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A study of NMR parameters of *para*-substituted polyfluorinated benzyl cations and their precursors

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ABSTRACT

^{13}C and ^{19}F NMR spectra of a series of *para*-substituted heptafluorotoluenes and hexafluorobenzyl cations were analyzed. The quantum-chemical calculations of δ_{13C} and δ_{19F} chemical shifts (CSs) as well as ^{19}F–^{19}F and ^{13}C–^{19}F spin–spin coupling constants (SSCCs) were performed. ^{19}F and ^{13}C CSs were predicted by the GIAO/PBE/L22 method. The accuracy of theoretical CSs values increased in the computation for cations in conjunction with anions as ionic pairs. The computation by the SOPPA(CCSD) method had enough accuracy for the prediction of ^{19}F–^{19}F, ^{13}C–^{19}F SSCCs and Ramsey contributions. Changes in various contributions to the spin–spin interaction along with their dependence on substituents at the *para*-position were also examined on passing from heptafluorotoluenes to the corresponding benzyl carbocations.

1. Introduction

Polyfluorinated benzyl cations are intermediates in electrophilic substitution reactions catalyzed by acids [1]. However, they can exist as long lived ions in super acidic media: these conditions are favorable for the NMR study of the characteristic features of these particles. The values of ^{13}C and ^{19}F chemical shifts (CSs) and ^{19}F–^{19}F and ^{13}C–^{19}F spin–spin coupling constants (SSCCs) can be used as effective tools for the electron structure investigation.

There are some successful studies on polyfluorinated benzyl cations [2], although a detailed interpretation of the spectral data has not been accomplished. The main difficulty with the interpretation of such spectra of fluorinated compounds is their complexity which results from magnetic inequivalence and strong couplings of nuclear spins (when the system is no longer first order). Therefore, a full quantum-chemical calculation of the NMR spectral parameters is becoming important for polyfluorinated benzyl cations and their precursors.

The aim of this study was to use the quantum-chemical methods to calculate the NMR parameters with sufficient accuracy for the iteration procedure to determine real CSs and SSCCs and explain the obtained data. We also wanted to determine the role of a perturbing action on the spin system of substituents with various donor-acceptor properties. For this purpose, we analyzed a series of *para*-substituted polyfluorinated benzyl cations and their chemical precursors (toluenes).

2. Materials and methods

2.1. Measurement of NMR parameters

^{13}C and ^{19}F NMR spectra were recorded on Bruker AV-300, AV-400, and AV-600 (75.5, 100.6, 150.9 MHz for ^{13}C and 282.4, 376.5, 567.7 MHz for ^{19}F respectively). Individual *para*-substituted heptafluorotoluenes were dissolved in $CDCl_3$ to a concentration of 1.0–2.0 M; hexafluorobenzene was added as the internal standard (δ_C C_6F_6 [TMS] = 138.3 ppm). The cations were generated by dissolving perfluorotoluenes in double-distilled SbF_5 to obtain 15–25 mol% concentrations. To reduce viscosity the solution was diluted with SO_2ClF (20 wt.%.). δ_{13C} and δ_{19F} of polyfluorobenzyl cations were measured relative to the external standard (a glass capillary with 1% C_6F_6 in acetone-d6) at a temperature varied from +10 to +30 °C in order to obtain the best resolution. Magnetic susceptibility corrections were not applied.

Broadband decoupling of protons and selective decoupling of fluorine atoms in both ^{19}F and ^{13}C spectra allowed us to decompose the nuclear spin systems of the compounds into simpler subsystems. We also used spectral data obtained from ^{13}C satellites which in the case of a subsystem of fluorine nuclei of the benzene ring were associated with the removal of symmetry (AA′BB′ becomes ABCDX, where X is a ^{13}C nuclei). Isotope shift

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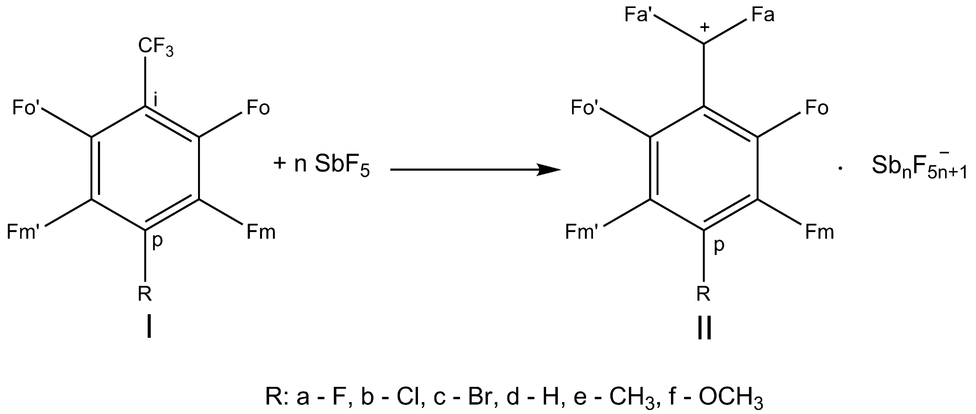

Scheme 1. Formation of *para*-substituted benzyl cations.

Table 1
Experimental *vs.* calculated values (in parentheses) of δ_F and δ_C relative to C_6F_6 (ppm).

Exp. (Calc.)	F_{ortho}	F_{meta}	F_{para}	$C\underline{F}_3$ $C\underline{F}_2$	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	$\underline{C}F_3$ $\underline{C}F_2$
Ia	22.6 (28.1)	2.6 (3.9)	15.3 (18.4)	106.0 (106.4)	−32.3 (−36.7)	6.9 (6.7)	0 (-0.2)	5.8 (5.7)	−17.4 (−9.2)
IIa	64.2 (74.1)	16.2 (19.5)	83.4 (96.8)	195.7 (191.4)	−45.2 (−48.6)	16.2 (15.3)	1.2 (1.7)	26.3 (25.5)	36.7 (32.1)
Ib	22.6 (28.2)	23.8 (28.8)	–	105.6 (105.9)	−29.5 (−33.7)	6.3 (6.2)	6.5 (6.6)	−20.8 (−21.9)	−17.5 (−9.3)
IIb	59.5 (69.2)	36.3 (41.5)		194.4 (192.1)	−43.7 (−46.9)	13.7 (13.0)	7.6 (8.0)	14.9 (11.7)	36.1 (31.7)
Ic	23.0 (29.0)	31.6(37.3)	–	105.6 (105.7)	−28.8 (−33.0)	6.3 (6.2)	7.4 (7.4)	−32.8 (−22.9)	−17.3 (−9.3)
IIc	58.4 (67.8)	44.3 (49.4)		193.6 (191.2)	−43.1 (−46.5)	12.8 (12.3)	9.0 (8.9)	8.2 (16.5)	35.9 (31.5)
Id	21.9 (29.2)	25.7 (32.8)	–	105.7 (105.4)	−27.2 (−30.4)	6.2 (6.1)	8.4 (8.2)	−28.2 (−37.2)	−17.2 (−9.1)
IId	62.6 (76.7)	38.9 (46.2)		202.0 (197.8)	−41.4 (−44.3)	14.7 (14.2)	8.9 (9.2)	0.9 (−8.4)	38.0 (33.2)
Ie	19.8 (25.2)	20.7 (24.5)	–	105.8 (105.7)	−30.8 (−33.7)	5.8 (5.5)	7.3 (7.1)	−16.9 (−23.2)	−17.0 (−8.9)
IIe	58.3 (69.9)	33.9 (38.6)		189.8 (189.9)	−44.4 (−47.5)	13.3 (12.7)	8.1 (8.4)	23.5 (15.1)	35.5 (32.0)
If	20.1 (23.7)	5.3 (0.4)	–	106.5 (106.5)	−35.5 (−41.2)	6.9 (6.6)	2.5 (0.5)	3.6 (−1.4)	−17.0 (−8.7)
IIf	54.0 (61.2)	15.1 (17.3)		163.3 (174.6)	−50.7 (−52.1)	14.0 (13.1)	1.3 (2.6)	30.0 (20.8)	29.9 (28.9)

differences are $^1\Delta F(^{13}C) - ^3\Delta F(^{13}C) = 45$ ppb for one pair of chemically equivalent fluorine nuclei and $^2\Delta F(^{13}C) - ^4\Delta F(^{13}C) = 18$ ppb for another. The calculated data were used for the interpretation of the observed NMR spectral parameters and as the initial set of values for the iteration of experimental NMR spectra. For that purpose the gNMR 5.0 software [3] was used. The experimental SSCC values were attributed to the signs of the calculated ones. A mismatch of signs for some experimental values with theoretical ones was mostly observed for small values and probably resulted from computation errors.

2.2. Computation details

Geometry optimization was performed using the quantum-chemical Priroda software [4] by the density functional theory (DFT) method with the PBE functional [5] and the L11 basis set [6] (Λ11, analog of cc-pCVDZ). We used the gauge including/invariant atomic orbital (GIAO) approximation in combination with DFT and the L22 basis set (Λ22, analog of cc-pCVTZ) for shielding computation. The values of CSs were calculated relative to the C_6F_6 shieldings obtained by the same approach. To get initial approximations of tight ion pairs with random coordinates, we used the Coalescence Kick software [7]. For each cation-anion pair, we generated five initial approximations and then optimized the geometric parameters in the Priroda software by the above method. The calculated CS values were averaged. The quantum-chemical Dalton 2.0 software package [8] was used for the computation of SSCCs by analogy, as described previously [9] at the DFT/B3LYP [10], SOPPA [11], and SOPPA(CCSD) [12] levels of theory in combination with aug-cc-pVTZ-J [9,13], aug-cc-pCVDZ [14], cc-pVDZ [15] basis sets as reported below. Also we used aug-cc-pVTZ-Jf (14s5p2d/8s4p2 d for F and C) basis set which was derived from aug-cc-pVTZ-J (15s6p3d1f/9s5p3d1f for F and C) by disregarding diffuse (1s1p1d) and f-functions in order to reduce the computation costs (see SI for more details). Equivalent constants were averaged for compounds with asymmetrical

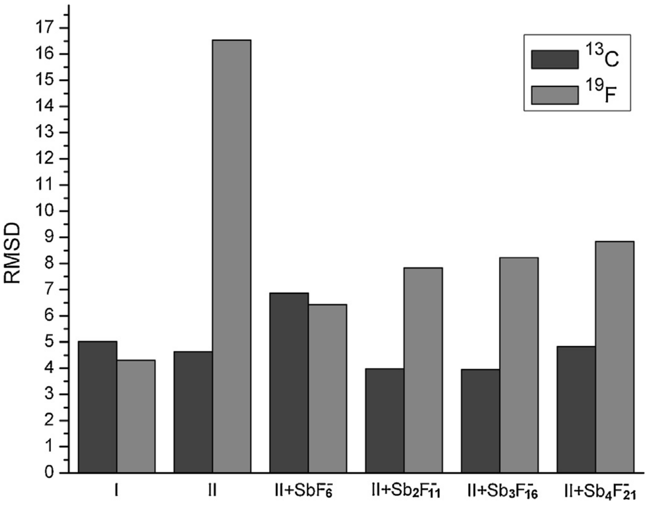

Fig. 1. Root mean square deviation of calculated chemical shifts (^{13}C-dark bars, ^{19}F-light gray bars) for toluenes I, cations II and cations II as ionic pairs with SbF_6^-, $Sb_2F_{11}^-$, $Sb_3F_{16}^-$, $Sb_4F_{21}^-$ anions.