluorine atom is in fact the cause of the result obtained. Indeed, in the case of the perfluoroallyl cation and its 2-hydro-derivative, i.e. on substitution of the fluorine atom by hydrogen in the 2-position which does not carry a positive charge, the opposite picture (10a) is observed.

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The main aim of the present review was to survey the results of the study of polyfluorinated allyl cations which had been regarded for a long time as hypothetical species and had been assumed to exist only as intermediates in electrophilic alkenylation reactions of fluoro-olefins. This uncertainty in the theroretical ideas about the mechanisms of the above reactions and in the chemistry of carbenium ions has now been eliminated as a result of the direct observation by ^{19}F and ^{13}C NMR of a series of polyfluorinated allyl cations (cyclic and acyclic) as both long-lived and kinetically independent species. Presumably data on the stability of allyl cations in solutions and on the distribution of their positive charge will extend the scope of the synthetic use of the reactions in which they are formed as intermediate species.

It may be hoped that the spectral signs of the formation of polyfluorinated allyl cations examined and surveyed in the present review will be of practical use to specialists working in the field of the NMR of organofluorine compounds which is nowadays developing rapidly. Analysis of the literature data devoted to the NMR spectra of fluorine-containing olefins and allyl cations has shown that such compounds can be used successfully as model molecules to establish new relations between spectra and structure.

REFERENCES

1. G.A.Olah, Angew. Chem., 1963, **75**, 800.
2. "Carbonium Ions", Wiley, New York–London–Sydney–Toronto, 1968, Vol.1; 1970, Vol.2.
3. B.I.Ionin, B.A.Ershov, and A.I.Kol'tsov, "YaMR Spektroskopiya v Organicheskoi Khimii" (NMR Spectroscopy in Organic Chemistry), Izd. Khimiya, Moscow, 1983, p.208.
4. G.Levy and G.Nelson, "Manual of Carbon-13 Nuclear Magnetic Resonance for Organic Chemists" (Translated into Russian), Izd. Mir, Moscow, 1975.
5. G.A.Olah and M.B.Comisarow, J. Amer. Chem. Soc., 1964, **86**, 5682.
6. G.A.Olah, M.B.Comisarow, C.A.Cupas, and C.U.Pittman, J. Amer. Chem. Soc., 1965, **87**, 2997.
7. G.A.Olah and A.M.White, J. Amer. Chem. Soc., 1969, **91**, 5801.

8. G.A.Olah and Y.K.Mo, Adv. Fluor. Chem., 1973, **7**, 109.
9. N.C.Deno, "Modern Problems of Physical Organic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1963, p.393.
10. "Carbonium Ions", Wiley, New York–London–Sydney–Toronto, 1972, Vol.3; 1974, Vol.4; 1976, Vol.5.
11. G.A.Olah, Uspekhi Khim., 1975, **44**, 793 [Russ. Chem. Rev., 1975(5)].
12. G.G.Belenkii and L.S.German, Soviet Sci. Rev., Section B. Chem. Phys., 1984, **5**, 183.
13. Yu.A.Kopevich, G.G.Belen'kii, and E.I.Mysov, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 1972, **7**, 236.
14. R.Chambers, A.Porkin, and R.S.Matthews, J. Chem. Soc. Perkin Trans. I. 1976, 2107.
15. B.E.Smart and G.S.Reddy, J. Amer. Chem. Soc., 1976, **98**, 5593.
16. R.Ewst and P.T.Kwitowski, J. Amer. Chem. Soc., **88**, 5280.
17. R.W.Taft, R.U. Martin, and F.W.Lampe, J. Amer. Chem. Soc., 1965, **87**, 2490.
18. I.L.Knunyants, Yo.G.Abduganiev, and E.M.Rokhlin, Tetrahedron, 1973, **29**, 595.
19. J.W.Emsley, L.Phillips, and V.Wray, "Progress in NMR Spectroscopy", Pergamon, Oxford–New York–Toronto–Sydney–Paris, 1977, p.111.
20. V.Wray, J. Amer. Chem. Soc., 1981, **103**, 2503.
21. T.J.Katz and E.H.Gold, J. Amer. Chem. Soc., 1964, **8**, 1600.
22. H.Mayr, W.Förner, and P.Schleyer, J. Amer. Chem. Soc., 1979, **101**, 6032.
23. G.A.Olah and R.J.Spear, J. Amer. Chem. Soc., 1975, **97**, 1539.
24. G.A.Olah, R.Clifford, Y.Halpern, and R.G.Johanson, J. Amer. Chem. Soc., 1971, **93**, 4219.
25. N.C.Deno and C.U.Pittman, J. Amer. Chem. Soc., 1964, **86**, 1871.
26. H.Mayr and G.A.Olah, J. Amer. Chem. Soc., 1977, **99**, 510.
27. G.A.Olah and H.Mayr, J. Amer. Chem. Soc., 1976, **98**, 7333.
28. D.N.Dytnerski, K.Ravgahagakubu, B.P.Singh, and T.S.Sorensen, Canad. J. Chem., 1982, **60**, 2993.
29. "Carbonium Ions", Wiley, New York–London–Sydney–Toronto, 1972, Vol.3, p.1007.
30. B.K.Carpenter, J. Chem. Soc. Perkin Trans. II, 1974, 1.
31. G.A.Olah, J.S.Staral, R.J.Spear, and G.Liang, J. Amer. Chem. Soc., 1975, **97**, 5489.
32. G.A.Olah and J.S.Staral, J. Amer. Chem. Soc., 1976, **98**, 6292.
33. J.B.Lambert, S.M.Wharrey, E.Block, and A.A.Bazzi, J. Org. Chem., 1983, **48**, 3982.
34. R.G.Rees and M.S.Green, J. Chem. Soc. B, 1968, 387.
35. G.A.Olah and G.Liang, J. Amer. Chem. Soc., 1972, **94**, 6439.
36. B.E.Smart, J. Org. Chem., 1976, **41**, 2377.
37. V.A.Petrov, G.G.Belen'kii, and L.S.German, Izv. Akad. Nauk SSSR, Ser. Khim., 1982, 2411.
38. V.A.Petrov, G.G.Belen'kii, M.V.Galakhov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1984, 2811.
39. M.V.Galakhov, V.A.Petrov, V.I.Bakhmutov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1985, 306.
40. M.V.Galakhov, V.A Petrov, G.G.Belen'kii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1986, 1063.
41. M.V.Galakhov, Yu.A.Borisov, V.A.Petrov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1986, 1761.
42. V.F.Snegirev, M.V.Galakhov, K.N.Makarov, and V.I.Bakhmutov, Izv. Akad. Nauk SSSR, Ser. Khim., 1985, 2302.
43. L.D.Kispert, C.U.Pittman, D.L.Allison, et al., J. Amer. Chem. Soc., 1972, **94**, 5979.
44. Yu.A.Borisov, M.V.Galakhov, and V.I.Bakhmutov, Izv. Akad. Nauk SSSR, Ser. Khim., 1986, 1498.
45. M.N.Lien and A.C.Hopkinson, J. Phys. Chem., 1984, **88**, 1513.
46. V.M.Karpov, T.V.Mezhenkova, V.E.Platonov, and G.G.Yakobson, J. Fluor. Chem., 1985, **28**, 121.
47. J.W.Emsley, J.Feeney, and L.A.Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy" (Translated into Russian), Izd. Mir, Moscow, 1969.
48. P.L.Cario and R.C.Hirst, J. Chem. Educ., 1969, **46**, 345.
49. H.Guenther, "NMR Spectroscopy. An Introduction to Proton Resonance Spectroscopy and Its Applications in Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1984, p.202.
50. G.M.D.Tiers, J. Amer. Chem. Soc., 1957, **79**, 5585.
51. G.M.D.Tiers, J. Chem. Phys., 1957, **29**, 963.
52. S.G.Frankiss, J. Phys. Chem., 1963, **67**, 752.
53. A.Saika and C.P.Slichter, J. Chem. Phys., 1954, **22**, 26.
54. G.J.Martin, M.L.Martin, and S.Odiot, Org. Magn. Reson., 1975, **7**, 2.
55. J.A.Pople, J. Chem. Phys., 1962, **37**, 53.
56. M.Karplus and J.A.Pople, J. Chem. Phys., 1963, **38**, 2803.
57. H.Spiesecke and W.G.Schnaider, Tetrahedron Lett., 1961, **468**.
58. T.Tokahiro and G.Fraenkel, J. Amer. Chem. Soc., 1969, **71**, 5005.
59. H.Baumann and H.Olsen, Helv. Chim. Acta, 1980, **63**, 2202.
60. R.T.Brownlee and D.J.Craic, Org. Magn. Reson., 1981, **15**, 248.
61. R.T.Brownlee and D.J.Craic, J. Amer. Chem. Soc., 1983, **105**, 872.
62. D.H.O'Brien, A.S.Hart, and C.R.Russel, J. Amer. Chem. Soc., 1975, **97**, 4410.
63. J.P.Begue and D.Bonnet-Delpon, Org. Magn. Reson., 1980, **14**, 349.
64. I.P.Bangov, Org. Magn. Reson., 1981, **16**, 296.
65. V.F.Snegirev, N.I.Delyagina, and V.I.Bakhmutov, Izv. Akad. Nauk SSSR, Ser. Khim., 1986, 1325.
66. I.N.Rozhkov, A.A.Stepanoff, and Yu.A.Borisov, IV Soviet-Japanese Meeting of Fluorine Chem. Kiev, 1985, 125.
67. V.I.Bakhmutov, M.V.Galakhov and E.I.Fedin, Izv. Akad. Nauk SSSR, Ser. Khim., 1987, 675.
68. M.V.Galakhov, Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1986.
69. W.H.Flygar and E.Goodisman, J. Chem. Phys., 1968, **49**, 3132.
70. F.B.Mallory, C.W.Mallory, and M.C.Federco, J. Amer. Chem. Soc., 1974, **96**, 3536.
71. V.I.Bakhmutov, M.V.Galakhov, and E.I.Fedin, Magn. Reson. in Chem., 1985, **98**, 971.
72. M.A.Natello, R.H.Contreras, H.O.Gavarini, and I.D.Rae, J. Chem. Phys., 1985, **98**, 270.
73. V.I.Bakhmutov, M.V.Galakhov, N.I.Raevskii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1987, 1884.
74. J.Hilton and L.H.Sutcliffe, Progr. Nucl. Magn. Reson. Spectr., 1970, **10**, 27.
75. T.Schaefer, K.Marat, A.Lemize, and A.F.Jansen, Org. Magn. Reson., 1982, **18**, 90.
76. R.F.Wasylishen and M.Barfield, J. Amer. Chem. Soc., 1975, **97**, 4545.
77. R.H.Contreras, C.G.Giribet, M.A.Natiello, et al., Austral J. Chem. V, **38**, 1779.
78. M.Barfield, E.W.Della, P.E.Pigou, and S.R.Walter, J. Amer. Chem. Soc., 1982, **104**, 3549.

79. M.Barfield, S.R.Walter, K.A.Clark, et al., Org. Magn., Reson., 1982, **20**, 92.
80. F.B.Mallory and C.W.Mallory, J. Amer. Chem. Soc., 1985, **107**, 4816.
81. V.N.Mamaev, Kh.A.Orazbendiev, and N.M.Sergeev, Dokl. Akad. Nauk SSSR, 1975, **220**, 877.
82. V.D.Shteingarts, Uspekhi Khim., 1981, **50**, 1407 [Russ. Chem. Rev., 1981(8)].
83. S.Duangthai and G.A.Webb, Org. Magn. Reson., 1979, **12**, 98.
84. M.V.Galakhov, V.A.Petrov, G.G.Belen'kii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1986, 1057.
85. M.V.Galakhov, G.G.Belen'kii, V.A.Petrov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1986, 1054.

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