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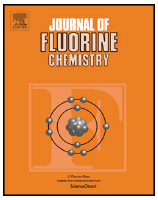

Full Length Article

The Investigation of NMR parameters of the heptafluoroindenyl cation

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ABSTRACT

The knowledge about parameters of ^{13}C and ^{19}F NMR spectra of the heptafluoroindenyl cation was expanded here. Quantum-chemical calculations were performed for ^{19}F- and ^{13}C-chemical shifts (CSs) as well as ^{19}F–^{19}F and ^{13}C–^{19}F spin–spin coupling constants (SSCCs). CSs were predicted by the GIAO/PBE/L22 method. The computation accuracy of CS values increased for the cation in conjunction with the anion SbF_6^-. The SOPPA method was used to calculate direct ^{13}C–^{19}F SSCCs and their Ramsey contributions. Other ^{13}C–^{19}F and ^{19}F–^{19}F SSCCs were predicted by the DFT/B3LYP method. The accuracy of these calculations was shown to increase when the anion influence was taken into account.

1. Introduction

In recent studies, we explored NMR parameters of polyfluorinated *para*-substituted benzyl cations [1], which are known to be aromatic compounds. In the latest study, we used the same approach to characterize a cation of a different and ambiguous nature: the heptafluoroindenyl cation [2]. Earlier, Karpov et al. made assignments of ^{19}F chemical shifts and determined absolute values of ^{19}F–^{19}F SSCCs in a set of fluorine-containing indenyl cations [2,3]. Nonetheless, we found that these data were insufficient to interpret the data from NMR spectra of the heptafluoroindenyl cation. The reason seems to be the complexity of these spectra because of magnetic nonequivalence and strong couplings of the nuclear spins. Moreover, it is necessary to consider the signs of SSCCs to reconstruct the spectra of the heptafluoroindenyl cation, but this information was not covered previously. In the present work, we report new spectral data as well as quantum-chemical calculations that were used for iteration and interpretation of spectral parameters of the heptafluoroindenyl cation.

2. Materials and methods

2.1. Measurement of NMR parameters

The cation was generated as described previously [2] by stirring octafluoroindene (~0.35 mmol) with a solution of double-distilled SbF_5 (~1.5 mmol) and SO_2ClF (~0.5 ml) at a temperature of $-50\,^{\circ}$C. ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV-400 and AV-600 instruments (100.6 and 150.9 MHz for ^{13}C; 376.5 and 567.7 MHz for ^{19}F, respectively) at $-35\,^{\circ}$C. Chemical shifts δ_{13C} and δ_{19F} were measured relative to the external standard (a glass capillary with 1% C_6F_6 in acetone-d6). Magnetic susceptibility corrections were not applied.

Selective decoupling of fluorine atoms in both ^{19}F and ^{13}C spectra allowed us to decompose the nuclear spin systems of the heptafluoroindenyl cation into simpler subsystems. We also used spectral data obtained from ^{13}C satellites that were associated with the removal of symmetry from the spin system. The calculated data were applied to interpretation of the observed spectral parameters and as the initial set of values for iteration of the experimental spectra. This iteration was carried out in the gNMR 5.0 software [4]. The experimental SSCC values were matched the signs of the calculated ones. A mismatch of signs between some experimental values and theoretical ones was mostly observed for small values and probably resulted from computational errors.

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2.2. Computation details

Geometry optimization was performed in the quantum-chemical Priroda software [5] by the density functional theory (DFT) method with the Perdew-Burke-Ernzerhof exchange-correlation (PBE) functional [6] and the L11 basis set [7] (Λ11, an analog of cc-pCVDZ). We used the gauge including/invariant atomic orbital (GIAO) approximation and the L22 basis set (Λ22, an analog of cc-pCVTZ) with DFT for CS computations. The values of CSs were calculated relative to the C_6F_6 shieldings obtained by the same approach. The solvent was included via modeling of microsolvation by means of a single anion: SbF_6^- or $Sb_2F_{11}^-$. We used the Coalescence Kick software [8] to determine the initial approximations of tight ion pairs with random coordinates. 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 values were presented as the Boltzmann average. The quantum-chemical Dalton2016.1 software package [9] was applied to computation of SSCCs in an analogous way, as described elsewhere [10] at the DFT/B3LYP [11] and SOPPA [12] levels of theory. We used the aug-cc-pCVDZ [13] basis set for the pair of atoms whose nuclei were involved in the SSCCs being calculated. For other atoms, we utilized the cc-pVDZ [14] basis set. In addition, we used the Stuttgart-Dresden (SDD) effective core potential (ECP) with the corresponding basis sets [15] for fluorine and antimony atoms in the SbF_6^- anion to facilitate the calculations of SSCC values when the influence of this anion was taken into consideration.

3. Results and discussion

3.1. Analysis of ^{19}F and ^{13}C chemical shifts

The GIAO/PBE/L22 method has been shown to be effective at prediction of δ_F and δ_C of uncharged polyfluorinated aromatic compounds [16]. In the case of polyfluorinated aromatic cations, the accuracy of calculations is higher for tight cation–anion pairs in comparison with calculations for naked cations in a gas phase [1]. The geometry optimization and calculations of δ_F and δ_C for the heptafluoroindenyl cation (Scheme 1) were conducted by the same approach.

The δ_F and δ_C values were calculated for a free heptafluoroindenyl cation as well as for ionic pairs with SbF_6^- and $Sb_2F_{11}^-$ anions (Table 1).

The best match of calculated δ_F and δ_C values with experimental ones was observed in the case of anion SbF_6^- as revealed by regression Eqs. (1) and (2).

$$\delta_C{}^{(exp.)} = 0.95\ \delta_C{}^{(theor.)} - 3.50;\ R^2 = 0.991 \qquad (1)$$

$$\delta_F{}^{(exp.)} = 1.05\ \delta_F{}^{(theor.)} - 4.62;\ R^2 = 0.987 \qquad (2)$$

The data from Table 1 are presented graphically in Fig. 1. The improvement of the ^{13}C shift values calculated with anion SbF_6^- was not as obvious as the improvement of ^{19}F shifts. We assumed that this result can be explained as follows: carbon nuclei were shielded by fluorine nuclei from interactions with the medium, whereas ^{19}F CSs are strongly sensitive to the effect of intermolecular interactions, which were not taken into account in the computation on the cation in the gas phase.

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

	Exp.	Theor.		
		$C_9F_7^+$	$C_9F_7^+ + SbF_6^-$	$C_9F_7^+ + Sb_2F_{11}^-$
C2	0.8	−2.0	−3.1	−2.5
C1,3	48.1	43.4	40.4	42.0
C8,9	−32.3	−37.9	−35.4	−38.1
C4,7	18.2	18.3	13.1	16.9
C5,6	11.9	13.4	11.7	12.4
F2	12.4	19.4	3.1	5.3
F1,3	141.6	166.3	143.7	150.6
F4,7	77.9	109.9	75.6	96.2
F5,6	38.7	68.6	43.9	50.4

3.2. Analysis of ^{13}C–^{19}F and ^{19}F–^{19}F spin–spin coupling constants

The double-resonance experiments enabled research into the nuclear spin system of the heptafluoroindenyl cation as a combination of simpler subsystems. This approach allowed us to decouple fluorine signals selectively one by one and to exclude the corresponding SSCCs. Fig. 2 shows a set of experimental spectra of F4,7 with selective homodecouplings and theoretical spectra obtained after iteration of the calculated SSCCs.

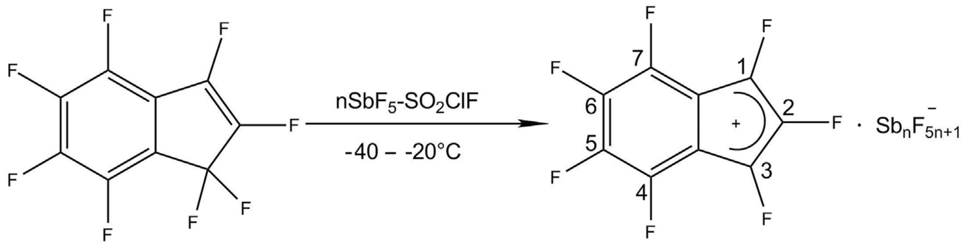
The values of $J_{F1\text{-}F3}$, $J_{F4\text{-}F7}$, and $J_{F5\text{-}F6}$ were determined by means of ^{13}C satellites in ^{19}F NMR spectra, where these constants appeared due to the loss of symmetry in the spin system of fluorine nuclei (Fig. 3).

Isotope shift differences were found to be $^1\Delta F(^{13}C) - {}^3\Delta F(^{13}C) = 120$ ppb in the case of $F_{1,3}$, $^1\Delta F(^{13}C) - {}^4\Delta F(^{13}C) = 49$ ppb in the case of $F_{4,7}$ and $^1\Delta F(^{13}C) - {}^2\Delta F(^{13}C) = 50$ ppb for $F_{5,6}$.

We employed B3LYP and SOPPA methods to calculate ^{19}F–^{19}F and ^{13}C–^{19}F SSCCs; these methods have been shown to be suitable for highly accurate prediction of these values in polyfluorinated cations and in their neutral precursors [1].

We compared ^{19}F–^{19}F and ^{13}C–^{19}F SSCCs calculated by these methods for the heptafluoroindenyl cation with those obtained for the cation microsolvated with the SbF_6^- anion. The results are presented in Table 2.

We found that SSCC calculations for the free cation yielded only a weak correlation with the experimental values both for DFT and for the SOPPA method. The model of an unsolvated heptafluoroindenyl cation in a gas phase did not seem to match the real system. It was shown that the accuracy of prediction could be increased in the case of calculations involving solvent interaction through explicit modeling of solvation by the SbF_6^- anion. As a



Scheme 1. Formation of the heptafluoroindenyl cation.