



Analysis of ^{19}F and ^{13}C NMR spectra of tetrafluorophthalic anhydride and its derivatives

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ABSTRACT

^{19}F and ^{13}C NMR spectra of perfluorinated compounds (i.e., tetrafluorophthalic anhydride, its hydroxyl- and amino-derivatives, N-pentafluorophenyltetrafluorophthalimide, and hexafluoroindan-1,3-dione) were analysed. Different signals in NMR spectra were assigned based on the analysis of spin–spin coupling constants. All assignments made were further confirmed by density functional theory (DFT) calculations of ^{13}C chemical shifts and $J_{\text{C},\text{F}}$ coupling constants.

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1. Introduction

Tetrafluorophthalic anhydride (4,5,6,7-tetrafluoroisobenzofuran-1,3-dione, **1**) and N-pentafluorophenyltetrafluorophthalimide (4,5,6,7-tetrafluoro-2-pentafluorophenylisoindoline-1,3-dione, **2**) are widely used as precursors for the synthesis of biologically active compounds [1,2] and condensation polymers [3,4]. Since chemical shifts of fluorine nuclei are highly sensitive to their coordination environment, the ^{19}F NMR spectroscopy can be effectively used for monitoring chemical transformations of fluorinated compounds [4]. It was suggested previously that ^{19}F NMR chemical shifts and substituent shielding parameters characterizing **1** and **2** can be used to predict spectra of polyfluorinated polyamidoacids and polyimides [5]. However, the precise analysis of ^{19}F NMR spectra characterizing compounds **1** and **2** was not reported by these authors [5]. Moreover, assignments of ^{19}F NMR chemical shifts provided in this case were substantially different from those reported in literature for the same compounds [2,6], as well as different from those reported for the hexafluoroindan-1,3-dione (**3**), compound with a similar structure [7]. It is noteworthy that in the case of compounds **1–3**, the fluorine nuclei of the tetrafluoroaromatic ring form an AA'XX' spin system, which gives two ^{19}F NMR signals with the similar fine structure. In such a case, assignments of ^{19}F NMR chemical shifts

are not possible based only on $J_{\text{F},\text{F}}$ coupling constants and the complete analysis of ^{13}C NMR spectra along with the analysis of ^{13}C -satellites in ^{19}F NMR spectra is required. While the ^{13}C NMR spectrum of anhydride **1** was described previously, the chemical shift values were not determined for all aromatic carbon signals as they appeared to be complex non-first-order multiplets [8]. The ^{13}C NMR spectra of imide **2** [2] and some other N-substituted 4,5,6,7-tetrafluoroisoindoline-1,3-diones [9] have been described without the analysis of $J_{\text{C},\text{F}}$ coupling constants. As a result, different assignments were suggested by these authors for the C₄–C₇ signals. These examples clearly illustrate that ^{19}F and ^{13}C NMR data available in the literature for compounds **1–3** are incomplete and mutually inconsistent.

In the present work, we provide a complete analysis of ^{19}F and ^{13}C NMR spectra characterizing compounds **1–3** as well as those characterizing 5-hydroxy- and 5-amino-4,6,7-trifluoro-isobenzofuran-1,3-diones (**4** and **5**, respectively) with the goal of providing rational assignments of signals in these spectra (see Fig. 1).

2. Experimental

2.1. Materials

Compounds **1–4** were prepared as described elsewhere [6,7,10,11] and their physical properties were found to be identical to those reported in the literature [2,6,7,10]. Compound **5** was prepared by dehydration of aminotrifluorophthalic acid. Melting point cannot be detected for this compound due to polymerization;

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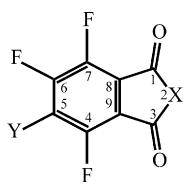


Fig. 1. The compounds analysed.

IR (KBr) bands at ν 3491, 3362 (NH₂), 1854, 1760 (C=O), 1649, 913, 885 (NH₂) cm⁻¹; ¹H NMR (CDCl₃) chemical shift δ at 4.86 ppm (br.s, NH₂); HRMS (calcd. for C₈H₂O₃F₃N: 216.9987, found: 216.9986).

2.2. Measurements

One dimensional ¹⁹F and ¹³C NMR spectra were collected using Bruker Avance 300, 400, and 600 MHz spectrometers. Samples were typically dissolved in CDCl₃ or acetone-d₆ to a concentration of approximately 1–2 mol/l and then scanned in 5 mm tubes. ¹⁹F NMR spectra of compounds **4** and **5** were recorded in both solvents. Standard pulse sequences with the 90° pulse angle were used to obtain NMR spectra at a FID resolution of 0.43 and 0.20 Hz or better for ¹⁹F and ¹³C spectra, respectively. Spectra were recorded in different spectral regions in order to detect all signals originating from each sample. Bruker Avance 400 and 600 MHz spectrometers were used for ¹⁹F-^{19}F and ¹³C-^{19}F double resonance experiments. All ¹⁹F and ¹³C NMR spectra were referenced with CFCl₃ and tetramethylsilane, respectively, signals of which were set to 0 ppm. The signal of C₆F₆ (−162.9 ppm) was used as an internal standard for ¹⁹F spectra and those of CDCl₃ (77.23 ppm) and/or acetone-d₆ (29.92 ppm) were used as internal standards for ¹³C spectra. XSIM.LINUX software (version 93.02.01) was used for modeling of NMR signals.

2.3. Calculations

The “Priroda-6” software [12] was used for quantum-chemical calculations of ¹³C NMR chemical shifts at the DFT level using a PBE method [13]. The basis set L22 [14] ((8s4p2d)/[3s2p1d] for H, (12s8p5d2f)/[6s5p3d1f] for C, N, O, F) was used to optimize the geometry parameters, while the basis set L33 [14] ((10s5p3d2f)/[4s3p2d1f]) with the GIAO approach [15] was used to calculate the

chemical shielding parameters. The ¹³C chemical shift values were obtained by subtracting the shielding of each individual atom from the shielding of the C₆F₆ standard and values thus obtained were further recalculated to the scale of the TMS reference which is characterized by a chemical shift value of 138.3 ppm [16].

Dalton 2.0 software [17] was used for DFT/B3LYP calculations [18] of spin–spin $J_{\text{C},\text{F}}$ coupling constants. These calculations were similar to those reported elsewhere [19] for $J_{\text{F},\text{F}}$ coupling constants. The basis set aug-cc-pVTZ-J [20] was used for carbon and fluorine nuclei interacting with each other, while the basis set cc-pVDZ [21] was used for remaining C, N, O, F nuclei. In the case of compound **4**, constants are reported as the average of values determined for structures having different OH group conformations but less than 0.3 kcal/mol differences in the enthalpy of formation.

3. Results and discussion

Chemical shifts of ¹⁹F and ¹³C nuclei in NMR spectra of compounds **1**–**5** are given in Table 1. Table 2 presents $J_{\text{F},\text{F}}$ and $J_{\text{C},\text{F}}$ coupling constants derived by modeling NMR signals with the XSIM.LINUX software. Table 3 shows the ¹³C/¹²C isotope effect on ¹⁹F chemical shifts, which was also determined from the analysis of NMR spectra with the XSIM.LINUX software.

To determine if coupling constants were negative or positive in the iteration procedure, it was assumed that $^3J_{\text{F},\text{F}}$ of fluorine nuclei in *ortho*-position to each other and $^1J_{\text{C},\text{F}}$ have negative values, consistent with previous reports [23,24]. Values of $^3J_{\text{F}-5,\text{F}-6}$, $^5J_{\text{F}-4,\text{F}-7}$, $^2J_{\text{C}-5,\text{F}-6}$, and $^4J_{\text{C}-4,\text{F}-7}$ coupling constants in spectra of compounds **1** and **3** as well as $^4J_{\text{C}-1,\text{F}-4}$, $^4J_{\text{C}-1,\text{F}-6}$, and $^3J_{\text{C}-1,\text{F}-7}$ coupling constants in spectra of compounds **4** and **5** were determined also experimentally by conducting ¹⁹F-^{19}F and ¹³C-^{19}F double resonance experiments. Experimental and simulated signals characterizing C-4 and C-5 in the ¹³C NMR spectrum as well as ¹³C-satellites of F-4 and F-5 signals in the ¹⁹F NMR spectrum of the compound **1** are shown in Fig. 2.

The results obtained enable us to provide unambiguous assignments for NMR signals characterizing ¹⁹F and ¹³C nuclei that are present in the aromatic ring of compounds **1**–**5**. It is evident that relative locations of signals are similar in NMR spectra characterizing compounds **1**–**3**. More specifically, signals characterizing F-5 and F-6 in the ¹⁹F spectrum are located upfield from those characterizing F-4 and F-7. This assignment is consistent

Table 1
Experimental and calculated ¹⁹F and ¹³C NMR chemical shift values δ (ppm) for compounds **1**–**5**.

1	2^a		3^b		4		5	
	CDCl ₃	Calculated values	Acetone-d ₆	CDCl ₃	CDCl ₃ (acetone-d ₆)	Calculated values	CDCl ₃ (acetone-d ₆)	Calculated values
F-4	−131.8		−136.0	−131.3	−133.6 (−133.2)		−133.8 (−133.3)	
F-5	−138.1		−142.9	−135.3	−		−	
F-6	−138.1		−142.9	−135.3	−141.7 (−142.6)		−144.4 (−145.6)	
F-7	−131.8		−136.0	−131.3	−134.5 (−137.4)		−136.7 (−139.2)	
C-1	156.4	154.5	160.3	180.1	(158.5)	154.5	(159.3)	154.5
C-3	156.4	154.5	160.3	180.1	(158.8)	155.1	(159.7)	155.7
C-4	144.5	143.1	144.9	144.7	(145.8)	141.3	(143.2)	139.0
C-5	146.7	146.3	146.4	147.7	(145.1)	138.3	(137.6)	125.1
C-6	146.7	146.3	146.4	147.7	(147.1)	144.1	(144.0)	141.4
C-7	144.5	143.1	144.9	144.7	(145.3)	142.9	(145.2)	142.9
C-8	113.7	106.1	115.2	121.6	(108.9)	101.8	(103.2)	97.0
C-9	113.7	106.1	115.2	121.6	(114.8)	106.2	(114.6)	106.6

^a Signals of the pentafluorophenyl group for **2**.

¹⁹F: −161.5 (F-3', F-5'), −151.0 (F-4'), −142.4 (F-2', F-6').

¹³C: 107.0 (C-1'), 144.9 (C-2', C-6'), 139.2 (C-3', C-5'), 143.5 (C-4').

Assignments of ¹³C signals are similar to those reported previously for other C₆F₅X compounds [16,22].

^b For **3** also signals of CF₂. ¹⁹F: −124.0, ¹³C: −100.9.

Table 2

Spin–spin coupling constants ${}^nJ_{F-i,F-j}$ and ${}^nJ_{C-i,F-j}$ characterizing ${}^{19}F$ and ${}^{13}C$ NMR spectra of compounds **1–5**.^a

1	2^b	3^c	4	5
CDCl ₃	Acetone-d ₆	CDCl ₃	Acetone-d ₆	Acetone-d ₆
${}^4J_{C-1,F-4}$			2.0	1.9
${}^4J_{C-1,F-6}$	{3.3} ^d		4.1 {3.9}	4.4 {4.4}
${}^3J_{C-1,F-7}$	~0		2.0	1.6
${}^4J_{C-3,F-4}$	~0		2.0	2.0
${}^4J_{C-3,F-6}$	{-1.7}		1.3 {-1.5}	1.0 {-1.3}
${}^3J_{C-3,F-7}$			2.0	1.9
${}^3J_{F-4,F-5}$	-20.3	-20.0	-19.7	-
${}^4J_{F-4,F-6}$	11.7	9.8	13.0	18.5
${}^5J_{F-4,F-7}$	17.3	16.9	18.2	16.4
${}^3J_{F-5,F-6}$	-18.8	-16.9	-18.2	-
${}^4J_{F-5,F-7}$	11.7	9.8	13.0	-
${}^3J_{F-6,F-7}$	-20.3	-20.0	-19.7	-19.8
${}^1J_{C-4,F-4}$	-273.2	-265.7	-274.5	-260.9
${}^2J_{C-4,F-5}$	12.5	12.2	11.4	-
${}^3J_{C-4,F-6}$	2.0	1.9	2.2	5.1
${}^4J_{C-4,F-7}$	3.7	3.1	3.9	2.1
${}^2J_{C-5,F-4}$	14.7	15.4	14.7	15.7
${}^1J_{C-5,F-5}$	-269.5	-262.1	-273.4	-
${}^2J_{C-5,F-6}$	13.3	13.1	13.1	13.7
${}^3J_{C-5,F-7}$	2.3	2.5	2.5	2.7
${}^3J_{C-6,F-4}$	2.3	2.5	2.5	5.3
${}^1J_{C-6,F-6}$	-269.5	-262.1	-273.4	-255.4
${}^2J_{C-6,F-7}$	14.7	15.4	14.7	13.7
${}^4J_{C-7,F-4}$	3.7	3.1	3.9	2.5
${}^2J_{C-7,F-6}$	12.5	12.2	11.4	13.3
${}^1J_{C-7,F-7}$	-273.2	-265.7	-274.5	-263.9
${}^3J_{C-8,F-4}$	-3.2	-1.4	-3.3	~1
${}^4J_{C-8,F-5}$	1.4	0.6	0.2	-
${}^3J_{C-8,F-6}$	3.1	4.1	3.9	1.4
${}^2J_{C-8,F-7}$	15.0	13.5	14.4	12.5
${}^2J_{C-9,F-4}$	15.0	13.5	14.4	12.1
${}^3J_{C-9,F-5}$	3.1	4.1	3.9	-
${}^4J_{C-9,F-6}$	1.4	0.6	0.2	2.3
${}^3J_{C-9,F-7}$	-3.2	-1.4	-3.3	1.5

^a Values are provided for specified solvents. Values shown in figured brackets were calculated, while those shown between lines were measured directly from spectra of the first order.

^b For the compound **2**: ${}^3J_{F-2',F-3'} = -21.8$, ${}^4J_{F-2',F-4'} = 2.8$, ${}^5J_{F-2',F-5'} = 6.3$, ${}^4J_{F-2',F-6'} = -6.6$, ${}^3J_{F-3',F-4'} = -21.0$, ${}^4J_{F-3',F-5'} = -1.5$.

^c For the compound **3**: ${}^1J_{C-2,F-2} = -264.8$ Hz.

^d The experimental value (${}^3J_{C-1,F-6} + {}^5J_{C-3,F-6}$) = (${}^4J_{C-1,F-6} + {}^5J_{C-1,F-5}$) = 2.0 Hz.

with that was suggested in the literature for compounds **1** and **2** [2,6] but differs substantially from assignments suggested for the same compounds in [5]. Chemical shifts characterizing F-4–F-7 nuclei in ${}^{19}F$ NMR spectra of compounds **1** and **3** have close values. In the case of imide **2**, however, all signals are shifted upfield as compared to those observed in ${}^{19}F$ NMR spectra of compounds **1** and **3**, which can be explained by both the modification of five-membered ring properties and by the change of the solvent from CDCl₃ to acetone-d₆.

Signals characterizing C-4–C-7 in the ${}^{13}C$ NMR spectrum of each of the compounds **1–3** have similar chemical shift values but their relative locations were found to be inverted when compared to those of corresponding F-4–F-7 nuclei in ${}^{19}F$ NMR spectra. It was established that signals characterizing C-4 and C-7 are located upfield as compared to those characterizing C-5 and C-6. Once again, this result is consistent with that was proposed in [9] but differs substantially from the data reported in [2].

Table 3

Isotopic shifts Δ (ppm) of NMR ${}^{19}F$ signals for ${}^{13}C$ isotopomeres of compounds **1–3**.

	1		2		3	
	${}^{13}C$ -4	${}^{13}C$ -5	${}^{13}C$ -4	${}^{13}C$ -5	${}^{13}C$ -4	${}^{13}C$ -5
$\Delta_{F-4} = \delta(F-4) - \delta(F-7)$	-0.058	-0.021	-0.078	-0.025	-0.068	-0.020
$\Delta_{F-5} = \delta(F-5) - \delta(F-6)$	-0.021	-0.048	-0.025	-0.062	-0.019	-0.049

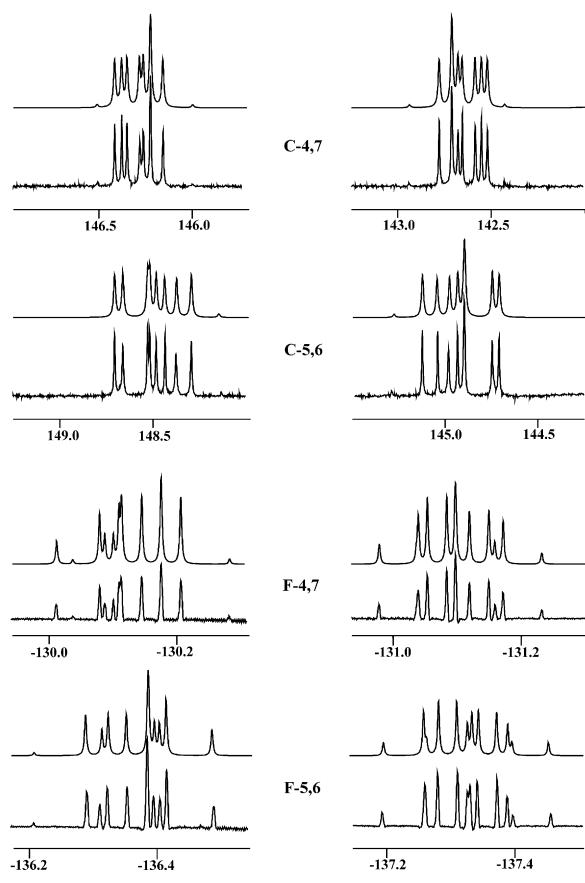


Fig. 2. Experimental (lower in pair) and simulated (upper in pair) signals of ${}^{13}C$ NMR and ${}^{19}F$ NMR spectra of anhydride **1** (spectra were recorded on the Bruker Avance 300 MHz instrument).

Assignments of carbon signals in the ${}^{13}C$ NMR spectra of compounds **1–5** made on the basis of the spin–spin coupling constants analysis are consistent with those calculated by the GIAO/DFT/PBE method for compounds **1**, **4** and **5**. In this case, however, calculated values of chemical shifts are somewhat smaller than experimental values. In the case of carbon atoms linked to fluorine, the difference between calculated and experimental values was found to be in the 2–4 ppm range, which is smaller than differences observed for nodal carbon atoms or those linked to oxygen or nitrogen atoms. The calculated ${}^{13}C$ chemical shift values for compounds **1**, **4** and **5** correlate well with those determined experimentally except for the nuclei C-1 and C-3 in compounds **4** and **5**. In the latter case, the difference between the C-1 and C-3 chemical shift values is small and comparable to the difference between the calculated and experimental values (see Fig. 3).

Therefore, $J_{C,F}$ coupling constant values determined experimentally for carbon atoms mentioned above were compared to those calculated by DFT/B3LYP. The data obtained from double resonance experiments show that ${}^4J_{C-1,F-6}$ has the largest absolute value equal to 4.1 Hz for **4** and 4.4 Hz for **5**, while both ${}^3J_{C-1,F-7}$ and ${}^4J_{C-1,F-4}$ values do not exceed 2 Hz. These results are consistent with ${}^3J_{C-1,F-7} = 2.0$ Hz and ${}^4J_{C-1,F-4} = 1.6$ Hz values observed in the spectrum of 4,7-difluoro-3-methylindan-1-one [25]. The values of ${}^4J_{C-1,F-6}$ and ${}^5J_{C-3,F-6}$ calculated for compounds **4** and **5** are close to those determined experimentally (see Table 2). Moreover, we also calculated ${}^4J_{C-1,F-6}$ and ${}^5J_{C-3,F-6}$ (${}^5J_{C-1,F-5}$) values for the compound **1**. In this case, C-1, F-5, and F-6 nuclei form the ABX system in ${}^{19}F$ and ${}^{13}C$ NMR spectra. Since F-5 and F-6 signals in the case of the isotopomer of **1** in which the ${}^{13}C$ atom is located in the position 1 (A

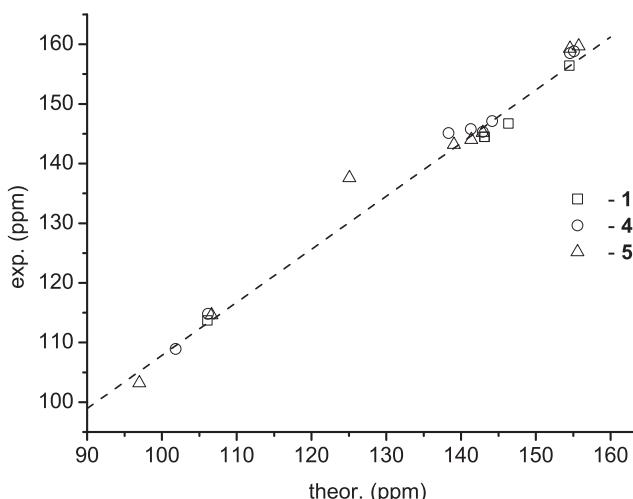


Fig. 3. Correlation of experimental and calculated ^{13}C NMR chemical shift values characterizing anhydrides **1**, **4**, **5**: (□) – **1** in CDCl_3 , (○) – **4** in acetone- d_6 , (△) – **5** in acetone- d_6 . $R^2 = 0.984$, slope = 0.894, RMSD = 4.48 ppm.

and B parts of the ABX system) are superposed with main signals of the compound **1** with all ^{12}C atoms, these signals cannot be isolated in spectra. In the case of the C-1 signal (the X part of the ABX system), only the sum of constants ($^4J_{\text{C-1,F-6}} + ^5J_{\text{C-1,F-5}}$) can be measured [26]. This value was found to be 2.0 Hz, which is in a good agreement with the calculated value (3.3–1.7 = 1.6 Hz). In the absence of experimental data which allow us to determine precisely if coupling constants are negative or positive, more explicit conclusions regarding the accuracy of calculations used cannot be made. However, the entire set of chemical shifts and coupling constants provided here appears to be reliable and internally consistent so that assignments for C-1 and C-3 signals in NMR spectra of compounds **4** and **5** can be made with confidence.

4. Conclusions

In summary, the ^{13}C and ^{19}F NMR spectra characterizing compounds **1**–**5** were analysed. The analysis of $J_{\text{F,F}}$ and $J_{\text{C,F}}$ coupling constants allows for the unambiguous assignment of the NMR signals originating from ^{19}F and ^{13}C nuclei. The data obtained can be used as reference values for interpreting NMR spectra of other derivatives of tetrafluorophthalic anhydride and tetrafluorophthalimide or polymers containing such fragments. Assignments of ^{13}C signals are consistent with the results of quantum-chemical calculations of carbon chemical shifts and $J_{\text{C,F}}$ coupling constants.

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