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^{13}C AND ^{19}F NMR SPECTROSCOPIC STUDY OF SUBSTITUENT EFFECTS IN α,α-DIFLUOROARYLCARBENIUM IONS [1]

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SUMMARY

In a series of α,α-difluoroarylcarbenium ions 1, one bond ^{13}C-^{19}F coupling constants and the ^{19}F chemical shifts at the cationic center have been used as criteria to follow the extent of fluorine non-bonded electron pair back donation. The electron demand at the cationic center was systematically altered by changing the nature of the substituents on the aryl ring and substituent effects were studied by ^{13}C and ^{19}F NMR spectroscopy.

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INTRODUCTION

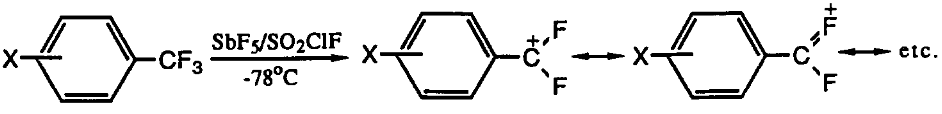
Stabilization of carbocations by halogen substituents, particularly fluorine atoms, adjacent to a carbocationic center is well recognized [2]. In spite of its high electronegativity, the fluorine atom stabilizes the cationic center through 2p non-bonded electron pair back donation (n-donation). Compared to other halogen atoms (i.e. Cl, Br, I) in the condensed state fluorine is not capable of stabilizing positive charge directly through the formation of bridged fluoronium ions [2].

We have recently utilized [3] one bond ^{13}C-^{19}F coupling constants as a measure to determine the extent of lone pair back-bonding (resonance) interaction in a series of substituted α-fluorodiarylcarbenium ions. The electron demand at the cationic center was systematically varied by changing the substituents on the phenyl rings. Previously Spear, Forsyth and Olah [4] had carried out similar studies on ring fluorinated benzyl cations.

We wish to report now studies on a series of substituted α,α-difluoroarylcarbenium ions, 1, generated under stable ion conditions by ^{13}C and ^{19}F spectroscopy. As previously [3] the one bond ^{13}C-^{19}F coupling constants have been used as a diagnostic means to measure the electron demand at the cationic center. The technique of gradual variation of electron demand at an arylcarbenium center by varying the nature of substituent on the aryl ring was first utilized by Gassman and Fentiman [5] to probe the extent of homoaromatic π-bond participation of 7-aryl-7-norbornenyl cations in solvolysis studies. Since that time the technique of so called "tool of increasing electron demand" has received much attention to measure the onset of π, πσ, n and σ-participations in a number of carbocations under superacidic stable ion conditions. The topic has recently been reviewed [6].

RESULTS AND DISCUSSION

A series of α,α-difluoroarylcarbenium ions 1 was prepared by the ionization of the corresponding α,α,α-trifluorotoluene precursors in SbF_5/SO_2ClF solution at -78°C. The ^1H and ^{19}F spectra of some of these ions were earlier reported by Olah and Comisarow in 1969 [7] and later by Olah and Mo in 1973 [8] . Previously unreported ^{13}C NMR spectra and ^{13}C-^{19}F coupling constants on the whole series of ions were now obtained. The complete ^{13}C and ^{19}F NMR data of the studied ions are tabulated in the Table. The chemical shift assignments were unequivocally made based on relative intensities of the carbon peaks and ^{13}C-^{19}F couplings, as well as by spin-echo experiments [9].



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X= 4-CH3, H, 4-F, 4-Cl, 4-Br, 4-CF3, 3,5(CF3)2

Structure 1

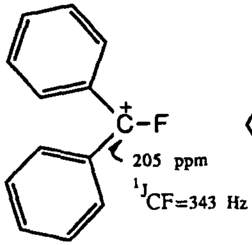
Before discussing the results in more detail, some conclusions common to all α,α-difluoroarylcarbenium ions can be drawn. While comparing chemical shifts of the α-fluorodiphenylcarbenium ion 2 [3] with the presently studied α,α-difluorophenylcarbenium ion, it is immediately evident that replacement of a fluorine atom by a second phenyl group causes a deshielding effect on the carbocationic center by 27.6 ppm.

TABLE

^{13}C and ^{19}F Chemical Shifts and Carbon-Fluorine[a] and Fluorine-Fluorine[b] Coupling Constants of α,α-Difluoroarylcarbenium Ions, **1**

X	C_1	C_2	C_3	C_4	C_5	C_6	CF_2^+	other	$\delta^{19}F^b$
4 - CH_3	106.5 (9.4)	143.3	134.4	179.4 (5.6)	134.4	143.3	174.7 (355.8)	24.8 CH_3	3.0
4 - Br	108.3 (9)	143.1 (8)	137.5	163.2 (4.5)	137.5	143.1 (8)	176.6 (360.3)		11.1
4 - Cl	107.9 (9.7)	144.3 (9.9)	134.5	170.9 (5.4)	134.5	144.3 (9.9)	176.1 (359.6)		7.6
4 - F	106.3 (9.9)	149.3 (19.4 t, 19 d)	122.7 (23)	182.1 (5.5 t, 303.8 d)	122.7 (23)	149.3 (19.4 t, 19 d)	174.9 (358.4)	-45 (4-F)	5.9 (20.1)
4 - H	109.8 (8)	144.6 (10.7)	133.2	158.7 (5.2)	133.2	144.6 (10.7)	177.4 (362.3)		14.9
3, 5, - CF_3	112.4 (8.5)	143.4	136.3 (37.5)	149.0	136.3 (37.5)	143.4	180.1 (370.6)	119.8 CF_3 (274); -65.2 CF_3	36.9

[a] J_{CF} in Hz in parenthesis; [b] J_{FF} in Hz in Parenthesis; [c] d = doublet, t = triplet, q = quartet



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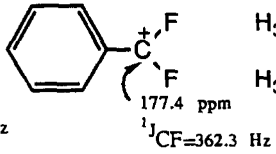
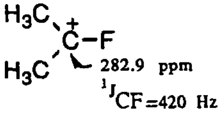


1-H



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Structure 2

This indicates the significance and magnitude of fluorine backbonding causing a larger shielding effect [10] than a phenyl substituent, despite its high electronegativity. Evaluation of the magnitude of the one bond fluorine coupling constants of the α-fluorodiphenyl 2 [3], α-fluorodimethyl 3 [2b] and α,α-difluorophenyl-carbenium ions shows the greatest degree of fluorine back-donation when no other resonance stabilization of the positive charge is possible as exemplified by the fluorodimethyl carbenium ion ($^{1}J_{C-F}$ = 420 Hz). The phenyl substituted α-fluorocarbenium ions benefit from additional charge delocalization through *ortho* and *para* quinoidal resonance structures. This can be seen by the relative constant value of the ^{13}C NMR chemical shift of the carbocationic centers studied herein. Going from electron releasing 1-(4-CH_3) to electron-withdrawing 1-(3,5-$(CF_3)_2$), the cationic center varies from $\delta^{13}C$ 174.7 to $\delta^{13}C$ 180.1, a small change of ^{13}C chemical shift for such a large variance in the nature of the substituents. This indicates that the α-fluorine atoms and the aryl group display a significant synergistic effect in stabilizing the positive charge. While the electron demand on the carbocationic center within these closely related ions is increased through electron withdrawing substituents on the phenyl ring, the α-fluorine atoms compensate this electron withdrawal by increased backbonding via their nonbonded electron pairs to maintain a relatively constant electron density at the cationic center, as indicated by the ^{13}C NMR chemical shifts.

In contrast the one bond ^{13}C-^{19}F coupling constants clearly reflects the change in electron demand at the cationic center. The magnitude of ^{13}C-^{19}F coupling constant varies from 355.8 Hz for $\underline{1}$-(4-CH_3) to 370.6 Hz in the case of $\underline{1}$-(3,5-$(CF_3)_2$). A plot of the one bond $^1J_{C\text{-}F}$ coupling constant versus Brown's σ^{C+} constants [11] of the respective substituents on the aryl group (Fig. 1) shows an excellent linear relationship, ($r^2 = 1$) thus supporting the validity of the suggestion.

The transmission of substituent effects and their compensation by increased 2π backbonding consequently occurs without perturbation by additional delocalization effects. When $^1J_{C\text{-}F}$ coupling constants were plotted against ^{13}C chemical shifts of the para carbon in the aryl ring, as a measure of relative charge delocalization into the aromatic ring, widely scattered points were obtained without any correlation as anticipated. However, perturbations causing such scatter are already accounted for, averaged out and/or compensated using Brown's σ^{C+} constants [11] which represent an overall electron demand on the more remote carbocationic center (3 or 4 bonds farther removed) originating from the intrinsic electronic properties of that substituent.

A plot of ^{19}F-chemical shifts versus σ^{C+} constants corroborates the findings of direct transmission of the electronic interactions through π-type fluorine lone pair backbonding . ($r^2 = 1$)

As expected the linear increase in the one bond coupling constants with increasing electron demand of the aryl ring (Fig. 1) is paralleled by the linear increase of ^{19}F-chemical shift values, (Fig. 2) since the changes in both parameters originate from the same causes. The differences in chemical shifts as well as in coupling constants in closely related systems are a function of the charge density of the charged center expressed quantitatively by the diamagnetic shielding constant σ_{dia} for chemical shift and by the Fermi contact term for coupling constants [10]. The other contributions determining the absolute sign and magnitude of the shielding and coupling constants are cancelled out or offset by means of evaluation of the data in terms of numerical differences (relative increase or decrease).

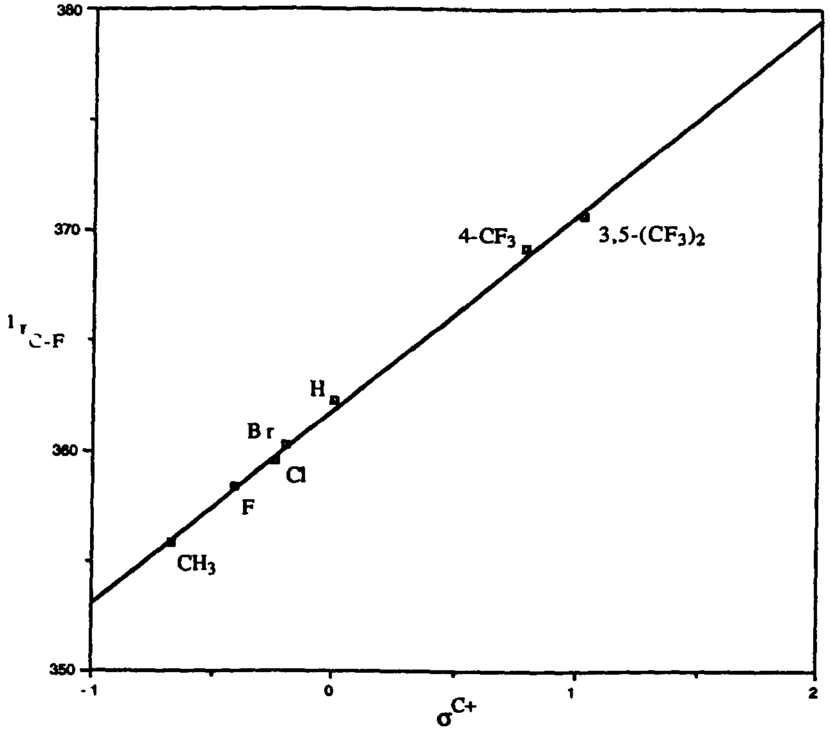

Fig 1 Correlation of one bond ^{13}C-^{19}F coupling constants of α,α-difluoroarylcarbenium ions 1 with σ^{C+} substituent constants.

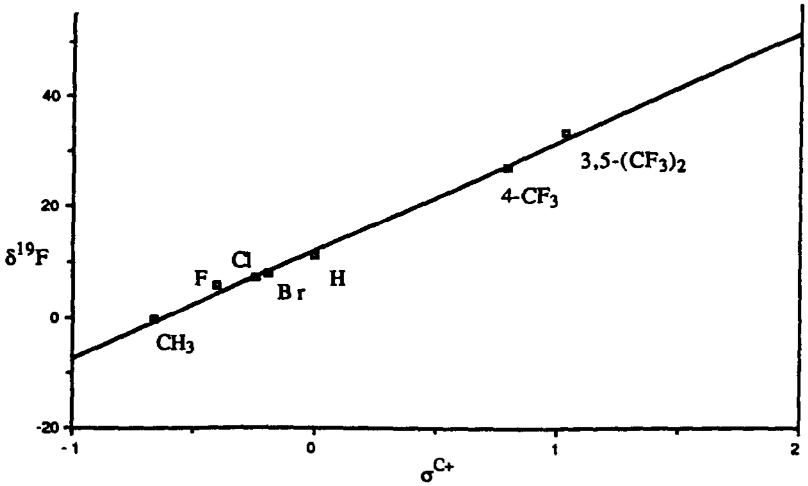

Fig. 2. Correlation of ^{19}F chemical shifts of α,α-difluoroarylcarbenium ions with σ^{C+} substituent constants

In closely related systems, like the one studied here, the only parameter varied is the substituent on the aryl ring, therefore the only quantity changing at the charged center is the electron withdrawal or release caused by the substituent. This change can be followed by monitoring the ^{19}F chemical shift or alternatively the $^1J_{C\text{-}F}$ coupling constant at the charged center. Numerical increase of the $^1J_{C\text{-}F}$ coupling constant reflects the compensation of increasing positive charge by fluorine π-backbonding through its nonbonded electron pairs.

EXPERIMENTAL

The ^{13}C and ^{19}F NMR spectra were obtained on a Varian Associates Model VXR-200 NMR spectrometer equipped with a ^{1}H/^{19}F-broad band 5mm variable temperature probe. ^{13}C and ^{1}H chemical shifts are referenced from capillary tetramethylsilane. ^{19}F shifts are referenced from the $CFCl_3$ signal. Substituted α,α,α-trifluorotoluenes (4-H, 4-F, 4-Cl, 4-CF_3, 3,5-$(CF_3)_2$) were commercially available (Aldrich, PCR) and used as received. 4-Methyl-α,α,α-trifluorotoluene was prepared by the following procedure.

Preparation of p-methyl-α,α,α-trifluorotoluene

1- Mmole of 4-bromo-α,α,α-trifluorotoluene (2.25 g) were added to 0.5 g Mg turnings (washed with HCl and dried in vacuo) in dry ether under gentle reflux to yield the Grignard reagent 4-BrMg-C_6H_4-CF_3. After completion of the reaction the solution was allowed to stir for 1 h at room temperature. The mixture was then cooled to 0°C and precondensed CH_3Br, 2.85 g (Matheson) is added via a precooled glass pipet. Then the reaction mixture was brought to room temperature, the ether is evaporated and the residual liquid slowly distilled at 70°C (20 mm Hz) to give 0.64 g of the product as a colorless liquid (40% yield). The compound gave satisfactory spectroscopic data. ^{1}H NMR ($CDCl_3$, δ), 1.1 (s, 3H); 5.9-6.4 (m, 4H), ^{13}C NMR ($CDCl_3$, δ): 141.8 (q, C-CF_3); 130.6 (C-CH_3), 123.9, 123.8, 123.3 (q, CF_3); ^{19}F NMR ($CDCl_3$, δ) -59.3 (CF_3).

Preparation of carbocations

Freshly distilled SbF_5 was used. To the superacid dissolved in about two-fold amount of SO_2ClF (total volume 1 ml) in a 5 mm NMR tube maintained at dry ice/acetone temperature (ca -78°C), was slowly added, with vigorous stirring and intermittent cooling, a cooled slurry or solution of the corresponding gem-difluoro precursor in SO_2ClF (0.5 ml), to give in an approximately 10% solution of the ion.

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