Polyfluorinated organic paramagnets*

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The review systematizes the methods for obtaining polyfluorinated organic radicals, considers features of their structure and physicochemical properties, and discusses the prospects for further development of this area.

Key words: organic radicals, organofluorine compounds, polyfluorinated compounds, paramagnets, structure-property correlations.

Introduction

Chemistry of organofluorine compounds is one of the most dynamically developing areas, which is interesting from the point of view of both fundamental research and solving applied problems.[1—6] Unique physical and chemical properties of these compounds play an utterly important role in the development of new materials for the energy, space, and medicine industries, agricultural preparations and pharmaceuticals, and in the development of modern technologies.[7—9]

Discoveries made at the intersection of various fields of science are of particular importance in the development of organofluorine chemistry. In many areas, affecting different spheres of science, researchers have gone far ahead. Some areas are still being formed. A promising direction that arose at the border of the chemistry of organofluorine compounds and organic paramagnets is among the latter. It is associated with the development of methods for the preparation and search for practical applications of stable polyfluorinated organic radicals.

Information on polyfluorinated organic radicals that appears from time to time in the literature is scattered across a large number of thematic reviews and monographs.**[3,9—15] At the same time, these radiacals are of a certain interest since there are numerous evidences of fundamental difference between polyfluorinated paramagnets and their counterparts, which do not contain fluorine atoms. It is precisely this family of compounds that we tried to draw attention to in this review.

Synthetic methods and properties of polyfluorinated organic radicals

Alkyl radicals

Introduction of several fluorine atoms into a core or nearest substituents of the paramagnetic moieties can significantly affect all the physicochemical properties of organic radicals, first of all, their stabilities. A striking example is represented by polyfluorinated *C*-centered radical **1a**, which was revealed by Russian researchers in 1983. It was isolated in the free form later by chemists from University of Southern California.[16] The preparative synthesis of paramagnet **1a** in the 90% yield is shown in Scheme 1. It consists in the reaction of perfluoroalkene **2a** with gaseous fluorine in perfluorohexane. The method has been successful in many ways. First, commercially available products, *viz.*, hexafluoropropene and fluorine, are used, which, in combination with the kilogram scale syntheses, makes paramagnet **1a** an easily available reagent.[17] Second, the developed synthetic concept proved to be promising, and highly stable paramagnets **1b**,**c** were prepared analogously from corresponding fluorinated alkenes **2b**,**c**.

Polyfluorinated radicals **1a**—**c** are characterized by rather high chemical and thermodynamic stability. For instance, at room temperature, radical **1a** does not undergo dimerization or, does not react with hydrogen without a catalyst, with oxygen, molecular chlorine, bromine, or iodine, does not interact with aqueous acids or alkalis. This unique radical can be distilled, isolated using chromatography, and analyzed by GC. Only at temperatures ⩾90 °C, paramagnet **1a** undergoes β-elimination with the formation of olefin **3** and trifluoromethyl radical CF_3 (see Scheme 1).[16] The latter feature determines the capability of radical **1a** of being an initiator of radical polymerization processes, including those leading to fluorinated polymers

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* Dedicated to Academician of the Russian Academy of Sciences R. Z. Sagdeev on the occasion of his 80th birthday.

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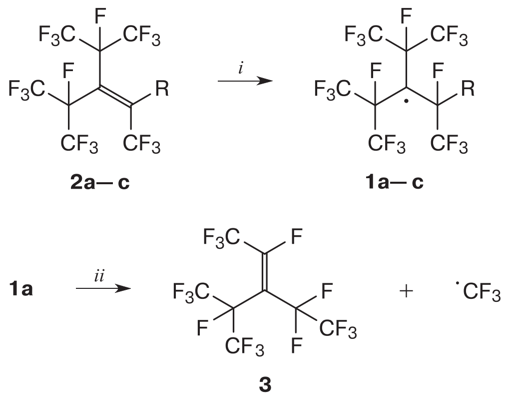
and co-polymers, and an efficient trifluoromethylating or trifluoromethylating and fluorinating agent.[16]

Scheme 1



R = F (**a**), CF_3 (**b**), *O-cyclo*-$C_6F_{10}SO_3C_2F_5$ (**c**)

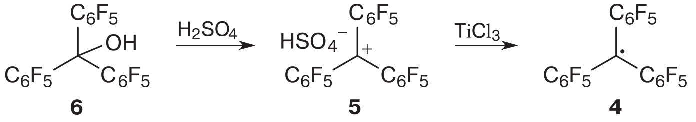
Reagents and conditions: *i.* F_2, C_6F_{14}, ~20 °C, 15—20 h. *ii.* Δ, τ 1/2 (**2a**), 90 °C, ~6 h or 100 °C, ~1.8 h.

Triarylmethyl radicals

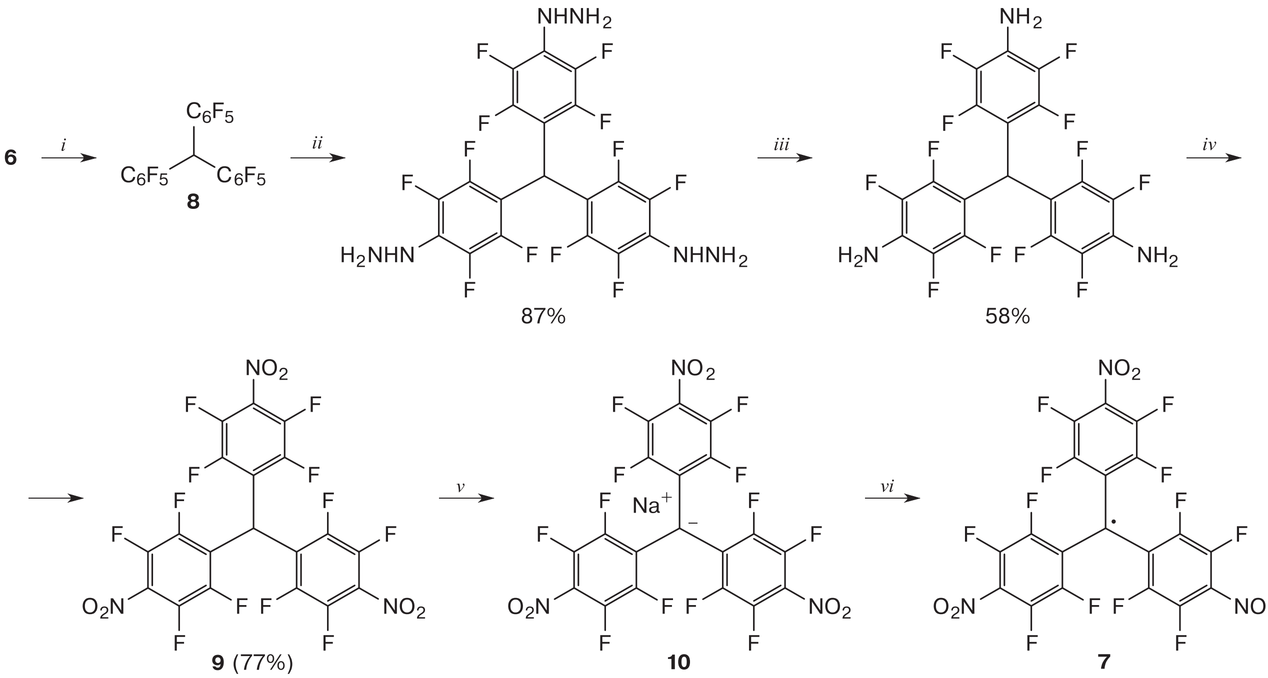
The series of perfluorinated carbon-centered radical is continued by triarylmethyl derivatives. Perfluorotriphenylmethyl radical **4** was synthesized by $TiCl_3$ reduction of corresponding carbocation **5** generated from alcohol **6** under the action of sulfuric acid (Scheme 2).[18] According to ESR spectroscopy data, the substance obtained by recrystallization from CCl_4 contained high, albeit different, amounts of radical **4**, which indicated that this radical was more stable than its non-fluorinated analog since the latter would dimerize in the course of the formation of the solid phase.

In contrast, tris(4-nitro-2,3,5,6-tetrafluorophenyl)methyl radical **7** was prepared according to Scheme 3, which includes a reaction of **6** with PBr_3 with the formation of tris(pentafluorophenyl)methane **8**. The latter was transformed into trinitro derivative **9** by consecutive treatment with hydrazine hydrate, hydroiodic acid, and concentrated hydrogen peroxide. Trinitro derivative **9** was then transformed to carbanion **10** by the action of alkali in dioxane and oxidized to radical **7** with 0.1 *M* aqueous $KMnO_4$ in dioxane (Scheme 3).[19]

Scheme 2



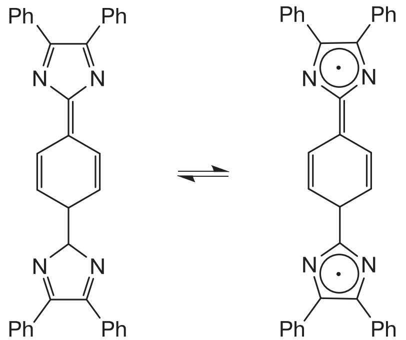
Scheme 3



Reagents and conditions:: *i.* PBr_3, 127 °C, 3 h. *ii.* $N_2H_4 \cdot H_2O$, dioxane, Δ, 20 h. *iii.* 48% HI, 127 °C, 44 h. *iv.* 98% H_2O_2, $(CF_3CO)_2O$, CH_2Cl_2. *v.* 0.1 *M* NaOH, dioxane. *vi.* $KMnO_4$, dioxane.

Imidazolyl biradicaloids

Considering polyfluorinated organic paramagnets, one should also pay attention to compounds with closed electron shells, which have a relatively low-lying excited triplet state. These compounds are called biradicaloids. Tetrafluoro-substituted 1,4-bis(4,5-diphenylimidazol-2-ylidene)cyclohexa-2,5-diene **11** can serve as an example of polyfluorinated biradicaloids. It was synthesized from 1,2,4,5-tetrafluorobenzene **12** (Scheme 4).[20] The final stage in the sequence of transformations is the oxidation of lophin derivative **13** with potassium ferricyanide under mild conditions in a two-phase KOH(aq)/benzene system. It is accompanied by a change in the color of the reaction mixture from pale yellow to blue-violet due to the formation of product **11**. After recrystallization from hot benzene, compound **11** isolated in the form of small blue-violet crystals transformed into a colorless product representing dimer **14** according to the X-ray diffraction data. Irradiation of this dimer in a benzene solution with 360 nm light leads to its decomposition to monomer **11**, which dimerizes again with the formation of compound **14** in darkness for 2 days. It is important to note that according to ESR spectroscopy data, the population of the biradical state of **11** at 293 K is 0.4%, which considerably exceeds that for non-fluorinated analog **15**.



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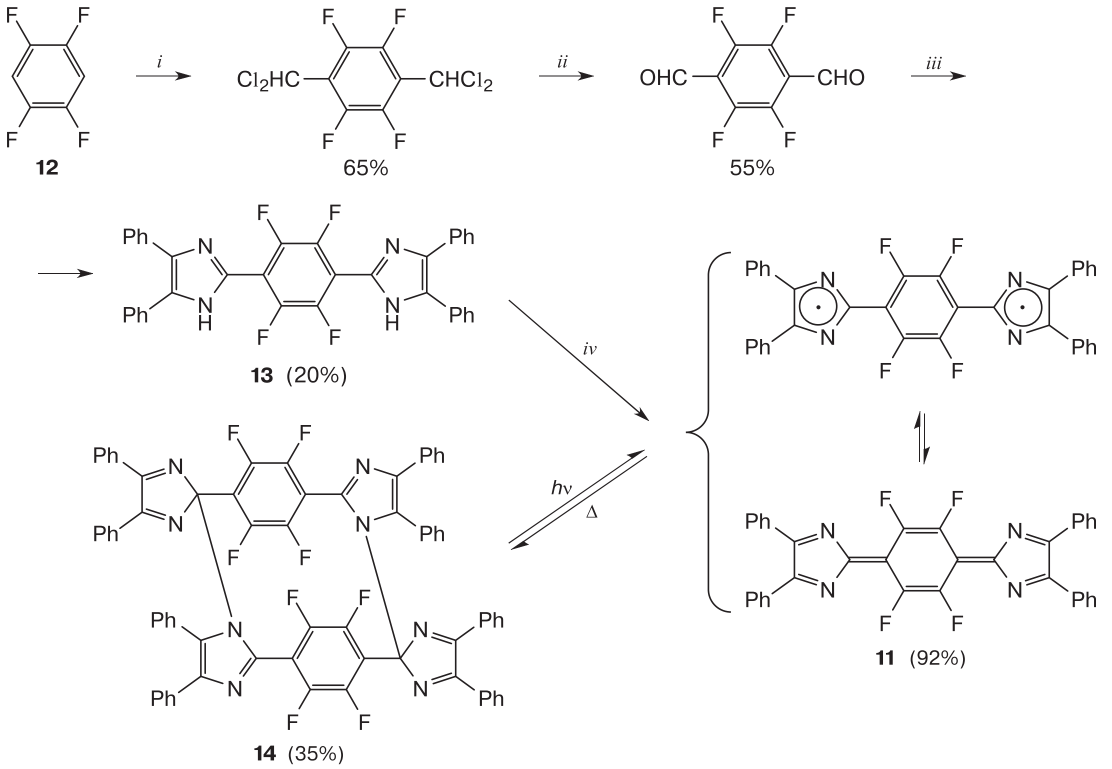
The intensity of the ESR signal of compound **11** decreases with decreasing temperature (Fig. 1). This corresponds to a decrease in the triplet state population, which according to estimations, is separated from the ground singlet state with a gap of 2.37 kcal mol^{-1}.

Aminyl radicals

Fluorine atoms have specific effect on stability of nitrenes and polynitrenes and their transformation into aminyl radicals.[21] It is shown that irradiation of 1,3-diazidobenzene in ethanol at 77 K does not resilt in its conversion in the corresponding diaminyl diradical. On

Scheme 4



Reagents and conditions: *i*. $AlCl_3$, $CHCl_3$, 70 °C, 24 h. *ii*. $FeSO_4$, H_2SO_4, 150 °C, 6 h. *iii*. PhC(O)C(O)Ph, $MeCO_2NH_4$, $MeCO_2H$, 130 °C, 24 h. *iv*. aqueous $K_3[Fe(CN)_6]$. KOH/C_6H_6, 20 °C, 24 h.

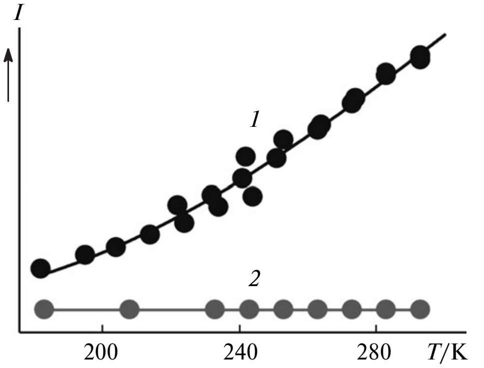
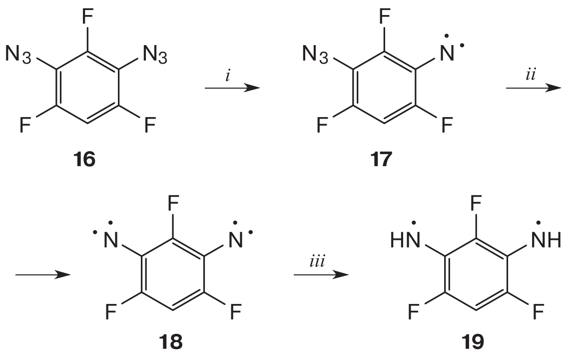


Fig. 1. Temperature dependences of intensities of ESR signals for solutions of **11** (*1*) and **15** (*2*) in toluene.[20] Image is reprinted with permission from the American Chemical Society.

the other hand, photolysis of 2,4-diazido-1,3,5-trifluorobenzene **16** at 77 K initially produces mononitrene **17** and then dinitrene **18** (Scheme 5). The latter has a larger affinity to hydrogen atoms due to electron withdrawing fluorine atoms. Therefore, upon brief warming of the reaction mixture to 100 K and subsequent cooling to 77 K, dinitrene **18** is transformed into triplet diaminyl diradical **19**,[22] which is characterized by the following parameters of zero-field splitting: $|D| = 0.019\pm0.0003$ cm^{-1}, $|E| \sim 0$ cm^{-1}.

Scheme 5

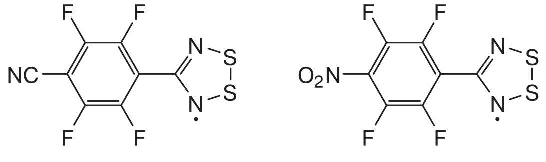


Reagents and conditions: *i*. 2-Methyltetrahydrofuran, 77 K, *hν*. *ii*. 77 K, *hν*. *iii*. 1) 100 K, 2) 77 K.

Dithiadiazolyl radicals

Properties of polyfluorinated species substantially differ from those of their non-fluorinated counterparts almost in all classes of organic radicals. This can be illustrated by considering the family of 1,2,3,5-dithiadiazolyl radicals **20**, which were discovered in the 70s of the last century and studied in detail later.[13,23]

In accordance with the X-ray diffraction data, 1,2,3,5-dithiadiazolyls are prone to the formation of dimers, the structure of which depends on the nature of substituents.[13] In some compounds, the energy of the antiferromagnetic exchange interaction is low. Therefore, the population of the excited triplet state noticeably increases with increasing temperature, determining the development of the paramagnetic properties of these compounds.[24,25]



20a **20b**

Introduction of polyfluorinated substituents suppresses the inclination of radicals **20** to dimerize. For instance, 4-cyanotetrafluorophenyl-substituted radical **20a** represents the first example of 1,2,3,5-dithiadiazolyl radicals remaining paramagnetic in the solid phase. Rather strong antiferromagnetic exchange interactions dominate in one of its modifications at −102 K, whereas upon cooling of the polycrystalline sample to 35.5 K, a magnetic phase transition to a magnetically ordered state takes place in it.[26—28] It is evidenced by the observation of the out-of-phase component of the AC magnetic susceptibility of paramagnet **20a** at frequency of 1 Hz (Fig. 2, *a*) and the absence of this component at 10, 100, and 1000 Hz, which excludes the occurrence of superparamagnetism and other frequency-dependent effects typical of small-sized magnetic particles. The occurrence of a magnetic phase transition in radical **20a** is additionally supported by the presence of a characteristic peak on the temperature dependence of heat capacity at 35.5 K, as well as by observation of difference peaks for two neutronograms recorded at 1.5 K (in the region of magnetic ordering) and 50 K (above the critical temperature).

Isotherms $M(H,T)$ obtained for radical **20a** in the range from 1.8 to 40 K show that with increasing the magnetic field strength, the spontaneous magnetization value $M_s(T)$ is quickly reached, and then there is a linear increase in M (Fig. 2, *b*). The spontaneous magnetization of radical **20a** is low and has a value much lower than the theoretical one (Fig. 2, *c*). This type of magnetic behavior characteristic of weak ferromagnets is determined by the absence of strictly antiparallel orientation of spins of two sublattices.

Another unique characteristic of radical **20a** consists in a significant increase in the critical temperature with increasing pressure. It reaches a value of 65 K at $\sim 16 \cdot 10^8$ Pa, which is a record value for purely organic ferromagnets.

The replacement of the nitrile group in radical **20a** with the nitro group fundamentally changes the magnetic behavior of the paramagnet. According to data of SQUID magnetometry, the ferromagnetic exchange interaction ($C = 0.368$ cm^3 K mol^{-1} at 1.6 K) prevails in the solid phase of nitro derivative **20b**. It causes an increase in the effective magnetic moment μ_{eff} at low temperatures

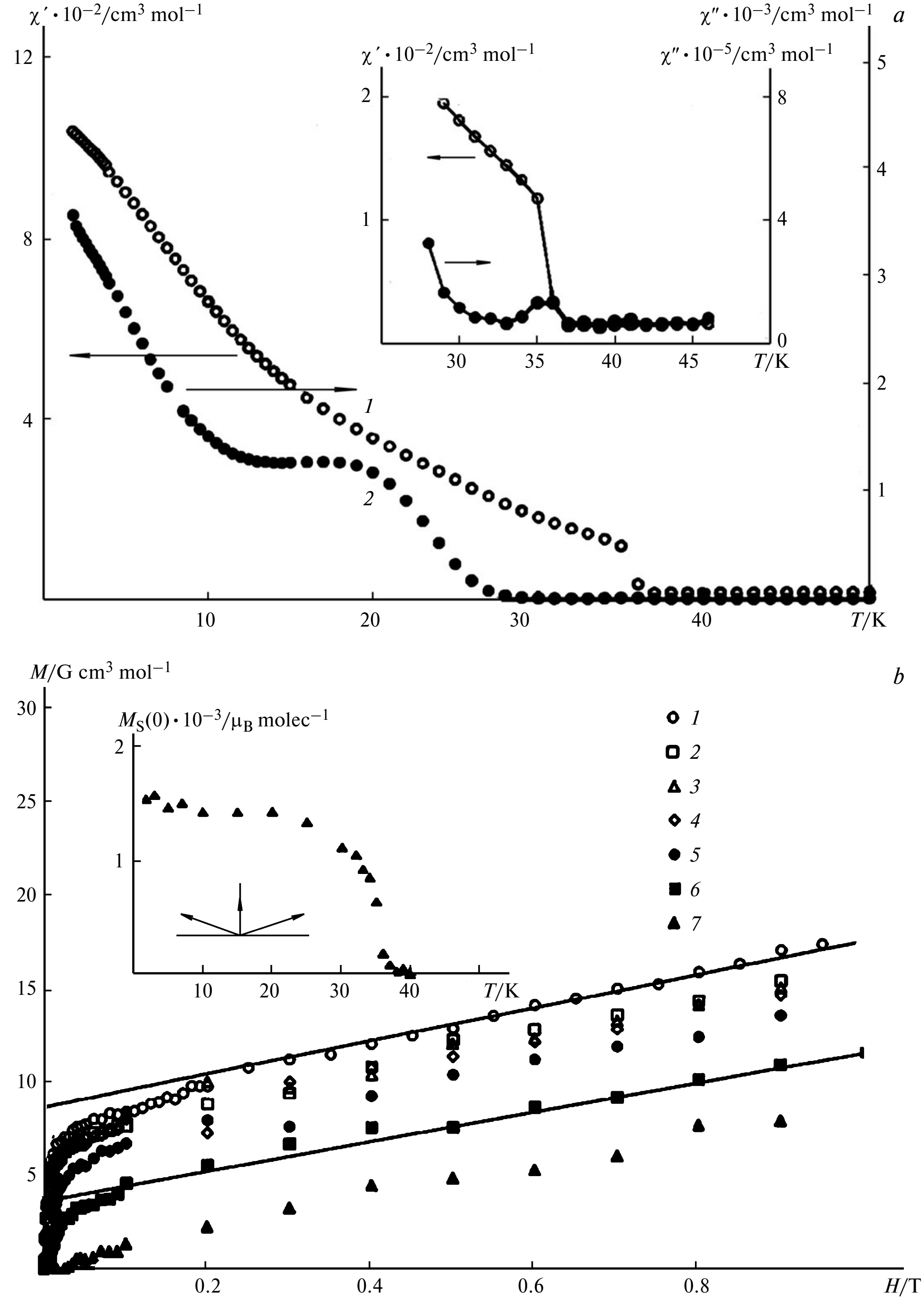


Fig. 2. (*a*) Temperature dependences of in-phase χ' (*1*) and out-of-phase χ'' (*2*) components of magnetic susceptibility of radical **20a**. (*b*) Magnetization isotherms and temperature dependence of spontaneous magnetization (inset) of **20a**; *T*/K: 1.8 (*1*), 5 (*2*), 10 (*3*), 20 (*4*), 30 (*5*), 35 (*6*), 40 (*7*).[28] Image is reprinted with permission from the American Physical Society.

(Fig. 3, *a*, *b*). At ~10 K, the μ_{eff} value has a maximum due to saturation effects in a field of 10 Oe.

Low-temperature studies of the in-phase component χ' of magnetic susceptibility of a monocrystal of **20b** at different orientations in a field of 2 G at 1.11 Hz revealed a sharp increase in the χ' values below 1.4 K, which is due to a transition of radical **20b** into the magnetically ordered state (Fig. 3, *c*). In this case, the magnitude of the jump

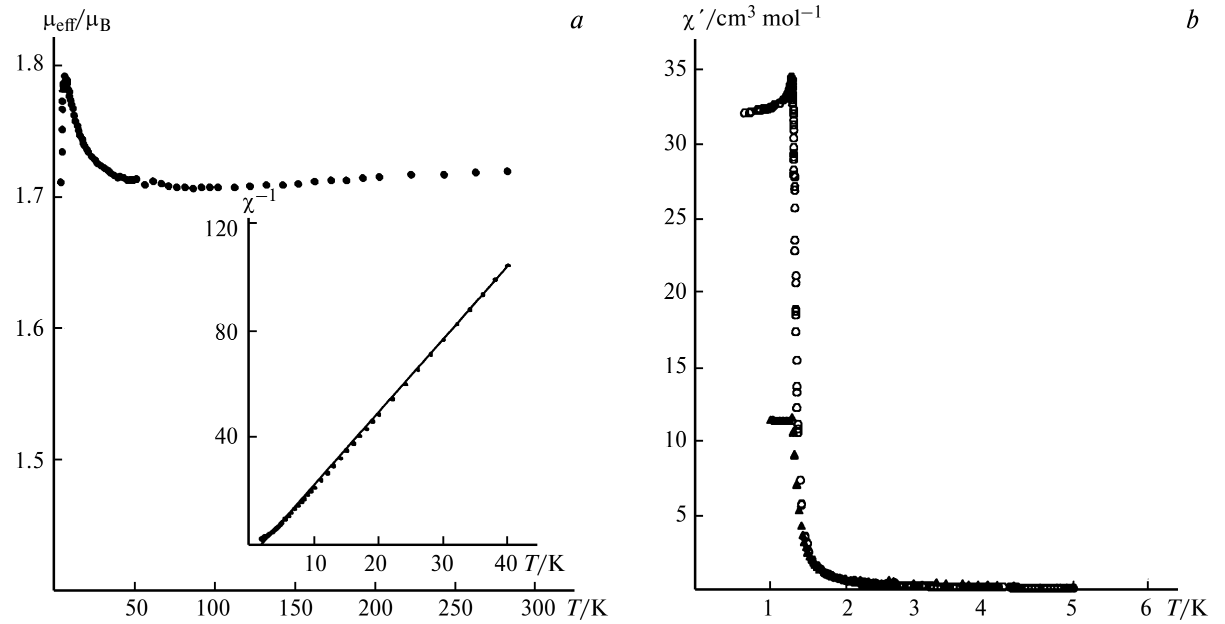
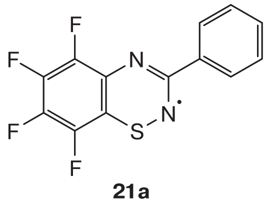


Fig. 3. (*a*) Temperature dependence (5—280 K) of effective magnetic moment for **20b** in a field of 10 Oe ($1/\chi$ *vs.* T in inset). (*b*) Temperature dependence of the in-phase component χ' of magnetic susceptibility of monocrystal of **20b** at different orientations in a field of 2 G at frequency of 1.11 Hz.[29] Image is reprinted with permission from John Wiley and Sons.

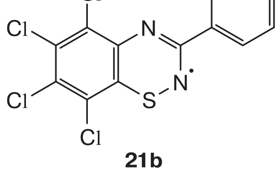
of the χ' value depends substantially on the orientation of the crystal relative to the magnetic field.[29]

Thiadiazinyl and dithiazolyl radicals

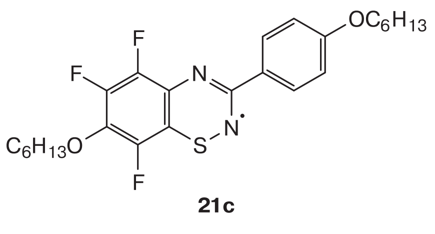
The introduction of fluorine (or chlorine) atoms into paramagnetic moieties possessing sufficiently high spin density promotes the stabilization of organic radicals. For instance, benzo-, pyrido-, and pyrazino-annulated 1,2,4-thiadiazinyl radicals are not stable enough to be isolated. In contrast, 1,2,4-thiadiazinyls **21a,b** annulated with tetrafluoro- and tetrachlorobenzene were isolated and completely characterized, in particular, using X-ray analysis.[30] Moreover, free hexyloxy-substituted 1,2,4-thiadiazinyl radical **21c** was successfully isolated for a study of liquid crystal paramagnets.[31]



21a



21b



21c

The introduction of polyfluorinated or polychlorinated substituents at position 5 of 1,2,3- dithiazolyl radicals, which is a position with a high spin density, reduces the tendency for these radicals to dimerize. According to the data of the Cambridge Structural Database, the structures of only two compounds among non-annulated 1,2,3-dithiazolyls were solved. Those are dichloro-5-isothiasolyl-substituted 4-chloro-1,2,3-dithiasolyl radical **22** and its pentafluorophenyl-substituted analog **23**. Note that the first compound is the only representative of 1,2,3-dithiazolyls with a crystal structure formed by non-dimerized radicals (Fig. 4, *a*).[32] Unlike compound **22** having a plane structure in the solid phase, the dihedral angle between the planes of phenyl and 1,2,3-dithiazolyl cycles in polyfluorinated derivative **23** is 58.3°. In addition, radicals **23** have packing in the form of co-facial dimers (Fig. 4, *b*) with the shortest S...S distance of 3.2987(13) Å, which is much smaller than the sum of van der Waals radii (3.6 Å).[33]

Nitroxyl radicals

Among nitroxyl radicals, polyfluorinated derivatives also stand out due to their unusual properties. Bis(trifluoromethyl)nitroxyl radical **24** was obtained already in the 60s of the last century by oxidation of the corresponding hydroxylamine with fluorine, chlorine, silver(I) or (II) oxide, mercury(II) oxide, potassium permanganate, cerium(IV) sulfate, potassium bromate, or other oxidants.[34—38] Organic radical **24** was the first representative obtained by electrochemical oxidation of hydroxylamine on platinum electrode (in 99% yield).[39] Under normal

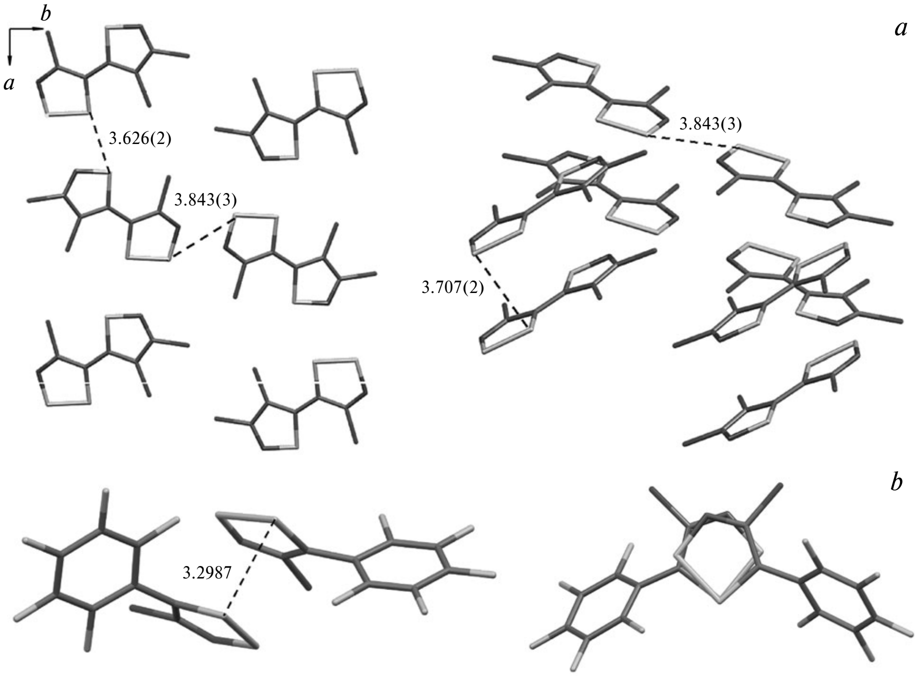
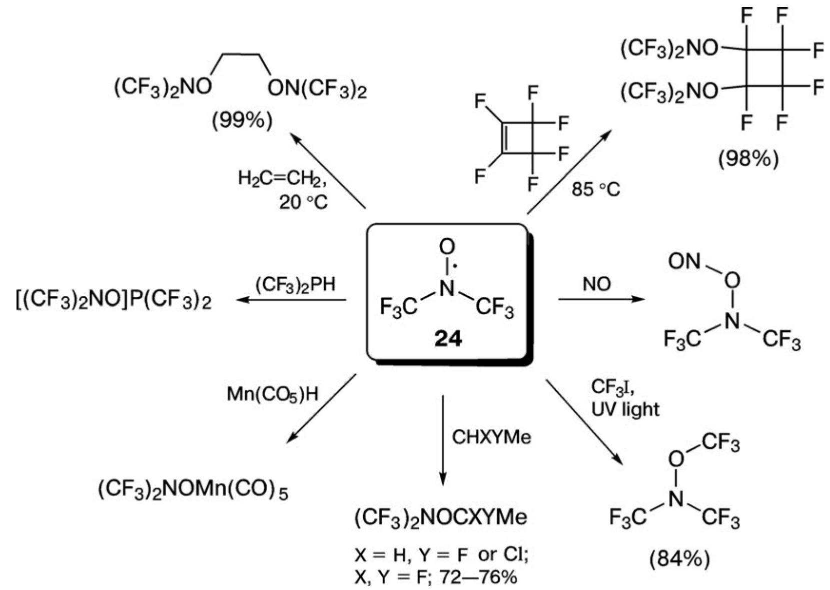


Fig. 4. A fragment of the crystal structure of 4-chloro-5-(3,4-dichlorothiazol-5-yl)-1,2,3-dithiazolyl **22** (*a*); structure of the dimer of 4-chloro-5-pentafluorophenyl-1,2,3-dithiazolyl radical **23** from two angles (*b*),[32] the shortest S...S distances are shown.

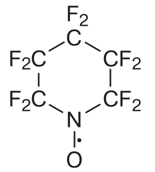
conditions, paramagnet **24** is a purple gas, which condenses at −25 °C, forming a dark violet liquid, and becomes solid at−55÷−70 °C and forms pale yellow crystals. It is soluble in water, its aqueous solution is pink-violet.[34] Nitroxyl radical **24** is very stable, it withstands heating up to 200 °C, does not react with water, 10% aqueous NaOH, air oxygen, stainless steel, or copper. At the same time, it easily reacts with other types of free radicals, *e.g.*, with NO, producing *O*-nitroso-bis(trifluoromethyl)hydroxylamine.[37] Moreover, radical **24** forms 2 : 1 adducts with olefins (ethylene, tetrafluoroethylene, perfluoropropene, and perfluorocyclobetene). It also reacts with various organoelement compounds possessing an element—H bond and haloalkanes, producing diamagnetic products of radical substitution of a hydrogen atom (Scheme 6).[40—42] The treatment of an excess of nitroxyl radical **24** with strong oxidants such as

Scheme 6



PtF_6, or $O_2^+SbF_6^-$ results in the decomposition of the paramagnet with elimination of trifluoromethyl radical, which recombines with starting compound **24**, producing $(CF_3)_2NOCF_3$ (38%).[43] In addition, $[(CF_3)_2NO]_2CF_2$ is formed in low yield (~17%) in the reaction with $O_2^+SbF_6^-$ (which is virtually $O_2^+SbF_6^- \cdot 0.73\ SbF_5$).

Other polyfluorinated nitroxyl radicals such as perfluoropiperidine *N*-oxyl **25** and perfluoromorpholine *N*-oxyl **26**, which are formed by photolysis of *N*-fluoroperfluoropiperedine and *N*-fluoroperfluoromorpholine, respectively, in the presence of oxygen and subsequent heating at ~140—175 °C,[44,45] also exhibit high stability. Nitroxyl radicals **25** and **26** are volatile blue-violet liquids (bp 51 and 60 °C, respectively). Their chemical properties are similar to those of nitroxyl radical **24**.



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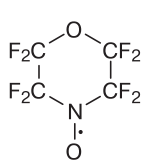

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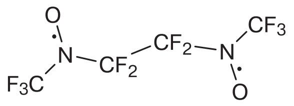
1,1,2,2-Tetrafluoro-*N*,*N*'-bis(trifluoromethyl)ethane-1,2-diamine-*N*,*N*'-dioxyl **27** was synthesized by hydrolysis of the adduct $2CF_3NO \cdot C_2F_4 \cdot PCl_3$ and subsequent oxidation with potassium permanganate in diluted sulfuric acid.[46] Polyfluorinated biradical **27** represents a dark violet liquid with bp 55 °C at 769 Torr and chemical properties analogous to those of nitroxyl radical **24**. Indeed, compound **27** easily reacts with perfluoroalkenes (tetrafluoroethylene, hexafluoropropene, *etc.*), mainly leading to polyfluorinated co-polymers together with minor amounts of polyfluorinated heterocycles.



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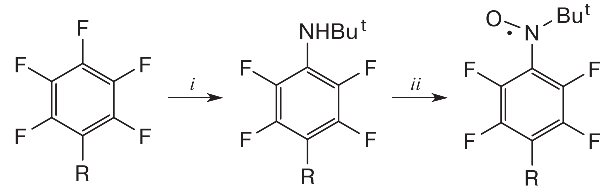
The method for synthesis of the first representative of polyfluoroaryl-*tert*-butylnitroxyl radicals, *viz.*, *N*-*tert*-butyl-*N*-[2,3,5,6-tetrafluoro-4-(1*H*-pyrrol-1-yl)phenyl]-nitroxyl radical **28**, which is unusually stable, was described.[47] This radical was prepared by conventional transformation of compound **29** into the corresponding lithium derivative and subsequent treatment with 2-methyl-2-nitrosopropane (Scheme 7). Hydroxylamine **30** obtained in the 32% yield was quantitatively oxidized to target radical **28**. According to the X-ray diffraction data, the dihedral angle between the plane of the $N(-O)C_{Bu}$ moiety and the plane of phenyl cycle in nitroxyl radical **28** is close to 90°. Crystal structure of radical **28** is formed by the packing of dimers, which arise due to the paired π-stacking of polyfluorophenyl and pyrrole cycles.

A wide range of polyfluoroaryl-*tert*-butylnitroxyl radicals was obtained in two steps. At the first step, the products of aminodefluorination are formed in the reaction of polyfluoroarenes with *tert*-butylamine. At the second step, *N*-*tert*-butyl-*N*-arylamines are oxidized to the corresponding nitroxyl radicals. The conditions used at the first step depend on the reactivity of the polyfluoroarene with respect to the nucleophile, *viz.*, with respect to *tert*-butylamine in this case. Polyfluorinated substrates, which are prone to nucleophilic aromatic substitution, such as octafluorotoluene **31a** and pentafluorobenzonitrile **31b** react with *tert*-butylamine already at room temperature, producing anilines **32a,b** in quantitative yield (Scheme 8). Oxidation of substituted

Scheme 8

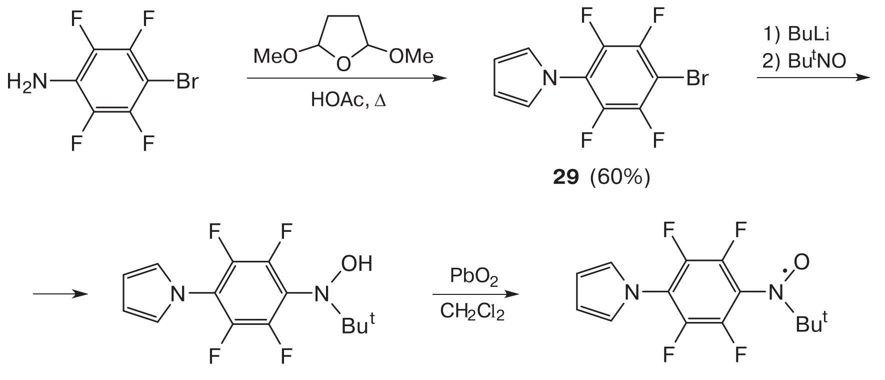


31a,b **32a,b** (99%) **33a,b** (90%)

R = CF_3 (**a**), CN (**b**)

Reagents and conditions: *i.* Bu^tNH_2, $CHCl_3$. *ii.* *m*-CPBA, $CHCl_3$.

Scheme 7

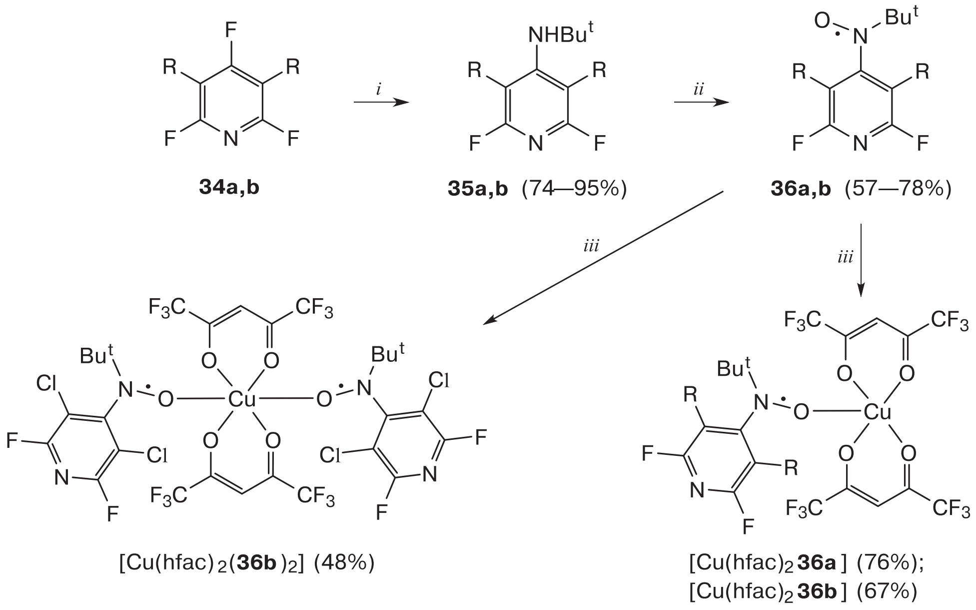


29 (60%)

30 (32%)

28 (100%)

Scheme 9



R = F (**a**), Cl (**b**)

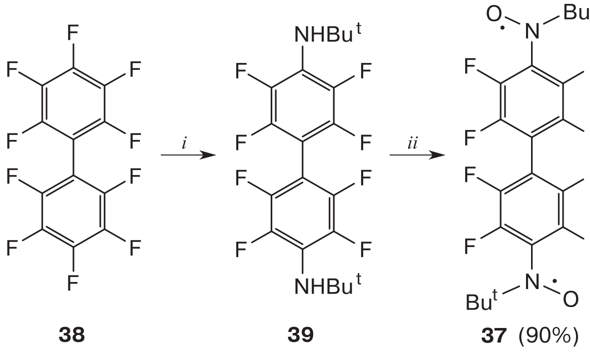
Reagents and conditions: *i.* Bu^{t}NH$_2$, CHCl$_3$, ~20 °C. *ii.* *m*-CPBA, CHCl$_3$, ~20 °C. *iii.* Cu(hfac)$_2$, hexane.

anilines **32a,b** with *m*-chloroperoxybenzoic acid leads to stable nitroxyl radicals **33a,b** in yield exceeding 90%.[48]

This method has proven itself to be effective in the synthesis of paramagnetic perfluoropyridine derivatives. For example, the reactions of pentafluoropyridine **34a** and 3,5-dichloro-2,4,6-trifluoropyridine **34b** with *tert*-butylamine gave products of *para*-substitution **35a,b**, oxidation of which led to radicals **36a,b** (Scheme 9). The latter turned out less stable than radicals **33a,b** and were not isolated pure. At the same time, stable molecular complexes of the 1 : 2 or 1 : 1 compositions, *viz.*, [Cu(hfac)$_2$(**36b**)$_2$], [Cu(hfac)$_2$**36a**], and [Cu(hfac)$_2$**36b**], are formed in moderate yields in the reaction of nitroxyl radicals **36a,b** with Cu(hfac)$_2$. An analysis of the X-ray diffraction data[49] showed that the nitroxyl group exists in the axial position in all obtained complexes, and the O$_{NO}$—Cu bond lengths vary from 2.402 to 2.481 Å. Heterospin complexes [Cu(hfac)$_2$(**36b**)$_2$], [Cu(hfac)$_2$**36a**], and [Cu(hfac)$_2$**36b**] exhibited high stabilities, they withstood heating to 104—112 °C (their melting points). In addition, they were highly volatile because of saturation with fluorine atoms. The complexes were quantitatively sublimed within 85—90 °C at pressure of 30 Torr, forming crystals, the structure of which was identical to that before sublimation.

In the case of polyfluorinated substrates with a reduced reactivity or if it is required to introduce two or more *tert*-butylamine groups, the other two methods are helpful. The first one is illustrated by the synthesis of nitroxyl biradical **37**, which is produced in a yield of up to ~90% by the reaction of perfluorobiphenyl **38** with an excess of lithium *tert*-butylamide and following oxidation of obtained diamine **39** (Scheme 10).

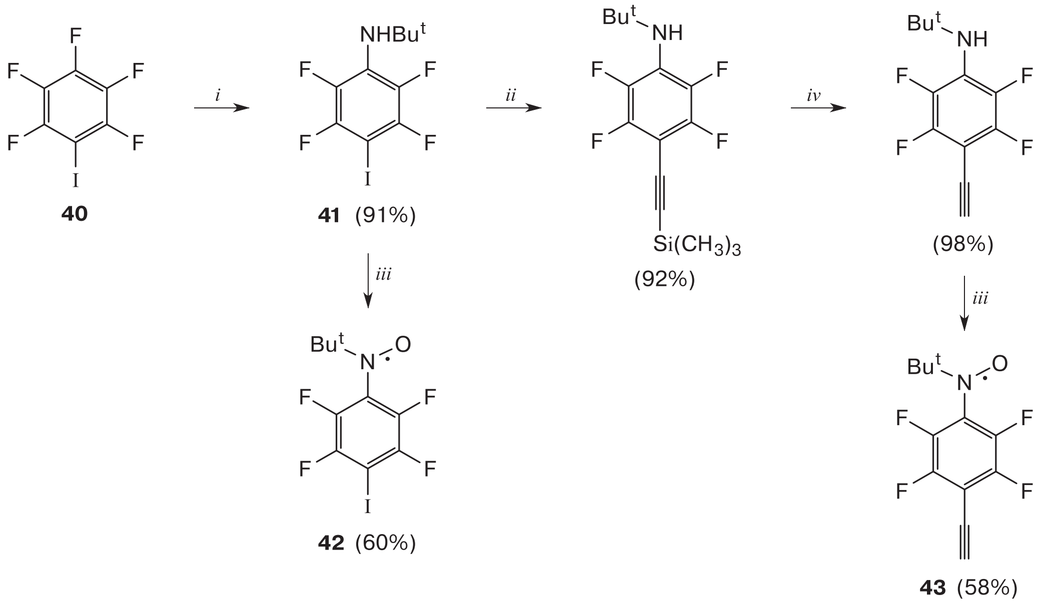
Scheme 10



Reagents and conditions: *i.* Bu^{t}NHLi, THF. *ii.* *m*-CPBA, CHCl$_3$.

The second method consists in heating a mixture of polyfluoroarene with an excess of *tert*-butylamine in an autoclave, which makes it possible to raise the temperature to the value necessary for the reaction to occur. For instance, heating of perfluoroiodobenzene **40** with *tert*-butylamine in an autoclave at 120 °C made it possible to obtain compound **41**, which represents a key tetrafluorinated derivative of iodoaniline, which became a precursor of two nitroxyl radicals **42** and **43** (Scheme 11). These radicals can serve as paramagnetic building blocks in the synthesis of spin-labeled compounds.[51]

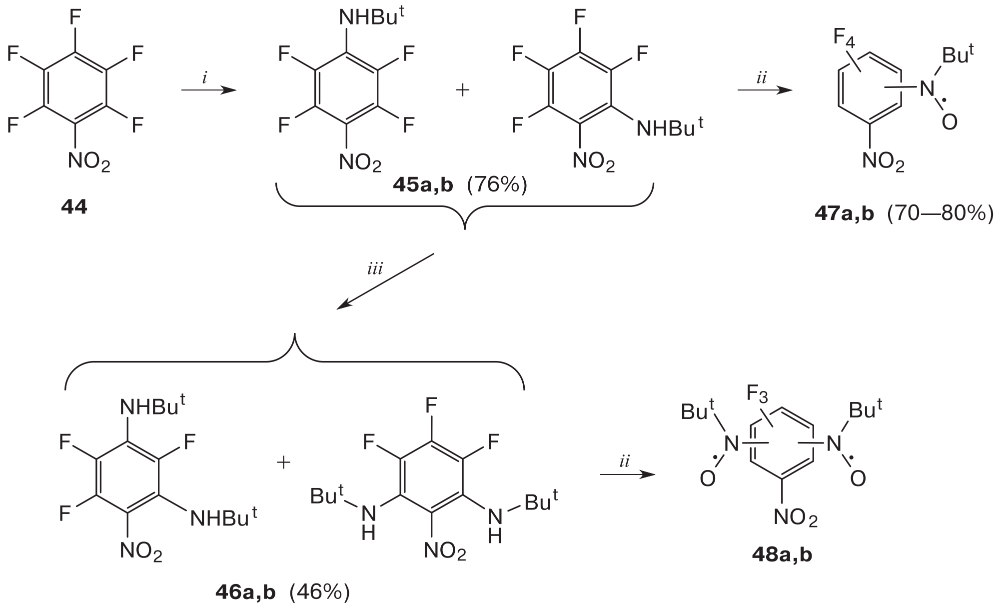
Scheme 11



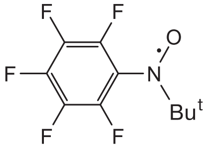
Reagents and conditions: *i*. Bu^tNH_2, 120 °C, autoclave. *ii*. $HC≡CSiMe_3$, ~20 °C, $Pd(PPh_3)_2$,CuI, Et_3N. *iii*. *m*-CPBA, $CHCl_3$, ~20 °C. *iv*. K_2CO_3, MeOH, ~20 °C.

Carrying out the reaction of polyfluorinated arenes with *tert*-butylamine in an autoclave at specified temperatures makes it possible to successively replace one, two, or more fluorine atoms in the aromatic substrate. In particular, one can obtain either mono- **45a,b** or bis(*tert*-butylamino)nitrobenzenes **46a,b** by the reaction of perfluoronitrobenzene **44** with *tert*-butylamine at different temperatures. Their oxidation with *m*-chloroperoxybenzoic acid leads to corresponding mono- **47a,b** and biradicals **48a,b** (Scheme 12). It should be noted that this approach results in the formation of only *meta*-substituted diamines, oxidation of which gives triplet diradicals **48a,b**.

Scheme 12



Reagents and conditions: *i*. Bu^tNH_2, 60 °C, autoclave. *ii*. *m*-CPBA, $CHCl_3$, ~20 °C. *iii*. Bu^tNH_2, 100 °C.



49

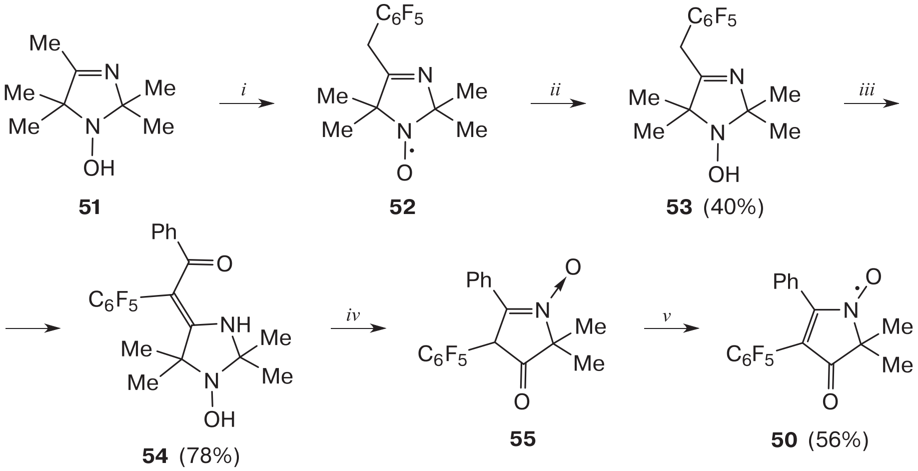
The advantage of *tert*-butylpolyfluoroarylnitroxyl radicals is their higher stability in comparison with their non-fluorinated analogs. In particular, pentafluorophenylnitroxyl radical **49** remains intact after prolonged boiling in benzene, whereas its non-fluorinated analog undergoes disproportionation to the corresponding amine and quinone derivative.[52,53] In the case of the fluorinated derivatives, this disproportionation is thermodynamically unfavorable because of higher strength of the C—F bond (116 kcal mol^{-1}) as compared to the C—H bond (98 kcal mol^{-1}).[2,54]

Consideration of a series of cyclic conjugated nitroxyl radicals can be started with pentafluorophenyl-substituted pyrrolinone 1-oxyl **50**, which is stable in contrast to its non-fluorinated analog. Multistage synthesis of oxyl **50** includes lithiation of 1-hydroxypentamethylimidazoline **51**, and the following reaction of the formed dianion with perfluorobenzene leads to intermediate radical **52**. Then, the paramagnetic product was reduced to hydroxylamine **53**, which was transformed into dianion and reacted with ethyl benzoate. Thus obtained amino enone **54** was transformed into cyclic β-oxonitrone **55**, oxidation of which led to target stable radical **50** (Scheme 13).[55]

N-Hydroxybenzimidazoles were proposed as convenient easily modified precursors of the corresponding *N*-oxyl radicals capable of catalyzing various reactions of functionalization of C—H bonds. It has been shown that the introduction of fluorine atoms into *N*-hydroxybenzimidazoles results in an increase in the dissociation energy of the OH bond and stabilization of the corresponding radicals, which substantially increases the yield of products of the C—H functionalization reaction.[56] The process of benzylic C—H amination of ethylbenzene **56** catalyzed by nitroxyl radicals, which are formed *in situ*, can be taken as an example. The use of polyfluorinated *N*-hydroxybenzimidazoles **57c,d** as catalysts significantly increases the yield of amination product **58** (Scheme 14).

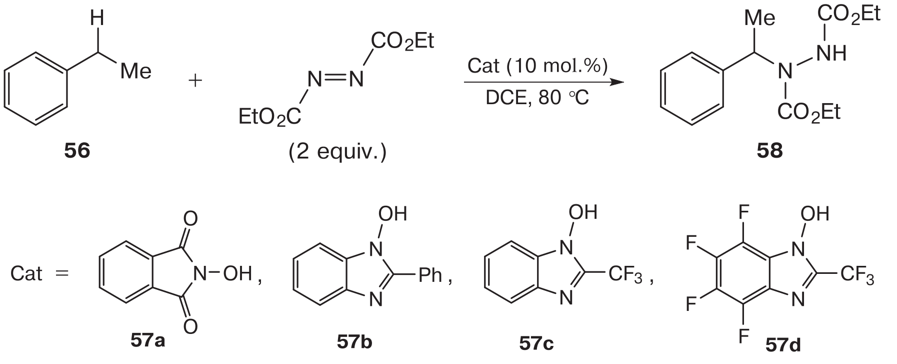
The use of polyfluorinated *N*-hydroxybenzimidazoles in the transformation of aldehydes such as compound **59** into acyl fluorides **60** under the action of Selectfluor also has a substantial effect on the product yields (Scheme 15).[56]

Scheme 13



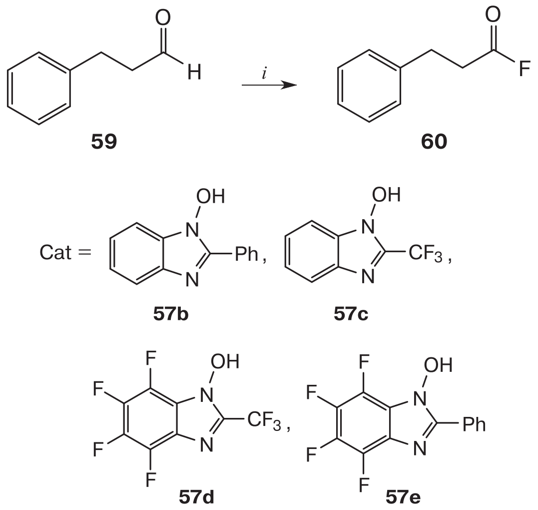
Reagents and conditions: *i*. 1) LDA, 2) C_6F_6, Et_2O. *ii*. Zn, NH_4Cl, MeOH. *iii*. 1) LDA, 2) $PhCO_2Et$, Et_2O. *iv*. HCl, MeOH. *v*. MnO_2, $CHCl_3$.

Scheme 14



Cat	Yield of **58** (%)
57a	55
57b	20
57c	56
57d	93

Scheme 15



Cat	Yield of **60** (%)	Cat	Yield of **60** (%)
57b	—	**57d**	61
57c	28	**57e**	33

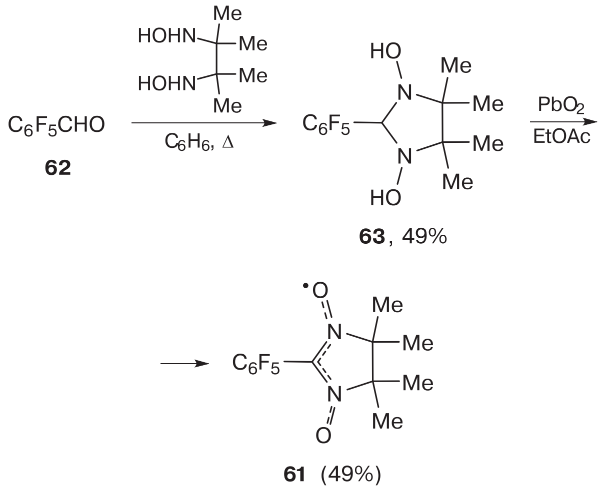
Reagents and conditions: Selectfluor (2 eq.), Cat (10 mol.%), MeCN, ~20 °C.

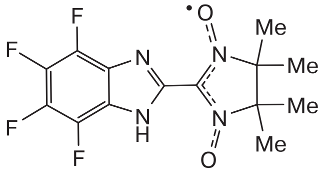
Nitronyl nitroxyl radicals

A well-studied class of cyclic nitroxyl radicals is 3-oxido-2-imidazolin 1-oxyl radicals,[57—63] which will be called below as nitronyl nitroxides. However, the number of polyfluorinated representatives of this class of radicals is not large. 2-Pentafluorophenyl-substituted nitronyl nitroxide **61** was synthesized in the 24% yield by the reaction of perfluorobenzaldehyde **62** and 2,3-bis(hydroxyamino)-2,3-dimethylbutane and subsequent oxidation of formed 1,3-dihydroxyimidazolidine **63** (Scheme 16).[64] In accordance with the X-ray diffraction data, radical **61** in the solid phase is characterized by the presence of intermolecular O...O contacts linking molecules into homogeneous magnetic chains.[65] At 3.4 K, nitronyl nitroxide **61** undergoes an unusual structural phase transition, which results in the transformation of homogenous antiferromagnetic chains into alternating chains. As a result, the magnetic behavior of radical **61** at low temperatures (0.5—2 K) is well described by the Heisenberg model of antiferromagnetic alternating chain with $2J/k_B$ = —5.6 K and $\alpha = 0.4$.[66,67] Note that such a structural phase transition was not revealed for the non-fluorinated analog of this radical.

Interesting structural-magnetic correlations are inherent in another polyfluorinated paramagnet, in tetrafluorobenzimidazolyl-substituted nitronyl nitroxide **64**.[68] In the solid phase, molecules of this radical form ribbons due to NH...N and NH...O hydrogen bond linkages. The exchange interactions of the ferromagnetic type take place within these ribbons (J/k_B = 22 K in the framework of the Heisenberg model of ferromagnetic chain).[69] A magnetic phase transition into a magnetically ordered state occurs at 0.7 K in nitronyl nitroxide **64**.[70]

Scheme 16



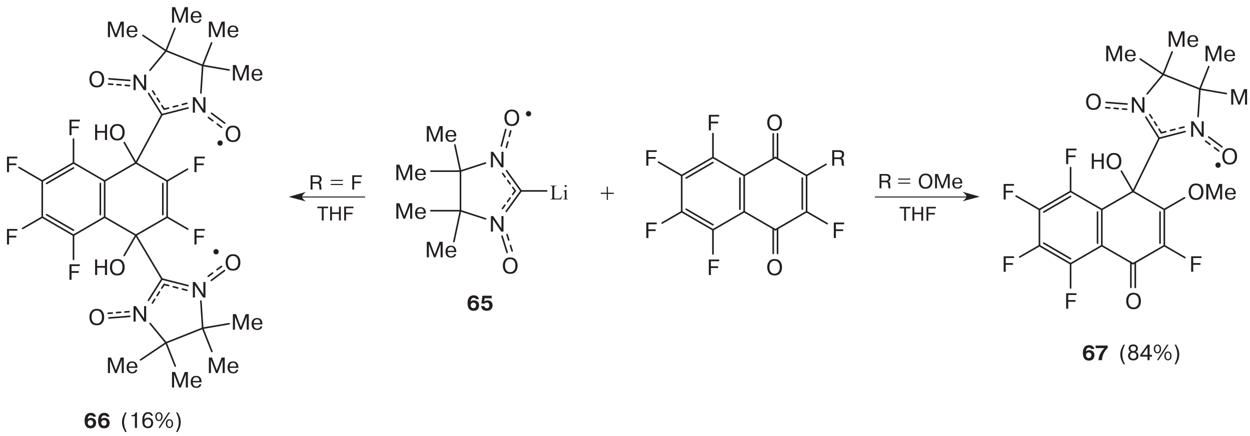


64

Additional possibilities in the synthesis of polyfluorinated paramagnets are opened by reactions proceeding with the retention of the paramagnetic moiety. For instance, adducts linked due to the carbonyl groups were obtained in the reaction of lithium derivative **65** with polyfluoro-1,4-naphthoquinones. It is noteworthy that the reaction of 2-methoxypentafluoro-1,4-naphthoquinones proceeds regioselectively with the formation of only 2-(3,5,6,7,8-pentafluoro-1-hydroxy-2-methoxy-4-oxo-1,4-dihydronaphthalen-1-yl)-4,4,5,5-teramethyl-4,5-dihydro-1*H*-imidazole 3-oxide 1-oxyl **66** (Scheme 17). A biradical adduct, 2,3,5,6,7,8-hexafluoro-1,4-bis(4,4,5,5-tetramethyl-3-oxido-1-oxylo-4,5-dihydro-1*H*-imidazol-2-yl)-1,4-dihydronaphthalene-1,4-diol **67** was prepared by the reaction of hexafluoro-1,4-naphthoquinone with an excess of nitronyl nitroxide **65**. Molecular and crystal structures of this compound were solved by the X-ray diffraction study.[71] It is interesting to note that according to ESR data, biradical **67** and monoradical **66** are stable in water, however in toluene solutions, they undergo rather fast deoxygenation to iminonitroxide derivatives.

In contrast to polyfluorinated quinones, in the case of polyfluoroarenes, the substitution of the fluorine atom resulting in the formation of the corresponding nitronyl nitroxide derivatives occurs under the action of radical **65**.

Scheme 17



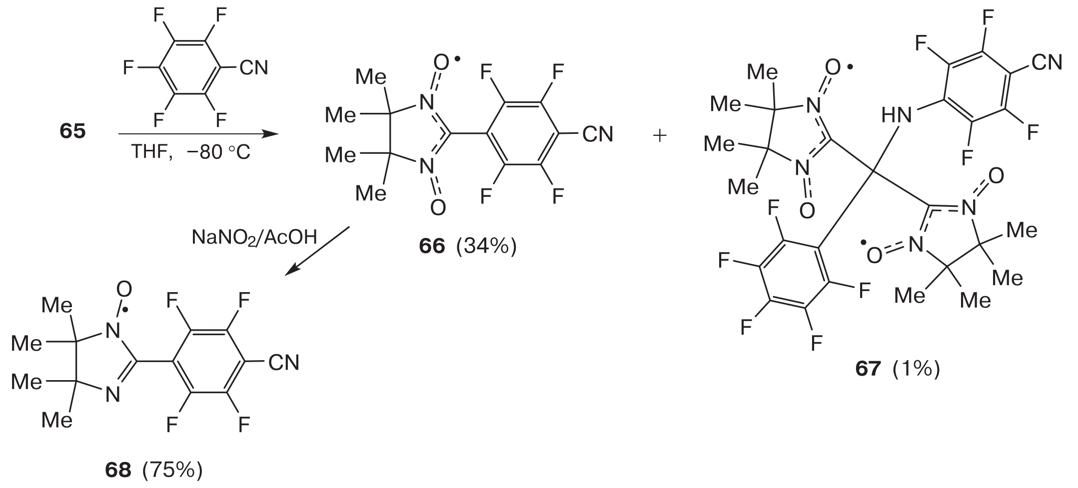
In particular, the reaction of compound **65** with perfluorobenzonitrile leads to 2-cyanotetrafluorophenyl-substituted radical **66** and a minor product, which is Csp^3-bound biradical **67** (Scheme 18). Nitronyl nitroxide **66** prepared using the $NaNO_2$/AcOH system easily undergoes deoxygenation, forming corresponding iminonitroxide radical **68** in a yield of up to 75%.[72]

Besides perfluorobenzonitrile, a wide range of polyfluorinated substrates are able to react with lithiated radical **65**, forming corresponding polyfluoroaryl-substituted nitronyl nitroxides **69**—**72**.[73,74] It is noticeable that the regioselective substitution of the fluorine atom in the *para*-position relative to the functional group of the polyfluorinated substrate takes place in all cases (Scheme 19).

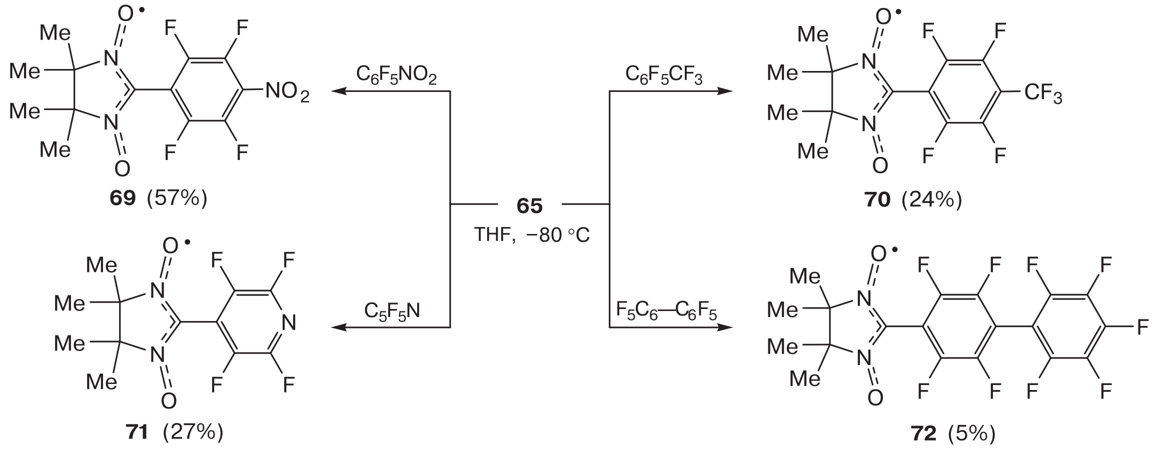
It is clear that the yields of the substitution products decrease with decreasing the substrate reactivity. The problem of low yields was not solved even when an alternative approach was used, which consisted in carrying out the cross-coupling of fluorinated iodides with an organogold derivative of nitronyl nitroxide.[75] The relevant examples are the interaction of iodide **73** with organogold derivative **74**, which produced target product **75** in a yield of only 4% (Scheme 20),[76] and an attempt to carry out a similar reaction with perfluoroiodobenzene, which was unsuccessful.[75,77,78]

Substituted benzimidazole 3-oxide 1-oxyls represent another family of nitroxide radicals. Their flat structures in combination with an efficient spin density delocalization promotes the appearance in the solid phase of rather strong intermolecular exchange interactions of both antiferromagnetic and ferromagnetic types. The highest energy of antiferromagnetic exchange, $J/k_B = 66$ K, was detected for one of crystalline modifications of 3-oxidobenzimidazole 1-oxyl radical containing the 2,6-difluorophenyl substituent **76a**.[79] On going to pentafluorophenyl derivative

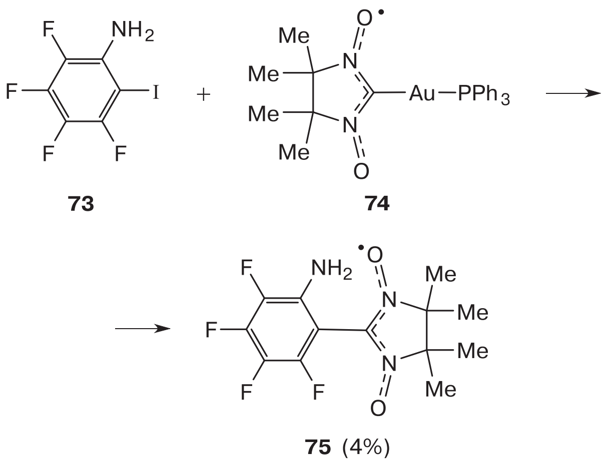
Scheme 18



Scheme 19

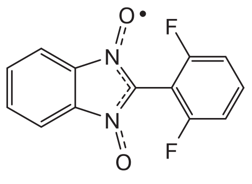


Scheme 20

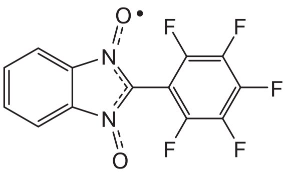


Reagents and conditions: $Pd(PPh)_3$, THF, Δ.

76b, the type of the exchange interactions is changed to antiferromagnetic (θ = −37°).



76a



76b

Radical cations and anions

Although a small, but very specific group of polyfluorinated radical cations and anions deserves a separate consideration. Paradoxically, the introduction of a large number of fluorine atoms into the aromatic substrate protects the radical cation formed in a one-electron oxidation from transformations both during production and during subsequent manipulations. For instance, the preparation of salts of the $C_6H_6^{\bullet+}$ radical cation remains unresolved problem, whereas salts of $C_6F_6^{\bullet+}$ were not only isolated, but also structurally characterized.[80] An undoubted achievement are the preparation of the salt $C_6F_6^{\bullet+}Os_2F_{11}^-$ in the crystalline form by the reaction of C_6F_6 with OsF_6 in HF in the presence of SbF_5 and synthesis of the salt $C_6F_6^{\bullet+}Sb_2F_{11}^-$ by the reaction of $O_2^+Sb_2F_{11}^-$ with C_6F_6 and the subsequent recrystallization of both salts from cold HF. According to the X-ray diffraction data, the radical cation $C_6F_6^{\bullet+}$ in these salts exists in two forms, which are the quinoid and bisallyl forms (Fig. 5).[80] It is noticeable that the lengths of all C—F bonds in these forms are shorter than in the starting perfluorobenzene.

Salts containing polyfluorinated radical anions such as radical anion of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF4)[81] are well known. In particular, stable complexes of 1 : 1 composition obtained by

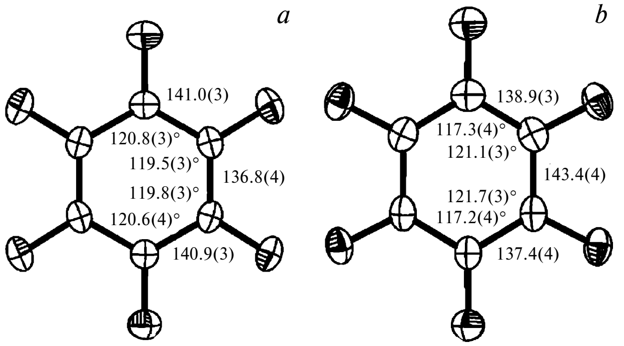
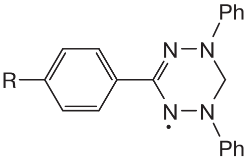


Fig. 5. Two types of molecular structures of the $C_6F_6^{\bullet+}$ radical cation in salt $C_6F_6^{\bullet+}Sb_2F_{11}^-$: a quinoid structure (*a*) and bisallyl structure (*b*); both are of D_{2h} symmetry within experimental error.[80] Image is reprinted with permission from John Wiley and Sons.

the interaction of equimolar amounts of verdazyl radicals **77a—c** and TCNQF4 were isolated in the pure form, and their molecular and crystal structures were established by X-ray diffraction.[82] Complexes {**77**·TCNQF4} are characterized by low magnetic susceptibility, which is attributed by the authors to strong antiferromagnetic spin interaction within stacks formed by TCNQF4$^{\bullet -}$ radical anions.



77a—c

R = MeO (**a**), Me (**b**), Cl (**c**)

Conclusions

Thus, the material presented in the review testifies to the ability of the fluorine atom to dramatically affect the chemical and physicochemical properties of organic radicals. The introduction of fluorine atoms into those moieties of paramagnets, in which an increased spin density is concentrated, significantly increases stability of these species. In particular, this makes it possible to replace bulky alkyl groups in organic radicals by significantly smaller CF_3 groups or even a fluorine atom, while maintaining or even increasing the stability of paramagnetic substrates. This effect can be useful in a wide variety of research areas.

In the field of molecular magnetics,[83,84] the use of polyfluorinated radicals opens the way to creation of stable carriers of unpaired electron density with a planar structure, which are necessary for the formation of solid phases with high energies of intermolecular exchange interactions. In addition, the use of polyfluorinated substrates and building blocks will undoubtedly lead to revolutionary changes in the design of stable high-spin organic systems and polymer magnets, as well as magnetic thermo- and photoinduced switches.

For the development of the field of magnetically active graphene nanoribbons[85] and quantum dots, the development of methods for assembling their derivatives with polyfluorinated edges will undoubtedly be of great importance. The study of such derivatives makes it possible to reveal the specific effect of fluorine atoms on the edge states of graphene nanostructures, their electronic structure, electrical conductivity, as well as interaction with the substrate and guest molecules.

The introduction of a fluorine atom into a paramagnetic molecule changes the solubility of the compound, increases its volatility, significantly affects the basicity and acidity of functional groups, as well as the tendency to form hydrogen bonds.[8,86] These properties, individually and collectively, can be useful in the production of thin films by physical vapor deposition and in the creation of two-dimensional heterospin structures or magnetically active frame materials. In addition, the transition to polyfluorinated derivatives of organic paramagnets significantly shifts the redox potentials relative to those of non-fluorinated analogs. Taking into account the increased stability of their reduced forms, such paramagnets can find application as effective cathode materials in electric batteries.

The world of polyfluorinated radicals is still poorly understood; in its unexplored corners, it still harbors many mysteries. We hope that this review will awaken the interest of representatives of different schools working in the field of organic radical synthesis in the preparation of polyfluorinated derivatives and their use in the design of new materials.

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This paper does not contain descriptions of studies on animals or humans.

The authors declare no competing interests.

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