



Quantum chemistry calculations of branched fluorocarbon systems

L.N. Ignatieva^{a,*}, V.M. Bouznik^b

^a Institute of Chemistry, FEBRAS, pr. 100 – letya Vladivostoka 159, Vladivostok 690022, Russia

^b A.A. Baikov Institute of Metallurgy and Material Science RAS, Leninsky pr. 49, Moscow 119334, Russia

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ABSTRACT

The calculations of energy properties and NMR spectra of C₁₄F₃₀ constitutional isomers were performed within the frames of the HF and DFT quantum chemistry methods. The formation of radicals and branches in fluorocarbon molecules has been discussed on the basis of the obtained results. The energetically preferred and possible isomers have been revealed. The possibility of using ¹³C and ¹⁹F NMR spectra to identify the formation of side trifluoromethyl groups and branches in chain fluorocarbon molecules C_nF_{2n+2} has been demonstrated.

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1. Introduction

Fluoropolymers having some properties uncharacteristic of regular polymers have found extensive application in many fields of science and industry [1] which predetermines the interest to studying their structure [2]. However, experimental studies of fluoropolymers are accompanied with a number of complications related to the sensitivity to external effects responsible for versatility of their molecular structure [3–5]. For example, a new band at 986 cm⁻¹ appears in the IR spectrum of PTFE at irradiation. This band is usually attributed to vibrations of the trifluoromethyl groups. First of all, it is necessary to prove and, in addition, the location of these groups remains unclear. The new bands appear in the other spectral regions (1600–1900 cm⁻¹) upon radiation or heat-treatment of PTFE samples. Such features reflect changes in the microstructure of the polymer macromolecules. There is some confusion in the interpretation of IR spectra. That complicates the understanding of the nature of the processes. The studies of PTFE and its co-polymers, for example, poly(tetrafluoroethylene-co-perfluoropropylene) showed changes of properties of these materials under irradiation in various conditions. NMR studies have shown a remarkable complication of the NMR spectrum in this case [6]. The interpretation of the observed changes is traditionally made using the experimental data for molecules of similar compositions, what is not always productive and unambiguous. In this situation it appears useful to apply

quantum chemistry calculations of the systems under study or respective model fragments [7,8]. Earlier [9–11] we demonstrated the efficiency of calculations of the above type during studies of the structure of products of pyrolysis of polytetrafluoroethylene (PTFE). The calculations enabled us to obtain the information on the topological structure (interatom distances, valent angles) of macromolecules and their energy properties, interpret vibration spectra, and identify chemical shifts of NMR spectra resonance lines.

The most complex studies are concerned with the products of radiation and chemical treatment of fluoropolymers used to create modified forms and novel products. In this case there emerge defects inducing not only the structural variations, but also changes in a number of macroscopic characteristics. The number of defects might be insignificant, which complicates their experimental registration, whereas their respective effect on polymer, in opposite, might be substantial. For instance, PTFE γ -irradiation above the temperature of the crystal phase melting increases the material wear resistance by four orders of magnitude [12]. Here the importance of quantum chemistry calculations increases, since they not only provide understanding of defect structures, but also facilitate revealing the mechanism of the defects effect on the materials properties.

Fluoropolymers, including the basic one (PTFE), are mainly formed by chain spiral macromolecules. Defects related to the formation of branches in the linear chains might emerge at using of different treatment methods.

We described the results of quantum chemistry calculations of model fluorocarbon unbranched molecules in the paper [13]. The present manuscript is a sequel to the author's previous paper [13]. It describes the results of quantum chemistry

* Corresponding author. Tel.: +7 4232 311 889; fax: +7 4232 311 889.
E-mail address: ignatieva@ich.dvo.ru (L.N. Ignatieva).

calculations of the ways of formation of branches in fluorocarbon molecules C_nF_{2n+2} and ^{19}F and ^{13}C NMR spectra of model molecules C_nF_{2n+2} with different structure of chain, with side CF_3 groups and branched one, formed through cross-linking and intersection.

2. Calculation details

Two methods were used in the present work: HF (restricted or unrestricted, basis 6-31G) and DFT B3LYP (restricted or unrestricted, basis 6-311+G(d)). The last one is widely used in the current method based on a combination of the Hartree–Fock method and the density functional theory [14]. The Gaussian-03 software [15] was used in the calculations. The recommendations of [16] and the data of our earlier works [8,10,17,18] were used in choice of the calculation methods and basis sets. To choose a suitable calculation method and an optimal basis set the above authors conducted test calculations of the geometry, vibrational frequencies and some energy properties of the molecules for which experimental data are available. The calculations were performed using the HF, MP2 and DFT (B3LYP functional) methods and variation of the 6-31G and 6-311+G(d) basis sets for every method. The value of the bond lengths CF, C–C and C=C in the molecules CF_4 , C_2F_6 , and C_2F_4 and oligomers C_nF_{2n+2} , C_nF_{2n} were shown in [10,17,18], as well as the angles quite are well described in the methods of DFT (B3LYP) (basis of 6-311+G (d)) and HF (basis 6-31G).

The values of the energy of C–F bond in the molecule of CF_4 , obtained by DFT (B3LYP, 6-311+G(d) basis), and even when using of 6-31G basis, are 493 kJ/mol and 476 kJ/mol, that is in good agreement with the experimental value (484 kJ/mol) [19]. Recalculation of the C–F bond energy by the method of radical distance extrapolation to infinity did not improve the result accuracy and, moreover, gave too high a value with using of the same basis.

The HF method provides a much lower value. However, when one analyzes not the absolute value of the total energy but the difference between the energies of the conformers or isomers, the situation is different. To verify the validity of the calculation of the energy properties obtained within the framework of the methods and the basis used the barriers of internal rotation of C_2F_6 molecules (conformation around the individual C–C bond) were calculated in the work [17] and the results were compared with experimental data. According to the results of calculations the structure of energetically more favorable conformation was the same at using both HF and B3LYP methods. The barriers of internal rotation for perfluorethane molecule, obtained from the total energies for two conformations with using of HF and B3LYP (basis 6-31G) were 4.4 and 3.3 kcal/mol, respectively, and 3.4 kcal/mol (B3LYP with the basis 6-311G (d)). This is in agreement with experimental data – 3.7 [20] and 3.9 kcal/mol [21].

The calculations of test molecules, as well as further performed studies for C_nF_{2n+2} , C_nF_{2n} have shown that, despite the fact that the best agreement with experiment is provided by the DFT method of with functional B3LYP, HF method with a proper basis selection can be successfully used to calculate the geometry of the fluorocarbon molecules and compare the energy performance. This refers to the trend of the energy or the difference of total energies. If one compares energy properties, for instance, energy change tendencies, the differences of full energies in isomers or bond dissociation energies in different parts of a molecule, both methods yield the same changing tendencies and similar results in good agreement with the experiments. This makes it possible to use the HF method for the

works like the present one, in particular, for large molecules and with much lower computer time expenditure.

The necessary condition at carrying out calculations within the frames of both methods, just like any other method, consists in holding to the same calculation conditions (preset calculation accuracy, method used, basis network, etc.). The criterion of adequacy of the obtained results is the comparison with experimental data.

Among of calculated compounds the authors chose the most stable isomers. Conformation around individual bonds CC were also calculated and taken into account.

The calculations of NMR spectra are facilitated by the fact, that in experimental studies one usually considers not absolute values of the nuclei magnetic shielding constants, but their differences, which are expressed in the chemical shifts relatively to a standard substance, for example, tetramethylsilane (TMS), hexafluorobenzene (C_6F_6), fluorotrichloromethane ($CFCl_3$). Cheeseman et al. [22] performed a systematic comparison of deferent levels of theory for calculating NMR shielding tensors. Their main conclusion is that the B3LYP/6-311+G(2d,p) level of theory predicts chemical shifts in quantitative agreement with experimental data. The authors acknowledge, however, that for very large molecules, in which the above level of theory is very expensive, accurate shielding tensors for ^{13}C are provided by the HF/6-31G* method. According to [16] here the calculation method requirements are not so strict, and even the HF method provides acceptable results.

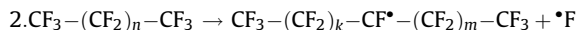
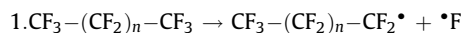
^{19}F NMR ^{13}C NMR spectra of $C_{14}F_{30}$ molecules were calculated by HF/HF/6-31G method. Since almost all the organofluorine chemists still use as an internal standard $CFCl_3$ in the present work shielding constants were calculated for this substance and chemical shifts are reported relative to the reference $CFCl_3$ in the present work.

3. Results and discussion

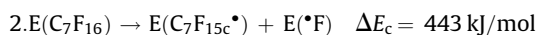
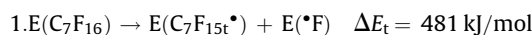
Polytetrafluoroethylene (PTFE) comprises a polymer consisting of chain macromolecules built from $-CF_2-$ units twisted into spirals. As known from experimental studies [1,2,23–25], PTFE radiation or thermal treatment results in macromolecules disruption. This process serves as a basis for the radiation method of PTFE destruction and powder fabrication from micron-sized particles and fluoropolymer modified forms [2,24]. PTFE irradiation results in formation of stable and unstable radicals [26] which can provide a source of different molecular groups linking, branches formation, and macromolecular chains intersection and cross-linking, thus facilitating the transformation of the polymer structure, including the formation of branched structures. Possible linking groups can be $\cdot CF_3$ radicals or more complex groups formed upon the chain disruption in the process of treatment. Addition of long chain fragments might result in chains intersection and/or cross-linking. The mentioned structural changes must result in variations of the fluoropolymer spectroscopic parameters, which can be identified using spectroscopy methods. As it was mentioned above, in IR spectra of the modified PTFE samples the emergence of new band was experimentally found. This band was assigned to the vibrations of side $-CF_3$ groups in the PTFE chain structure (C–F and C–C vibrations in branching nodes). However, in experimental IR spectra the above mentioned bands might not be distinguished from other C–F and C–C vibrations. As it was shown in [11,13], the ^{19}F and ^{13}C NMR spectra could appear more convenient and informative. Indeed, the chemical shifts of ^{19}F NMR signals from fluorine atoms in CF_3 , CF_2 , and C–F groups differ significantly (by more than 40 ppm, according to [13]). One can expect the same regularity for signals from the carbon atom.

3.1. Formation of branches in fluorocarbon molecules

The process of PTFE chain disruption was studied experimentally in a number works [2,26,27]. The radical formation in a model short-chain molecule C_nF_{n+2} can be represented by the following schemes:



The fluorine atom binding energies in different chain sites (intrachain (c) and end (t)) were calculated for the C_4F_{10} molecule [13]. The calculation for C_7F_{16} molecule performed in this paper within the frames of DFT (B3LYP, 6-31G(d) basis) yielded similar results:

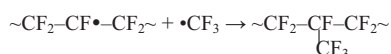


According to the performed calculations, the fluorine atom binding energy in the chain end (in CF_3 terminal group) is higher 38 kJ/mol than that inside of the chain (in CF_2 group). The respective C–F bond lengths differ between the chain middle part and its end ($R(C-F_c) = 1.32 \text{ \AA}$, $R(C-F_t) = 1.30 \text{ \AA}$). One should mention that C–F bond energy is close to the experimental one in polytetrafluoroethylene (480 kJ/mol) [27].

Calculations for the C_4F_{10} molecule performed by HF (6-31G) in the work [13] ($\Delta E_t = 262 \text{ kJ/mol}$, $\Delta E_c = 223 \text{ kJ/mol}$) albeit differing in absolute values, provide a tendency and lead to the same conclusion, moreover the difference in the C–F bond disruption energies between conformations is virtually absent (39 kJ/mol). Calculations for longer molecules $C_{10}F_{30}$ and $C_{17}F_{38}$ performed in the present work provide the same tendency and similar results (34 kJ/mol). Although the energies difference is minor, if the fluorine atom detachment takes place under external effects, the obtained results indicate that this goes on predominantly inside the chain, so that the possibility of the emergence of defects in chains and branched conformations is grounded.

Based on the ratio between bond energies in the PTFE chain, namely, on the fact that the C–C bond is significantly weaker than C–F ($\Delta E(C-C) = 290 \text{ kJ/mol}$, $\Delta E(C-F) = 480 \text{ kJ/mol}$ [27]), it was assumed that the PTFE irradiation disrupts predominantly weaker C–C bonds, whereas C–F bonds remain intact [28]. This is not in agreement with the assumption on the formation of branches in the PTFE chain upon irradiation [29].

According to [29] branches in PTFE are probably formed on the reaction:



The fact that branches are formed on the account of formation of side trifluoromethyl groups in a chain was assumed in the works [2,29,30] on the basis of studies of IR spectra of PTFE samples that underwent radiation, thermal, and mechanical treatment. The calculations of energy properties of the process of bonding of the CF_3 radicals to C_4F_9 ones using the DFT (B3LYP, 6-311+G(d)) method [13] demonstrated that bonding of the CF_3 radical to the formed (for example, upon irradiation) C_4F_9 radical resulted in the system stabilization. Here the stabilization occurs independently of the site of the trifluoromethyl radical bonding: inside the chain or to its end. The stabilization energies estimated from the difference between the sum of the fragments energies and the energy of the formed system are close. That is why, if one assumes that irradiation yields the fluorine atoms detachment and, as a result, the radicals formation, the trifluoromethyl group bonding

would occur to the site of the radical formation. Calculations performed in this work within the frames of the HF(6-31G) method for a longer molecule produce the same conclusions.



(c – intrachain radical, t – terminal radical, d – chain with CF_3 side group, u – unbranched chain).

The emergence of the trifluoromethyl radical near the radical formed upon the effect on the fluorocarbon molecule is quite understandable. This radical may be formed upon the C–C bond disruption at the chain end. Such a process is possible because the energy required to disrupt the C–C bond at the chain end is lower than that the inside of the chain by $\sim 8 \text{ kJ/mol}$. In this case the formation of the terminal and trifluoromethyl radicals takes place.

The emergence of defects (side branches in chains) due to substitution of one of the fluorine atom in the chain by the $-CF_3$ fragment results, as was showed by the calculations, in charge redistribution in systems, and as a consequence in the elongation of C–C bonds from 1.54 to 1.57 Å, emergence of remote fluorine atom (1.38 Å), and changes in the dihedral angle from 161 to 165° (spiral twistedness degree) at the side where trifluoromethyl group is bonded. Thus, the chain distortion occurs in the point of the $-CF_3$ group bonding. These factors could yield the changes in elasticity, mobility, regularity, and, therefore, crystallinity of the polymer. The latter is in agreement with the emergence of a band at 986 cm^{-1} in IR spectra of UPTFE (ultradispersed PTFE) revealed in [30], which is assigned to vibrations of the side trifluoromethyl group and increase of the degree of the sample amorphousness.

Interestingly, the relationship between the total energies of the constitutional isomers d and u is not preserved upon the chain elongation. For example, in the isomer $C_5F_{12}(d)$ (with the side trifluoromethyl group) is the most stable [17] one, whereas for the isomers C_6F_{14} , C_7F_{16} , C_8F_{18} , $C_{15}F_{32}$ and $C_{16}F_{34}$ the unbranched chain (u) is more stable. One should mention that the same tendency was obtained during calculations by both B3LYP(6-311+G(d)) and HF(6-31G) methods, in spite of the fact that the absolute values were different. These data explain the fact of the predominantly chain (unbranching) structure of long PTFE macromolecules. But according to the calculations data, the isomers' energy differences are not large. For example, the energy difference for $C_{14}F_{30}$ and $C_{18}F_{38}$ molecules is $\sim 12 \text{ kJ/mol}$ (unbranched and one CF_3 side group). This fact grounds the possibility of formation of defect structures upon mechanical or radiation impacts, especially when short molecules appearance in the structure.

To reveal the way of packing of CF_3 in a chain, let us compare the energy of structures of the $C_{14}F_{30}$ molecule with different quantity of side trifluoromethyl groups and constitutional isomers with the same quantity of CF_3 groups (Table 1).

As seen from the table, the highest stability characterizes the unbranched chain (the most stable conformer is discussed). Since in the site of the $-CF_3$ group there occurs chain distortion, which requires the energy consumption, one should expect that the larger is the number of branches, the less preferable is the specific conformation. This was corroborated by the calculation results. The full energy of the constitutional isomer of the $C_{14}F_{30}$ with one side trifluoromethyl group differs from that of respective unbranched molecule by 12.3 kJ/mol. The most energetically favorable place of the CF_3 group attachment was found in [18]. Here we have considered the most preferred conformation of attachment of the CF_3 group to this carbon atom. The isomer $C_{14}F_{30}$ with four side trifluoromethyl groups (4) is less energy preferred by 49 kJ/mol. This value reduces to 38 kJ/mol for $C_{16}F_{34}$ and to 26 kJ/mol for $C_{17}F_{38}$. Here we consider the most energetically preferred among the constitutional isomers (4–9).

Table 1Relative energies of C₁₄F₃₀ constitutional isomers (in kJ/mol relative to the most stable, unbranched isomer).

Molecule	E_{rel}	Constitutional isomer
CF ₃ (CF ₂) _n CF ₃ (1)	0	
CF ₃ (CF ₂) ₄ CF ₂ CF ₃ (CF ₂) ₆ CF ₃ (2)	12.3	
CF ₃ (CF ₂) ₂ CF ₂ CF ₃ (CF ₂) ₃ CF ₂ CF ₃ (CF ₂) ₃ CF ₃ (3)	30.4	
(CF ₃) ₂ CF ₂ CF ₂ CF ₂ CF ₃ (CF ₂) ₂ CF ₂ CF ₃ CF ₂ CF ₃ (CF ₃) ₂ (4)	49	
(CF ₃) ₂ CF ₂ CF ₂ CF ₂ CF ₃ (CF ₂) ₂ CF ₂ CF ₃ CF ₂ CF ₃ (5)	110	
CF ₃ CF ₂ CF ₂ CF ₂ CF ₃ CF ₂ CF ₂ CF ₃ CF ₂ CF ₂ CF ₃ CF ₂ CF ₃ (6)	115	
(CF ₃) ₂ CF ₂ CF ₂ CF ₂ CF ₃ CF ₂ CF ₂ CF ₃ CF ₂ CF ₃ CF ₂ CF ₃ (7)	80	
CF ₃ (CF ₂) ₂ CF ₂ CF ₃ CF ₂ CF ₃ CF ₂ CF ₃ CF ₂ CF ₃ (CF ₂) ₂ CF ₃ (8)	152	
(CF ₃) ₂ CF ₂ CF ₂ CF ₃ (CF ₂) ₄ CF ₂ CF ₃ CF ₃ (CF ₃) ₂ (9)	99	

Table 1 (Continued)

Molecule	E_{rel}	Constitutional isomer
Intersecting chains (10)	104	
Cross-linking chains (11)	104	

In our opinion, these results are important for fluoroparaffins having similar molecular dimensions.

Some authors repeatedly put forward the assumption on the possibility of PTFE chains intersecting. We considered two types of chain linking: configuration of intersecting and the cross-linking chains. The calculation data (models 10 and 11, Table 1) provide grounds to assume possible emergence of such isomers, but only under external effects, for instance, radiation. The difference of full energies of unbranched chain and these entities are equal to 104 kJ/mol.

3.2. Identification of branches by NMR method

Nuclear magnetic resonance is a convenient method for identification of side groups in a chain. In [11] we obtained, using calculations, the values of signals in ^{19}F NMR spectra of the chain molecule $\text{C}_{10}\text{F}_{22}$ relatively to the C_6F_6 signal and of the same molecule with side trifluoromethyl groups. To continue this work, we performed calculations of ^{19}F and ^{13}C NMR spectra of the $\text{C}_{14}\text{F}_{30}$ molecules of different structures: unbranched chain, chains, with different quantities and locations of side CF_3 groups, and branched molecules formed from two intersecting or cross-linking chains (models 10 and 11, Table 1). Since the charges of carbon atoms in terminal and side CF_3 groups and CF_2 groups inside the chain differ significantly, the NMR spectra of ^{13}C , just like those of ^{19}F , must be sensitive to the emergence of side branches. The advanced NMR spectrometers allow the measurement of NMR ^{13}C . The changes in the ^{13}C NMR spectrum of PTFE, which as authors believe is cross-linked by radiation, are shown in the work [31].

Fig. 1 shows the calculated models and the values (or region of the signals for CF_2 groups) of chemical shifts of ^{19}F and ^{13}C NMR (relatively to CFCl_3). The data presented in Fig. 1 provide grounds for assuming that in ^{19}F and ^{13}C MAS NMR spectra the signals of carbon and fluorine atoms of terminal CF_3 and intrachain CF_2 groups can be identified. One should mention that the calculated values of chemical shifts of ^{19}F NMR (for CF_2) for chain molecules $\text{C}_{13}\text{F}_{28}$ and $\text{C}_{14}\text{F}_{30}$ are in good agreement with experimental data for PTFE [32], its low-molecular form FORUMTM, and low-molecular fraction separated from the FORUMTM material that mainly consists of short $\text{C}_n\text{F}_{2n+2}$ ($n = 7-10$) formations [11].

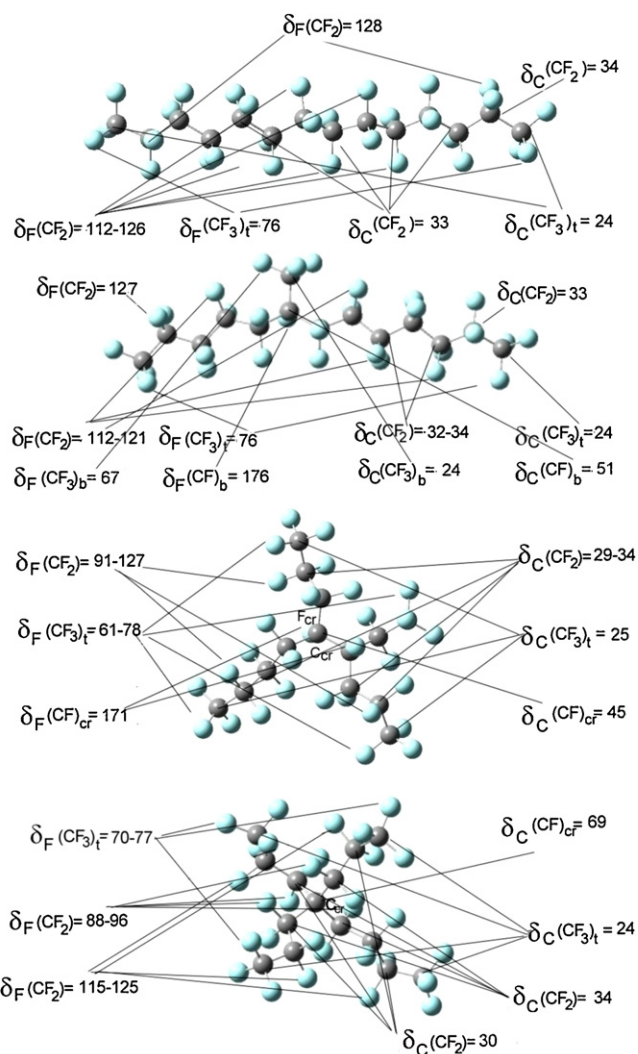


Fig. 1. Calculated models and chemical shift values of ^{19}F and ^{13}C NMR (relatively to CFCl_3) in the $\text{C}_{14}\text{F}_{30}$ constitutional isomers.

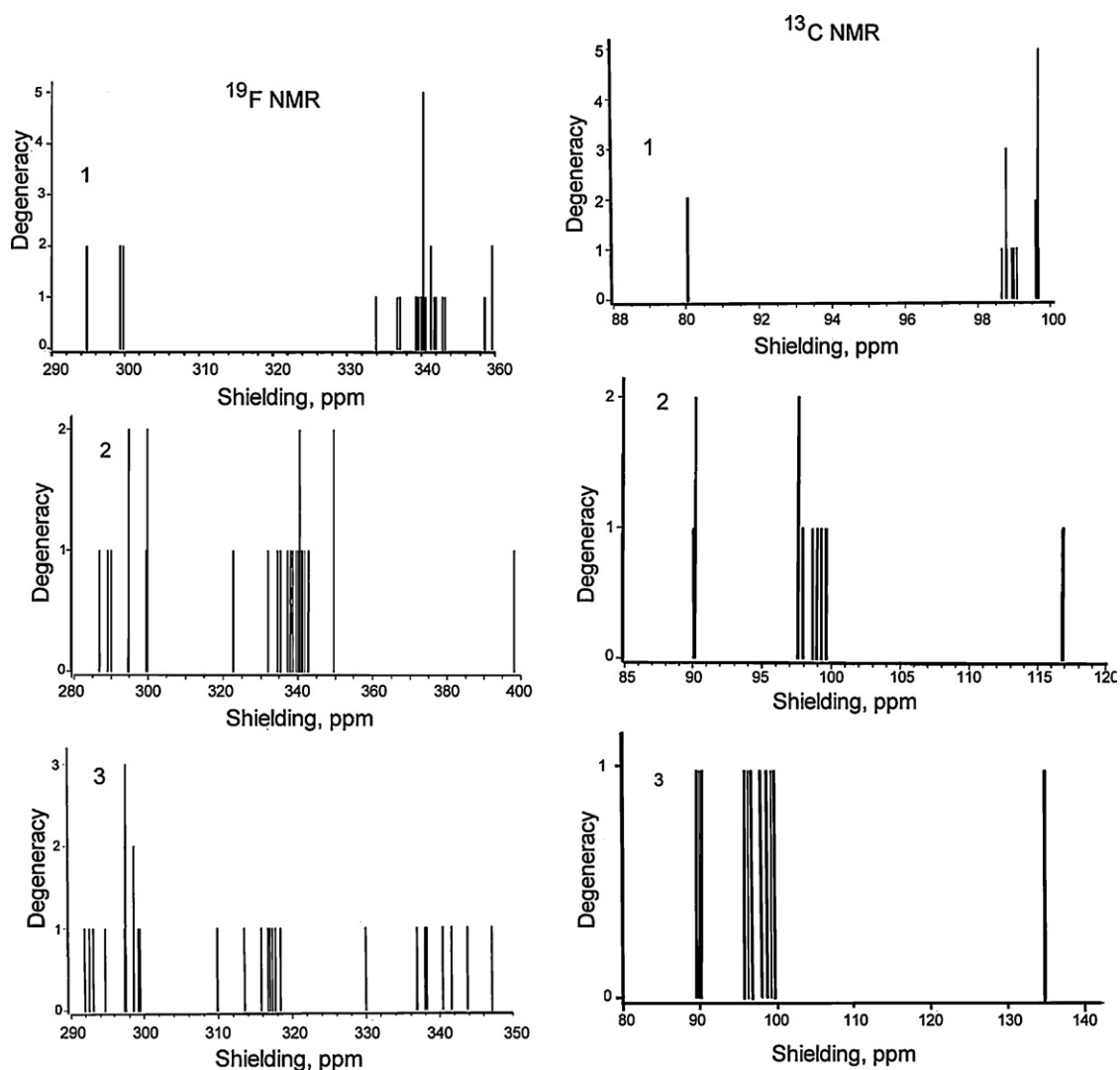


Fig. 2. ^{19}F and ^{13}C NMR spectra model molecules $\text{C}_{14}\text{F}_{30}$ (1, 2, 11, Table 1): 1 – unbranched chain, 2 – chain with one side group, 3 – structure of intersecting chains.

According to the performed calculations, in ^{19}F NMR spectra the emergence of the side CF_3 is accompanied with that of new signals in the range 67 ppm and 176 ppm (relatively to CFCl_3) corresponding to fluorine atoms signals in side CF_3 and C–F groups, respectively, which are absent in ^{19}F NMR spectra of the unbranched $\text{C}_{14}\text{F}_{30}$ molecule. In the ^{13}C NMR spectrum, there emerges a signal at 51 ppm corresponding to the carbon atom signal in the C–F group.

Regrettably, as seen from Fig. 1, if one examines only the areas of the signals locations, the above isomer might be confused with that built from cross-linking chains. Accurate calculated values of chemical shifts of $\delta_c(\text{CF})_{\text{cr}} = 45$ and 48.3 ppm of carbon atoms for chains cross-linking (C_{cr}) are close to the value $\delta_c(\text{C–F})_{\text{b}}$ of the signal corresponding to the carbon atom of the side CF_3 group (51 ppm). According to the calculations, the intersecting and cross-linking chain isomers are not preferable but are possible.

The differences of ^{19}F and ^{13}C NMR signals of atoms of the side trifluoromethyl groups and cross-linking chain are mostly minor, signals from C–F group disappears in the spectrum of intersecting chain. These constitutional isomers can be distinguished by the widths of observed bands caused by the change of the quantities of nonequivalent groups and, as a result, the change of the number of signals (Fig. 2).

4. Conclusions

The calculations of energetic properties and NMR spectra of $\text{C}_n\text{F}_{2n+2}$ ($n = 13\text{--}16$) constitutional isomers were performed within the frames of the HF and DFT quantum chemistry methods. The formation of radicals and branches in fluorocarbon molecules has been discussed on the basis of the obtained results. The energetically preferred and possible constitutional isomers have been revealed. The possibility of using NMR spectra to identify the formation of side trifluoromethyl groups and branches in chain fluorocarbon molecules $\text{C}_n\text{F}_{2n+2}$ has been demonstrated.

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