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Synthesis, structures and reactivity of polyhalo[60]fullerenes †

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Abstract. Methods for the synthesis of polyfluoro(chloro, bromo) derivatives of C_{60} fullerene and their structures are described. The reactivity of these compounds is demonstrated considering redox reactions, nucleophilic substitution, radical addition, cycloaddition and electrophilic arylation. The bibliography includes 185 references.

I. Introduction

Polyhalofullerenes are the best studied fullerene polyadducts, and halogenation reactions were among the first reactions of fullerenes performed in the early 1990s.[1–8] These compounds have attracted interest primarily because they hold promise for the design of new materials, which would be expected to exhibit unique properties. In particular, an idea of the synthesis of chemically inert perfluorinated fullerene $C_{60}F_{60}$ similar in properties to Teflon (the so-called 'Teflon Buckyballs') was very popular at one time.[1,9] However, later it has been found[10,11] that polyfluorofullerenes are not as chemically stable as polyfluoroalkanes, and it is impossible to prepare exohedral $C_{60}F_{60}$. Nevertheless, polyhalofullerenes have continued to attract attention, and investigations into halogenation of fullerenes for more than one decade led to the development of efficient methods for the synthesis of polyfluoro-, polychloro- and polybromofullerenes. The structures of individual polyhalofullerenes were established.

Compounds containing an aromatic annulene fragment bearing conjugated C=C bonds only in *trans* configuration (all-*trans* annulenes or trannulenes) were first synthesised based on polyfluorofullerenes.[12] It has been repeatedly suggested[12–15] that polyhalofullerenes hold promise for the synthesis of donor–acceptor dyads with improved electron-withdrawing properties and for the design of molecular devices. This has stimulated studies of the redox,[16,17] electrochemical[18–21] and photophysical[22–24] behaviour of polyhalofullerenes and their derivatives. The design of new polyhalofullerene-based materials requires that both physical and chemical properties of these compounds were known. The aim of the present review is to systematise and analyse methods for the synthesis, structural features, chemical properties and characteristics of chemical transformations of polyhalo derivatives of the C_{60} ([60]fullerene) molecule.

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II. Synthesis, structures and physical properties of polyhalo[60]fullerenes

Being polyunsaturated compounds, fullerenes are prone to be involved in radical and nucleophilic addition and cycloaddition reactions, but they very rarely react with strong electrophilic reagents.[25,26] Polyhalofullerenes are usually synthesised by the reactions of fullerene with a wide range of halogenating agents. Preparative procedures for the synthesis of various polyfluoro-, polychloro- and polybromofullerenes are available. Polyiodofullerenes are presently unknown, although the existence of molecular crystals with the composition $C_{60} \cdot 2\,I_2$ was proved.[27,28] In spite of the fact that the number of possible geometric isomers of polyhalofullerenes is very large, in practice only a few of them were prepared by halogenation of fullerene. The formation of particular isomers is generally controlled by thermodynamic factors and only in rare cases by kinetic factors.

The present review deals only with polyhalo derivatives of C_{60} fullerene. Polyhalogenated C_{70} fullerenes and polyhalogenated higher fullerenes have been studied in much less detail. However, the available data suggest that their chemical properties are analogous to those of polyhalo[60]fullerenes.

1. Synthesis and structures of polyfluoro[60]fullerenes

Polyfluorofullerenes are most numerous of all isolated and characterised polyhalofullerenes (Fig. 1).[29–36] For example, the structures of $C_{60}F_{18}$ with the symmetry group C_{3v},[37–39] three isomers of $C_{60}F_{36}$ (with *T*, C_3 and C_1 symmetry)[40–42] and D_3 and S_6 isomers of $C_{60}F_{48}$ (Refs 43 and 44) were studied. Polyfluorofullerenes $C_{60}F_{2n}$ ($n = 1-4$),[45,46] C_s-$C_{60}F_{16}$

† Dedicated to the memory of Roger Taylor.

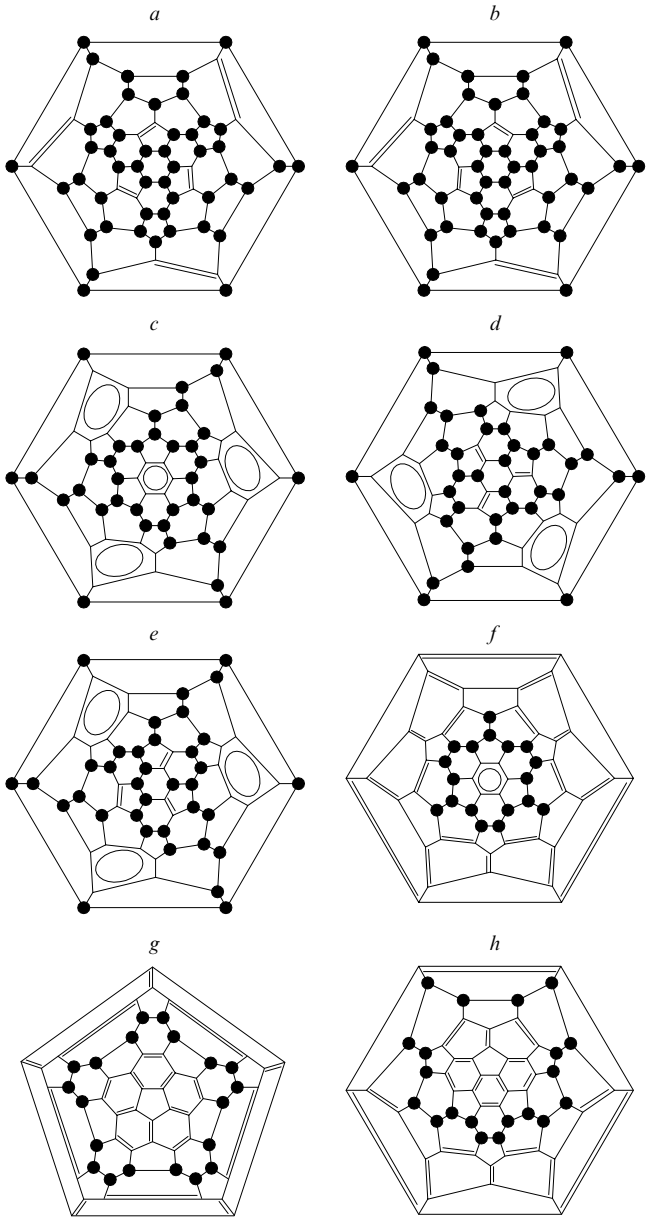


Figure 1. Schlegel diagrams of polyfluorofullerenes $C_{60}F_{48}$ [D_3 (*a*) and S_6 isomers (*b*)], $C_{60}F_{36}$ [T (*c*), C_3 (*d*) and C_1 isomers (*e*)], C_{3v}-$C_{60}F_{18}$ (*f*) and two projections of D_{5d}-$C_{60}F_{20}$ (*g*, *h*). Hereinafter, the solid circles indicate the binding sites of halogen atoms.

(see ‡),[47] D_{5d}-$C_{60}F_{20}$,[48,49] T_h-$C_{60}F_{24}$ (Ref. 50) and $C_{60}F_{38}$ (Ref. 51) were isolated and partially characterised.

The methods for the synthesis of polyfluoro derivatives of fullerenes can be divided into three groups: (1) fluorination of fullerene by molecular fluorine either directly or in metal fluoride matrices, (2) fluorination of fullerene by fluorides of transition metals in high oxidation states and (3) fluorination of polychloro- and polybromofullerenes.

Higher polyfluorofullerenes, in particular, $C_{60}F_{48}$, can easily be synthesised by the reaction of fullerene with molecular fluorine (see Section II.1.a).[43] However, attempts to use this procedure for the synthesis of less fluorinated fullerenes led to the formation of complex mixtures of products. This is due to the fact that direct fluorination occurs by a radical mechanism. The range of synthetically accessible polyfluorofullerenes was substantially extended due to the use of high-oxidation-state metal fluorides as fluorinating agents. In this case, the reaction apparently proceeds by a mechanism of single-electron oxidation of fullerene (and its partial fluorination products) by metal cations followed by the addition of the fluoride ion to the intermediate radical cation. This assumption is consistent with the observed dependence of the degree of fluorination of fullerene on the metal oxidation potential.[35,52] The selective formation of polyfluorofullerenes $C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ was also observed in the reactions of fullerene with molecular fluorine in MnF_2, CoF_2 or NiF_2 matrices.[53–55] The advantage of this approach is the possibility to synthesise polyfluorofullerenes in a flow reactor, which is of importance for the development of industrial apparatus. Fluorination of polyhalofullerenes under mild conditions affords thermodynamically unstable but kinetically stable T_h-$C_{60}F_{24}$ (see Sections II.1.d and V).[50]

a. Polyfluorofullerene $C_{60}F_{48}$

Fluorination of [60]fullerene with molecular fluorine was historically one of the first studied functionalisation reactions of C_{60}. Early experiments on fluorination of this fullerene often gave complex mixtures of fluoro derivatives of [60]fullerene, the composition of the products varied depending on the reaction temperature and time.[1,11,56,57] In 1994, Tuinman and Gakh[43] developed a preparative procedure for the selective synthesis of $C_{60}F_{48}$ involving two fluorination steps.

$$C_{60} \xrightarrow[250\ ^\circ C,\ 20\ h]{NaF,\ F_2} C_{60}F_{46} + C_{60}F_{48} \xrightarrow[275\ ^\circ C,\ 30\ h]{NaF,\ F_2} \underset{(60\%)}{C_{60}F_{48}}$$

The reaction was performed in the presence of NaF to decrease the exothermicity of fluorination, which made it possible to decrease the degree of 'combustion' of fullerene in fluorine atmosphere and increase the yield of the target product. Initially, C_{60} and NaF were heated in a stream of fluorine at 250 °C for 20 h. The resulting mixture of isomers of higher polyfluorofullerenes $C_{60}F_{46}$ and $C_{60}F_{48}$ was extracted with $CFCl_3$ and subjected again to fluorination but at higher temperature (275 °C, 30 h). Polyfluorofullerene $C_{60}F_{48}$ was obtained in yields up to 60%. All attempts to perform further fluorination of $C_{60}F_{48}$ at high temperatures failed. Decomposition of the carbon skeleton of the molecule giving rise to a complex mixture of polyfluorocarbons C_nF_m ($n = 16-30$, $m = 30-50$) occurred instead of the addition of the fluorine atom.[58] Based on this fact, it was concluded that the maximum possible degree of fullerene fluorination is achieved in polyfluorofullerene $C_{60}F_{48}$. Improved procedures for the synthesis of $C_{60}F_{48}$ were described.[55,59]

One- and two-dimensional ^{19}F NMR correlation spectroscopy demonstrated that polyfluorofullerene $C_{60}F_{48}$ thus synthesised is a mixture of isomers with the point groups D_3 and S_6 (see Fig. 1 *a*, *b*).[43] The structures of the D_3 and S_6 isomers were conclusively established by X-ray diffraction.[44] These molecules are characterised by the presence of six shortened double bonds (1.301 Å), which are located in six five-membered rings of the fullerene cage and are completely shielded by the surrounding fluorine atoms. The F···F distance between the opposite fluorine atoms at the double bond is 4.2 Å. Since the van der Waals diameter of the fluorine atom is 2.7 Å, the open space around the C=C bond is at most 1.5 Å. Such a substantial steric shielding of the double bond is one of the factors that preclude further fluorination of $C_{60}F_{48}$ without destruction of the fullerene cage.[11]

‡ The point symmetry group of the compound is given in italics as a prefix to the formula.

b. Polyfluorofullerene $C_{60}F_{36}$

Heating of C_{60} with MnF_3,[60] CeF_4 [35] or $MPbF_6$ (M = Mg, Ca, Sr or Ba) [61] at 380 °C under dynamic vacuum affords a mixture of *T*, C_3 and C_1 isomers of $C_{60}F_{36}$ in a yield of >70% (see Fig. 1 *c*–*e*).

$$C_{60} \xrightarrow[380\ ^\circ C,\ <10\ Pa]{MnF_3} \underset{(70\%-80\%)}{C_{60}F_{36}}$$

The structures of the isomers have been initially suggested based on ^{19}F NMR spectroscopic data.[40,62] More recently, the structures of *T*- and C_3-$C_{60}F_{36}$ were established by X-ray diffraction.[41,42] Each isomer contains isolated cyclohexatriene fragments. An analysis of the C–C bond lengths in these rings demonstrates that all these distances are averaged and are similar to the typical bond lengths in aromatic compounds (for example, 1.373 Å for *T*-$C_{60}F_{36}$ and 1.368 Å for C_6F_6). Taking into account efficient π-electron density delocalisation and small deviations from planarity (about 0.01 Å) of the cyclohexatriene fragments, these rings can be considered as benzenoid. In the most symmetrical isomer *T*-$C_{60}F_{36}$, the fluorine atoms are arranged so that four isolated benzenoid fragments are retained. The molecules of the less symmetrical isomers (C_3-$C_{60}F_{36}$ and C_1-$C_{60}F_{36}$) contain three such fragments, whereas the remaining three double bonds are localised in the five-membered rings. It should be noted that all three isomers of $C_{60}F_{36}$ are structurally related to each other and can easily be derived from each other as a result of the 1,3-shift of one fluorine atom (interconversions of the C_3 and C_1 isomers) [63] or three fluorine atoms (interconversions of the *T* and C_3 isomers) within one or three five-membered rings, respectively. These rearrangements are also confirmed by the fact that fluorination of isomers of $C_{60}F_{36}$ by molecular fluorine affords higher polyfluorofullerenes D_3- and S_6-$C_{60}F_{48}$, which cannot occur without migration of the fluorine atom over the surface of the fullerene sphere.[64] It should be noted that analogous mechanisms were proposed for the explanation of interconversions of polyhydrofullerenes $C_{60}H_{36}$ isostructural to isomers of $C_{60}F_{36}$.[65]

c. Polyfluorofullerenes $C_{60}F_{18}$ and $C_{60}F_{20}$

Polyfluorofullerene $C_{60}F_{18}$ can be prepared in yields of up to 60% by heating (465 °C) a mixture of C_{60} and K_2PtF_6 under dynamic vacuum.[37,39] The compounds Cs_3PbF_7,[61] Rb_2PtF_6 and Cs_2PtF_6 (Ref. 66) can be recommended as alternative fluorinating agents for the synthesis of $C_{60}F_{18}$. The use of $KMnF_4$,[46] K_3CoF_6,[67] Li_4CeF_8 or the $KF-MnF_3$ system [49,67] leads to an increase in the percentage of low-fluorinated by-products or a decrease in the degree of conversion of C_{60}. Hence, these reactions are less attractive for the synthesis of $C_{60}F_{18}$.

$$C_{60} \xrightarrow[465\ ^\circ C,\ <10\ Pa]{K_2PtF_6} \underset{(40\%-60\%)}{C_{60}F_{18}}$$

The only isomer of polyfluorofullerene $C_{60}F_{18}$ with symmetry C_{3v} (see Fig. 1,*f* and 2) was isolated. An important difference between this compound and the above-considered polyfluorofullerenes is that all fluorine atoms in this compound are located in one half of the fullerene cage, whereas another hemisphere remains unfunctionalised. As a result, the molecule assumes a large dipole moment estimated to be 8–15 D.[38,68] According to the X-ray diffraction data,[38,39] the fullerene hemisphere containing fluorine atoms is substantially flattened (see Fig. 2 *b*). This hemisphere includes the cyclohexatriene pole, in which the bond lengths are equalised and are typical of aromatic systems (1.372 Å). Therefore, like isomers of $C_{60}F_{36}$, polyfluorofullerene $C_{60}F_{18}$ contains a

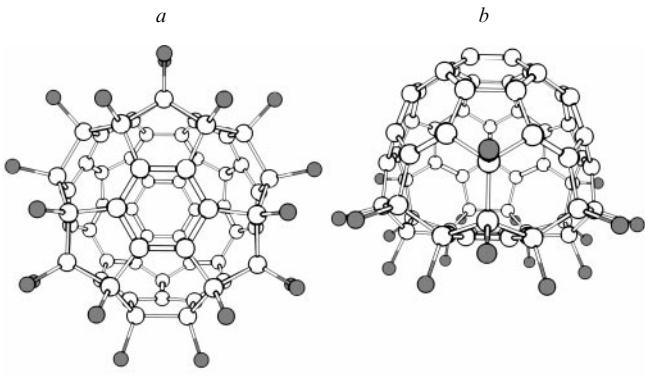


Figure 2. Three-dimensional structure of C_{3v}-$C_{60}F_{18}$: top view (*a*) and side view (*b*).

benzenoid fragment. The bond lengths and the shape of the pole of the fullerene hemisphere free of fluorine atoms are very similar to the corresponding parameters of non-modified fullerene. The $C_{60}F_{18}$ molecule contains four types of fluorine atoms, one of which is sterically most accessible, and the distance from such fluorine atoms to the carbon atoms bearing them (1.396 Å) is larger than the lengths of the other fluorine–carbon bonds (1.361–1.385 Å). Evidently, this longest bond is the weakest one, *i.e.*, this type of fluorine atoms is most reactive in the $C_{60}F_{18}$ molecule. The higher reactivity of this type of atoms compared to other fluorine atoms is also attributed to the fact that the involvement of the latter in chemical transformations results in a deviation from planarity and destabilisation of the aromatic π system of the benzene-like fragment.

Polyfluorofullerene $C_{60}F_{20}$ was isolated from fluorination products of C_{60} with complex manganese and cerium fluorides in 5%–8% yields.[48,49,66,69] (It should be noted that this compound was found in trace amounts, if at all, among the reactions products of fullerene with K_2PtF_6 and Cs_2PtF_6, but it was detected in the analogous reaction with Rb_2PtF_6). A ^{19}F NMR spectroscopic study demonstrated that all 20 fluorine atoms in the $C_{60}F_{20}$ molecule are equivalent. This is consistent with the structure shown in Figs 1 *g*,*h* and 3.[48] Fullerene D_{5d}-$C_{60}F_{20}$ contains the equatorial belt of sp^3-hybridised carbon atoms $(CF)_{20}$, which divides the fullerene cage into two equivalent dehydrocorannulene fragments. Although the alternative structure of $C_{60}F_{20}$ described in Ref. 48 formally satisfies the condition of equivalence of 20 fluorine atoms, conclusive evidence in favour of the initially proposed structure containing the equatorial $(CF)_{20}$ belt was

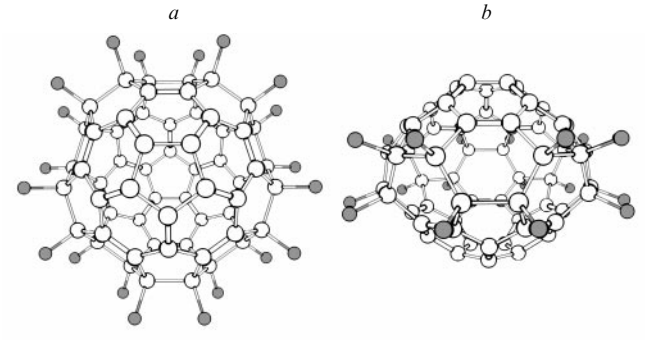


Figure 3. Three-dimensional structure of D_{5d}-$C_{60}F_{20}$: top view (*a*) and side view (*b*).

given in a more recent study.[49] Evidently, polyfluorofullerene D_{5d}-$C_{60}F_{20}$ cannot be generated from C_{3v}-$C_{60}F_{18}$ without substantial rearrangements of the fluorine atoms. This suggests that the pathways giving rise to these two compounds include different intermediate fluorination products.[48]

Due to the presence of two dehydrocorannulene fragments, which are located at the poles of the $C_{60}F_{20}$ molecule and can independently bind donor or acceptor groups, these derivatives are promising starting compounds for the formation of donor – acceptor complexes and polymers.[70]

d. Polyfluorofullerene T_h-$C_{60}F_{24}$

A possible method for the synthesis of polyhalofullerenes is based on the replacement of one halogen atom by another halogen. In early studies,[71, 72] it has been demonstrated that chlorine (bromine) atoms in polychloro(bromo)fullerenes can be replaced by fluorine atoms in reactions with molecular fluorine or XeF_2. However, the authors failed to isolate individual compounds. By contrast, bromination of lower polychloro derivatives $C_{60}Cl_n$ (n = 6, 8, 12 or 14) by liquid bromine affords T_h-$C_{60}Br_{24}$,[73] the chlorination of which by antimony pentachloride at high temperature gives rise to T_h-$C_{60}Cl_{24}$.[74]

Fluorination of T_h-$C_{60}Br_{24}$ with xenon difluoride in anhydrous HF at room temperature is the only known example of the successful selective formation of polyfluorofullerene by the substitution reaction.[50]

$$T_h\text{-}C_{60}Br_{24} \xrightarrow[-BrF_3]{XeF_2,\ HF,\ 25\ ^\circ C} T_h\text{-}C_{60}F_{24}$$

Under the above-mentioned conditions, bromine atoms in polyhalofullerene are replaced by fluorine atoms. According to the ^{19}F NMR spectroscopic data, this reaction produces the highly symmetrical T_h-$C_{60}F_{24}$ compound isostructural to the starting $C_{60}Br_{24}$ compound (Fig. 4). According to quantum chemical calculations,[50] this polyfluorofullerene is metastable and, consequently, can undergo isomerisation or disproportionation to form more stable structures. However, this process is kinetically hindered; at least, it was not detected at room temperature.

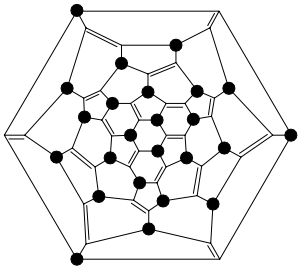


Figure 4. The Schlegel diagram of T_h-$C_{60}F_{24}$.

e. Other polyfluoro derivatives of [60]fullerene

In addition to $C_{60}F_{18}$ and $C_{60}F_{20}$, fluorination of C_{60} fullerene by complex metal fluorides (K_2PtF_6, $KMnF_4$, Cs_2PbF_6, Li_4CeF_8, *etc.*) gives other lower polyfluorofullerenes [$C_{60}F_{2n}$ (n = 1 – 3),[45, 46] two isomers of $C_{60}F_8$,[45, 46, 75] $C_{60}F_{12}$, $C_{60}F_{14}$,[49] $C_{60}F_{16}$ (Ref. 47)], oxopolyfluorofullerenes [$C_{60}F_2O$,[45] $C_{60}F_{2n}O$ (n = 2 – 4),[76] $C_{60}F_{16}O$,[77] $C_{60}F_{18}O$,[78 – 80] $C_{60}F_{18}O_2$ (Ref. 81)] and mixed perfluoroalkylfluoro derivatives [$C_{60}F_7CF_3$,[45, 46] $C_{60}F_{17}CF_3$, $C_{60}F_{17}C_2F_5$ (Ref. 82)]. Impurities of oxopolyfluorofullerenes and perfluoroalkylpolyfluorofullerenes are always present in certain amounts among fluorination products of fullerenes. These compounds are formed because of imperfections in vacuum apparatus used for their preparation, due to the presence of traces of oxygen in crystalline fullerene, reagents or on the surface of the reactor and as a result of thermal destruction of polyfluorofullerenes (for more details, see Section III.4.b). Although the percentage of these compounds is low (the yields are usually lower than 5%), they were isolated by chromatography and partially characterised. The structures of most of these compounds were proposed based on ^{19}F NMR spectroscopic data. The structures of some derivatives were confirmed by the results of other spectroscopic methods (for example, by IR and Raman spectroscopy) interpreted with the use of quantum chemical calculations. The structures of some compounds were established by X-ray diffraction. For example, it was demonstrated that the C_s and C_1 isomers of fullerene $C_{60}F_{17}CF_3$ are isostructural to $C_{60}F_{18}$. These molecules contain the CF_3 group instead of one of three sterically most accessible fluorine atoms.[82] An X-ray diffraction study showed that oxohomofullerene C_s-$C_{60}F_{18}O$ dominates among oxygen-containing products.[80] In this compound, the oxygen atom is introduced into the longest [5,6] C(F) – C(F) bond § of the $C_{60}F_{18}$ molecule, which is accompanied by cleavage of this bond.

2. Solubility of polyfluoro[60]fullerenes

Only a few studies were concerned with the determination of solubility of polyfluorofullerenes and investigation of their stability in solution.[83 – 85] It should be noted that the lack of information on stability of polyfluorofullerenes in different solvents led to erroneous interpretation of the experimental data in some early studies in favour of the formation of $C_{60}F_{60}$.[1, 86, 87]

Stability of polyfluorofullerenes in solution depends on the chemical properties of these compounds. As will be demonstrated below, polyfluorofullerenes are prone to nucleophilic substitution reactions, in particular, to hydrolysis and can act as oxidising agents. Hence, to prevent non-destructive dissolution of polyfluorofullerenes, it is necessary to avoid the use of nucleophilic or protic solvents (for example, alcohols, amines, pyridine, *etc.*), solvents that are difficult to purify from traces of water or alcohols (for example, acetone and chloroform) and solvents that are readily involved in redox reactions (ethers, particularly, for higher polyfluorofullerenes).

Among the solvents recommended for use in experiments with polyfluorofullerenes, hydrocarbons (alkanes and arenes) and their halogeno derivatives should be mentioned. The solubilities of C_{60} and polyfluorofullerenes $C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ in some organic solvents are given in Table 1.

3. Synthesis and structures of polychloro[60]fullerenes

Unlike polyfluoro[60]fullerenes, polychloro derivatives of fullerene C_{60} have been less studied. For example, only $C_{60}Cl_6$ has been synthesised (by the reaction of fullerene with iodine monochloride) so far and reliably characterised.[89 – 91]

$$C_{60} \xrightarrow[-I_2]{ICl,\ 25\ ^\circ C} C_{60}Cl_6 \quad (70\%)$$

Fullerene C_{60} is known to react only with highly reactive electrophiles; however, this compound is readily involved in radical addition reactions. Hence, it is reasonable to suggest

§ The carbon – carbon bond between the five- and six-membered rings is enclosed in brackets [5,6].

Table 1. Solubility of C_{60} and polyfluoro[60]fullerenes in organic solvents at 25 °C (in mg ml^{-1}).

Solvent	C_{60}	$C_{60}F_{18}$	$C_{60}F_{36}$	$C_{60}F_{48}$
Aromatic hydrocarbons				
Benzene	1.5 [a]	0.48 [b]	–	1.5
Toluene	2.9 [a]	0.52 [b]	–	1.4
o-Xylene	8.7 [a]	0.75 [b]	–	4.8
m-Xylene	1.4 [a]	1.23 [b]	–	11.1
p-Xylene	5.9 [a]	0.96 [b]	–	9.1
Mesitylene	2.4 [a]	–	–	0.31
n-Alkanes				
n-Pentane	–	–	0.36	19.4 [c]
n-Hexane	–	–	0.50	11.6 [c]
n-Heptane	–	–	0.60	10.8 [c]
n-Octane	–	–	0.44	11.6 [c]
n-Nonane	–	–	0.89	9.9 [c]
n-Decane	–	–	0.61	9.0 [c]
n-Undecane	–	–	–	6.5 [c]
Tolyl halides				
o-MeC_6H_4Cl	–	5.6	2.1	14.8
m-MeC_6H_4Cl	–	6.4	3.3	18.2
p-MeC_6H_4Cl	–	8.2	2.1	8.2
o-MeC_6H_4Br	–	5.6	1.6	8.2
m-MeC_6H_4Br	–	6.4	2.2	6.4
p-MeC_6H_4Br	–	4.2	1.8	6.4
p-MeC_6H_4F	–	4.2	3.4	11.4

[a] Ref. 88, [b] Ref. 83, [c] Ref. 85. Other values were taken from Ref. 84.

that chlorination of C_{60} proceeds by a radical mechanism.[89] This assumption is consistent with the influence of solvents on the reaction rate. It was found that the reaction proceeds more rapidly in benzene or chlorobenzene than in toluene. Evidently, toluene captures part of the radicals, resulting in a decrease in the rate of chlorination of fullerene. Since ICl is a weak Lewis acid, chlorination of C_{60} in benzene or toluene gives aryl-containing fullerenes as by-products.[91,92] Apparently, this reaction proceeds analogously to arylation of fullerenes and polychlorofullerenes in the presence of aluminium chloride [93] (see Section IV.2). The yields of aryl-containing fullerenes that are formed as by-products can be substantially decreased using monochloro- and dichlorobenzenes, which are less reactive in Friedel – Crafts reactions, and by removing unconsumed ICl from the reaction mixture as quickly as possible.[91,94]

The structure of polychlorofullerene $C_{60}Cl_6$ (Fig. 5 *a*) was established by ^{13}C NMR spectroscopy [89] and was then confirmed by X-ray diffraction.[95] In the molecule, five chlorine atoms surround one of the pentagonal faces of the fullerene, whereas the sixth chlorine atom is directly attached to this five-membered ring to form a 1,2 contact with the adjacent chlorine atom (this structure is generally described as a truncated pentagonal pyramid). This addition pattern of addends to the fullerene cage was demonstrated [96] to be energetically most favourable in the presence of bulky substituents, including chlorine atoms. To the contrary, the formation of *trans*-chains of 1,2 contacts (the so-called *S* addition pattern) is favourable for small substituents, such as H and F atoms. This difference is evidently associated with steric strain due to interactions between the adjacent bulky groups. The presence of one 1,2 contact between chlorine atoms in the $C_{60}Cl_6$ molecule leads to a slight elongation of the corresponding C – Cl bond and, as a consequence, to its weakening. At the same time, most reactions with $C_{60}Cl_6$ consist of the replacement of all five chlorine atoms surrounding the five-membered ring with retention of the chlorine atom in the ring. This is due to the fact that elimination of this atom as the chloride anion should give rise to a fragment of the cyclopentadienyl cation with pronounced antiaromatic properties. By contrast, elimination of other chlorine atoms affords stable allyl-type cations.

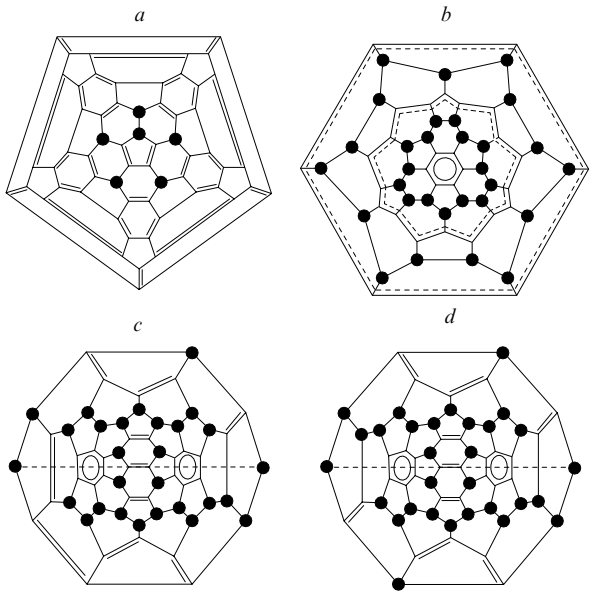


Figure 5. The Schlegel diagrams of C_s-$C_{60}Cl_6$ (*a*), D_{3d}-$C_{60}Cl_{30}$ (*b*), C_1-$C_{60}Cl_{28}$ (*c*) and C_2-$C_{60}Cl_{30}$ (*d*).

Syntheses of a series of polychloro derivatives of fullerene C_{60} with a larger number of chlorine atoms [for example, $C_{60}Cl_8$, $C_{60}Cl_{10}$,[94] $C_{60}Cl_{12}$,[4,94,97] $C_{60}Cl_{14}$,[94,97] $C_{60}Cl_{24}$,[2] $C_{60}Cl_{26}$ (Ref. 94)] were documented. However, only indirect evidence for the formation of these molecules was presented, and these data can be interpreted ambiguously. Higher polychlorofullerenes, *viz.*, T_h-$C_{60}Cl_{24}$, C_1-$C_{60}Cl_{28}$, C_2-$C_{60}Cl_{30}$ and D_{3d}-$C_{60}Cl_{30}$ (see Fig. 5), have been synthesised and structurally characterised only very recently.[74] These compounds can be prepared by heating fullerene with such chlorinating agents as ICl, PCl_5, $SbCl_5$, VCl_4, $KICl_4$, $MoCl_5$ or $VOCl_3$.[74,98] Polychlorofullerene T_h-$C_{60}Cl_{24}$ is isostructural to the halogeno derivatives T_h-$C_{60}Br_{24}$ and T_h-$C_{60}F_{24}$. The structure of the compound D_{3d}-$C_{60}Cl_{30}$ (see Fig. 5 *b*) contains two benzenoid poles and the [18]trannulene 'equator' (see Section III.2.c) with a high degree of delocalisation. The aromatic character of these fragments is confirmed by the C – C bond lengths (1.368 and 1.375 Å in the six-membered rings and 1.386 and 1.392 Å in the trannulene ring).[99] In the D_{3d}-$C_{60}Cl_{30}$ molecule, the C=C double bonds are involved only in aromatic rings, due to which this polychlorofullerene is thermally more stable (T_{decomp} = 450 – 500 °C) than other polychlorofullerenes (T_{decomp} = 280 – 350°C).[74,99,100] Although the reactivity of these compounds remains unstudied, their unusual structures will undoubtedly attract attention of researchers in the nearest future.

4. Synthesis and structures of polybromo[60]fullerenes

Polybromo[60]fullerenes can be synthesised by the reaction of C_{60} with liquid bromine or its solution in an appropriate

solvent. For example, dissolution of C_{60} in liquid Br_2 affords orange crystals of $C_{60}Br_{24} \cdot n\,Br_2$.[7]

$$C_{60} \xrightarrow{Br_2} C_{60}Br_{24} \cdot Br_2 \quad (86\%)$$

The structure of $C_{60}Br_{24}$ was established by X-ray diffraction.[7, 101] All the attached bromine atoms are located in the fullerene cage so that 1,2 contacts between these atoms are absent (Fig. 6 *a*). There is the only possible arrangement for 24 attached bromine atoms without 1,2 contacts. It corresponds to the structure with high symmetry T_h. The average C–Br, C–C and C=C bond lengths are normal for these types of bonds (1.994, 1.510 and 1.344 Å, respectively). Further addition of the bromine atoms leads to appearance of 1,2 contacts between these atoms, and, as a result, to destabilisation of the molecule due to strong steric strains caused by repulsions between the bulky substituents. Therefore, the highest degree of bromination of C_{60} is apparently achieved in polybromofullerene $C_{60}Br_{24}$.

Bromination of [60]fullerene by molecular bromine in some organic solvents affords polybromofullerenes $C_{60}Br_6$ and (or) $C_{60}Br_8$, the selectivity being dependent on the nature of the solvent.[5] In CS_2 or $CHCl_3$, dark-brown crystals of $C_{60}Br_8$ containing solvated bromine molecules precipitate from the reaction mixture (in 80% and 50% yields, respectively).[5]

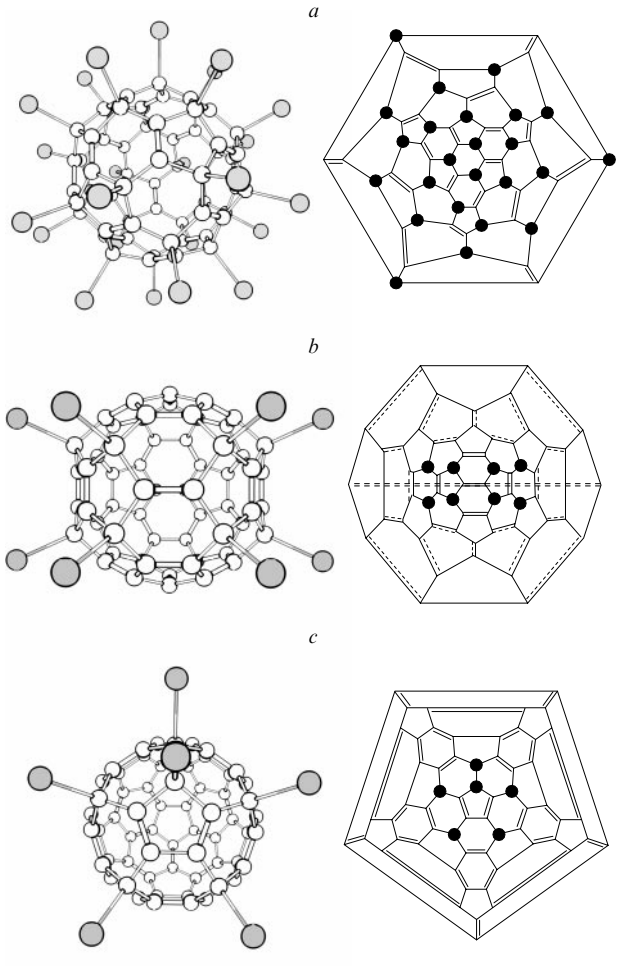


Figure 6. Three-dimensional structures and the Schlegel diagrams of polybromofullerenes T_h-$C_{60}Br_{24}$ (*a*), C_{2v}-$C_{60}Br_8$ (*b*) and C_s-$C_{60}Br_6$ (*c*).

$$C_{60} \xrightarrow{Br_2} \begin{cases} \xrightarrow{CS_2} C_{60}Br_8 \cdot Br_2 \ (80\%) \\ \xrightarrow{CCl_4} C_{60}Br_6 \cdot Br_2 \ (92\%) \end{cases}$$

Bromination of C_{60} in benzene or CCl_4 gives rise to $C_{60}Br_6$ (in ~50% and 92% yields, respectively) as dark-claret plates.[5]

In the study cited,[5] the observed selectivity of the formation of polybromofullerenes in various solvents was attributed to selective precipitation of insoluble polybromofullerene, due to which it does not undergo further transformations. However, more recent investigations demonstrated [102] that the reagent ratio also has a principal effect on the selectivity of formation of polybromofullerenes. In particular, both $C_{60}Br_6$ and $C_{60}Br_8$ were synthesised in nearly quantitative yields with the use of 1,2-dichlorobenzene as the solvent in the reactions with a 40- and 400-fold excess of Br_2, respectively.[102]

The structures of polybromofullerenes $C_{60}Br_6$ and $C_{60}Br_8$ (see Fig. 6 *b*, *c*) were unambiguously established by X-ray diffraction.[5, 101, 103] The molecules have C_s and C_{2v} symmetry, respectively. The C–Br bond lengths vary in a narrow range (1.986–1.998 Å). The changes in the C–C bond lengths in the molecule C_s-$C_{60}Br_6$ compared to those in C_{60} fullerene are substantial only for the brominated hemisphere, the largest elongation being observed for the bonds involving sp^3-hybridised carbon atoms. Five bromine atoms surround the five-membered ring containing the butadiene fragment with two double $C(sp^2)=C(sp^2)$ bonds (1.350 Å) and one elongated $C(sp^2)-C(sp^2)$ single bond (1.462 Å). The characteristic features of the addition pattern of the bromine atoms in the molecule C_{2v}-$C_{60}Br_8$ are responsible for the presence of the isolated C=C double bonds with typical lengths of 1.333 and 1.339 Å in the brominated fragment of the fullerene cage. The $C(sp^2)-C(sp^3)$ bonds of predominantly ordinary character have an average length of 1.510 Å. The remote region of the fullerene sphere is characterised by the C–C bond lengths typical of [60]fullerene.

Polybromofullerenes are the thermally least stable polyhalo derivatives of fullerenes and decompose to give C_{60} and molecular bromine upon heating to 100–200 °C, the thermal stability being increased in the series $C_{60}Br_6 < C_{60}Br_8 < C_{60}Br_{24}$.[7, 102] Polybromofullerenes are characterised by low solubility and low stability in solution, which limits their use in organic synthesis.[89-

III. Reactions of $C_{60}F_{18}$ and other polyfluoro[60]fullerenes

In the previous sections, it was noted that $C_{60}F_{18}$ is a synthetically accessible, rather stable and reactive polyfluorofullerene. Its structure is characterised by the presence of a flattened fluorine-substituted fragment and the unfluorinated fullerene hemisphere. These structural features are responsible for the diversity of chemical transformations of this compound, such as redox, nucleophilic substitution, arylation and cycloaddition reactions. Hence, it is not surprising that the chemical properties of this compound have been studied in most detail. In addition to the reactivity of $C_{60}F_{18}$, scarce published data on the chemical properties of other polyfluoro[60]fullerenes are considered below.

1. Redox reactions

It is known that C_{60} fullerene exhibits oxidation properties and forms the $C_{60}^{-\bullet}$ radical anion at a relatively positive potential [the first half-wave potential $E^{I}_{1/2} = -0.59$ V in CH_2Cl_2 *vs.* the saturated calomel electrode (SCE)].[18, 19, 21] The addition of electronegative groups to the fullerene cage should, on the

whole, lead to an increase in electron-withdrawing properties. As a result, the reduction potentials of polyfluorofullerenes are more positive. This shift achieves 1.38 V for $C_{60}F_{48}$ against C_{60}.[21] The high electron affinity of polyfluorofullerenes is also confirmed by the fact that long-lived polyfluorofullerene dianions[20,21,104–106] and even the $C_{60}F_{48}^{3-\bullet}$ trianion[17] were detected in the gas phase by mass spectrometry.

The processes that occur during electrochemical reduction of polyfluorofullerene $C_{60}F_{48}$ were studied in detail.[21] One-electron reversible reduction of $C_{60}F_{48}$ giving rise to the $C_{60}F_{48}^{-\bullet}$ radical anion occurs at the potential $E^{I}_{1/2} = 0.79$ V (CH_2Cl_2, SCE). Since the reduction potential of $C_{60}F_{48}$ is more positive than the oxidation potentials of the I^-/I_3^- (0.26 V, SCE) and I_3^-/I_2 pairs (0.65 V, SCE), the reaction of $C_{60}F_{48}$ with the iodide anion occurs with elimination of molecular iodine.[21,107] This process is accompanied by the formation of the long-lived (>20 s) $C_{60}F_{48}^{-\bullet}$ radical anion.

Further reduction of $C_{60}F_{48}$ at potentials $E^{II}_{1/2} = 0.44$, $E^{III}_{1/2} = 0.37$ and $E^{IV}_{1/2} = -0.12$ V (CH_2Cl_2, SCE) leads to irreversible processes accompanied by defluorination of polyfluorofullerenes.[21] To elucidate the mechanism of these processes, the reaction products of $C_{60}F_{48}$ with various reducing agents were studied by electrospray ionisation mass spectrometry. The reducing agents were chosen in such a way that their oxidation potentials were as close to the potential of the corresponding process as possible. For example, reduction of $C_{60}F_{48}$ with ferrocene (Fc) with the oxidation potential [$E(Fc/Fc^+) = 0.31$ V *vs.* SCE] close to the second reduction potential of polyfluorofullerene affords the $C_{60}F_{47}^-$ anion. It was hypothesised that the reaction initially produces the unstable $C_{60}F_{48}^{2-}$ dianion, which decomposes to form the F^- and $C_{60}F_{47}^-$ anions. The latter yields $C_{60}F_{47}^{2-\bullet}$. The reaction of $C_{60}F_{48}$ with the stronger reducing agent, *viz.*, decamethylferrocene [$E(DmFc/DmFc^+) = -0.11$ V *vs.* SCE], produces $C_{60}F_{46}^{2-}$. In the authors' opinion, the latter is formed as a result of elimination of F^- from the initially formed $C_{60}F_{47}^{3-}$ trianion. The schemes of the reactions involved in the successive reduction of $C_{60}F_{48}$ and their reduction potentials in CH_2Cl_2 *vs.* SCE are given below.

$$C_{60}F_{48} + e^- \longrightarrow C_{60}F_{48}^{-\bullet},\ E_{1/2} = 0.79\ V;$$

$$C_{60}F_{48}^{-\bullet} + e^- \longrightarrow C_{60}F_{48}^{2-} \longrightarrow F^- + C_{60}F_{47}^-,\ E_{1/2} = 0.44\ V;$$

$$C_{60}F_{47}^- + e^- \longrightarrow C_{60}F_{47}^{2-\bullet},\ E_{1/2} = 0.37\ V;$$

$$C_{60}F_{47}^{2-\bullet} + e^- \longrightarrow C_{60}F_{47}^{3-} \longrightarrow F^- + C_{60}F_{46}^{2-},\ E_{1/2} = -0.12\ V.$$

It should be noted that the process is not stopped at this moment, and the percentage of polyfluorofullerenes containing a smaller number of fluorine atoms increases with time.

Electrochemical transformations of polyfluorofullerenes containing smaller amounts of halogen have been investigated.[16,18,19,108] Reduction of these compounds was demonstrated to be accompanied by a loss of fluorine atoms. For example, the reaction of $C_{60}F_{18}$ with chloroanil produces the $C_{60}F_{17}^-$ ion,[108] and reduction of $C_{60}F_2$ and $C_{60}F_4$ affords the $C_{60}^{-\bullet}$ anion.[18]

The reduction potential of polyfluorofullerenes monotonically increases with increasing number of the attached fluorine atoms or upon introduction of other electron-withdrawing fragments into the molecule (Table 2). The arrangement of the fluorine atoms at the fullerene cage also has an effect on the potential. For example, of the three studied isomers of $C_{60}F_{36}$, it is most difficult to reduce the *T* isomer; the C_1 and C_3 isomers are reduced at 30 and 80 mV higher potentials, respectively.[108] This fact correlates with higher chemical stability of the *T*-$C_{60}F_{36}$ isomer compared to the C_1 and C_3 isomers (see Section III.2.a).[109,110]

Interesting results were obtained in the study of the trannulene dyads $C_{60}F_{15}[C(CO_2Et)_2CO_2R]_3$ (R = Et, pyrene-, perylene-, ferrocene- or tetrathiafulvalene-containing fragments).[14,22,111] The first reduction potential of these compounds corresponding to the single-electron reversible transfer varies from −0.005 to −0.10 V (CH_2Cl_2, SCE), which is substantially higher than the reduction potential of $C_{60}F_{18}$ (−0.33 V, CH_2Cl_2, SCE).[108] The observed process is attributed to reduction of the [18]trannulene fragment in the compounds under study.

Table 2. Reduction potentials of polyfluorofullerenes and some their derivatives in CH_2Cl_2.

Compound	$E^{I}_{1/2}$/V		Ref.
	vs. SCE	*vs.* C_{60}/C_{60}^-	
C_{60}	−0.59	0.00	18, 19, 21
$C_{60}F_2$	−0.55	0.04	18
$C_{60}F_4$	−0.51	0.08	18
$C_{60}F_{18}$	−0.33	0.26	108
$C_{60}F_{18}O$	−0.28	0.31	108
$C_{60}F_{15}[C(CO_2Et)_2CO_2R]_3$ [a]	−0.10 to −0.005	0.49–0.51	14, 22, 111
T-$C_{60}F_{36}$	0.04	0.63	108
C_1-$C_{60}F_{36}$	0.07	0.66	108
C_3-$C_{60}F_{36}$	0.12	0.71	108
$C_{60}F_{36}$ [b]	0.24	0.82	19
$C_{60}F_{48}$	0.78	1.38	21, 108

[a] R = Et, pyrene-, perylene-, ferrocene- or tetrathiafulvalene-containing fragments; [b] a mixture of the *T*-$C_{60}F_{36}$ and C_3-$C_{60}F_{36}$ isomers (1 : 10).

Polyfluorofullerenes are stronger oxidising agents than fullerene, which was demonstrated back in early studies. A mixture of higher polyfluorofullerenes $C_{60}F_{44}$ and $C_{60}F_{46}$ was found to oxidise the iodide anion to I_2.[107] Reduction of polyfluorofullerenes is accompanied by a loss of fluorine atoms to form a complex mixture of compounds, from $C_{60}F_{36}$ to $C_{60}F_{40}$. The reactions of higher polyfluorofullerenes with Br^- proceed with difficulty and are accompanied by elimination of only a small amount of Br_2.

Organic compounds can also be oxidised and even fluorinated by higher polyfluorofullerenes. For example, heating of a mixture of $C_{60}F_{44}$ and $C_{60}F_{46}$ in Pr^iOH affords acetone,[107] whereas heating of solutions of polyfluorofullerenes in aromatic solvents in the presence of Lewis acids leads to defluorination of fullerenes[112–114] accompanied by partial fluorination of solvent molecules. Under these conditions, even pyridine, which exhibits low reactivity in electrophilic substitution reactions, gives 2-fluoropyridine in a yield of up to 10%.[107] In the presence of higher polyfluorofullerenes, polymerisation of THF occurs;[87,110,115] an analogous process is also observed upon dissolution of these compounds in acetone (in the latter case, a polymer is formed as a result of aldol condensation induced by HF).[1]

Therefore, polyfluorofullerenes are very strong oxidants, the redox reactions involving these reagents being accompanied by defluorination of the starting polyfluorofullerenes. The degree of defluorination is generally determined by the strength of the reducing agent and the possibility of competitive substitution and addition reactions. Some other examples of reduction of polyfluorofullerenes observed in the course of nucleophilic substitution and cycloaddition reactions are given in Sections III.2 and III.4.a.

2. Nucleophilic substitution reactions

The mechanisms of nucleophilic substitution in polyhalofullerenes are virtually unknown. The ideas about the processes involved in these reactions changed with time. However, numerous uncertainties and ambiguities concerning these

mechanisms still persist. The problem is that the substitution of different nucleophiles and polyhalofullerenes occurs apparently by different pathways. Hence, there is good reason to discuss the most probable mechanisms of these reactions in the present review. We expect that further experimental studies will provide conclusive information on these mechanisms.

a. Reactions with O-nucleophiles

Even in early studies, it was found that polyfluorofullerenes, which have initially been believed to be chemically inert, are involved in nucleophilic substitution reactions.[56, 86, 115, 116] These reactions have been discovered accidentally. The mass spectrometric analysis of fluorination products of C_{60} fullerene revealed the presence of oxopolyfluoro derivatives containing from 1 to 18 oxygen atoms.[8, 57, 117]

It is unlikely that oxygen atoms are inserted into polyfluorofullerene molecules upon oxidation by atmospheric oxygen because solid samples of polyfluorofullerenes were found [29, 59, 86] to be unchanged in air for an indefinitely long period of time. However, dissolution of highly fluorinated fullerenes in polar solvents (for example, THF) containing traces of water is accompanied by an exothermic reaction resulting in a loss of fluorine atoms.[110, 115] Hence, it was hypothesised that oxo derivatives of polyfluorofullerenes are formed through the nucleophilic displacement of F by OH followed by elimination of HF from the adjacent F and OH substituents.[57, 115, 116] This transformation occurs so easily that oxopolyfluorofullerenes have long been considered as primary reaction products.[57, 117] However, hydroxypolyfluorofullerenes are precursors of these compounds, as has been recently exemplified by the individual isomers C_3- and C_1-$C_{60}F_{36}$.[109]

The discovery of 'accidental' [34] epoxidation of polyfluorofullerenes has inflated studies of targeted nucleophilic displacement of fluorine atoms by oxygen-containing nucleophiles. It was found that $C_{60}F_{36}$ (Ref. 40) and higher polyfluorofullerenes [115, 116] are easily hydrolysed in the presence of organic cosolvents (the presence of the latter is necessary because polyfluorofullerenes are insoluble in water). For example, dissolution of $C_{60}F_{36}$ in wet toluene or chloroform affords the compounds $C_{60}F_{35}OH$, $C_{60}F_{33}(O)OH$ and $C_{60}F_{32}(O)_2$.[118] The treatment of polyfluorofullerenes with methanolic NaOMe leads to methoxydefluorination. The nucleophilic displacement of fluorine atoms with sodium acetate in acetic acid was also documented.[115] Therefore, unlike polyfluoroalkanes and most of their derivatives, polyfluorofullerenes are rather good substrates for nucleophilic substitution reactions. The mechanism of this reaction deserves a detailed discussion.

The nucleophilic substitution involves the carbon–leaving group bond cleavage and the carbon–nucleophile bond formation. These processes can be either concerted (the so-called S_N2 mechanism) or sequential. The concerted mechanism is impossible for polyhalofullerenes because it involves the backside attack of a nucleophile with respect to the leaving group, *i.e.*, from the inside of the the fullerene sphere. In early studies on nucleophilic substitution in polyhalofullerenes, the direct nucleophilic displacement of halogen has been believed to be a result of the frontal attack of a nucleophile. However, this mechanism was rejected in more recent studies. Actually, the frontal attack of a nucleophile is a forbidden process according the orbital symmetry rules. *Ab initio* quantum chemical studies with an extended basis set taking into account diffuse and polarisation functions demonstrated that the energy barrier to the frontal attack is 165–190 kJ mol^{-1} higher than that to the backside attack even in simplest halomethanes.[119]

Nucleophilic substitution reactions at a carbonyl carbon atom or at a silicon atom proceed by an addition–elimination mechanism (the leaving group is eliminated only after the formation of a bond with a nucleophile). However, it is evident that this mechanism is impossible for polyfluorofullerenes. The S_N1 mechanism can also be rejected. First, the formation of carbocations from electron-deficient polyfluorofullerenes in the absence of Lewis acids is hardly probable. Second, the substitution reaction rate was found to depend on the strength of a nucleophile. For example, up to 65% of fluorine atoms are replaced in the reaction with sodium methoxide in methanol for 12 h, whereas only 15% of fluorine atoms are replaced in the reaction with the weaker nucleophilic agent, *viz.*, sodium acetate, in acetic acid (which is often used as the solvent in S_N1 reactions) even after 550 h.[115]

The nucleophilic substitution reaction can be considered as a single-electron transfer from a nucleophile to the leaving group. Before the reaction, the nucleophile bears a lone electron pair, whereas the leaving group contains one electron of the R–X bond. After completion of the reaction, the nucleophile bears one electron of the R–Y bond, whereas the leaving group contains a lone electron pair. This electron density shift can occur either simultaneously with the bond cleavage–formation steps or independently of these processes (or one of these processes).

All possible nucleophilic substitution mechanisms can be represented by a three-dimensional reaction diagram (Fig. 7).[120–122] The degree of the R–Y bond formation is on the *x* axis; the degree of the R–X bond cleavage, on the *y* axis; the degree of electron density transfer from one fragment to another, on the *z* axis. The S_N1 mechanism is described by the movement of the system from the point *A* to the point *C* through the point *B*. The movement along the *ADC* path corresponds to the addition–elimination mechanism. The transformation of the system from the state *A* to the state *C* without intersections of other nodes in the diagram corresponds to the concerted S_N2 reaction.

If the electron shift from the nucleophile (Y:) to the substrate (RX) is not accompanied by the Y–R bond formation and the R–X bond cleavage, the mechanism involves the single-electron transfer (path *A*–*F*). If the electron shift is not accompanied by the formation of the Y–R bond but is accompanied by the cleavage of the R–X bond, the mechanism involves the dissociative electron transfer (path *A*–*G*). The strong electron-withdrawing properties of fullerene and, particularly, of polyfluorofullerenes suggest the possibility of the single-electron transfer mechanism.

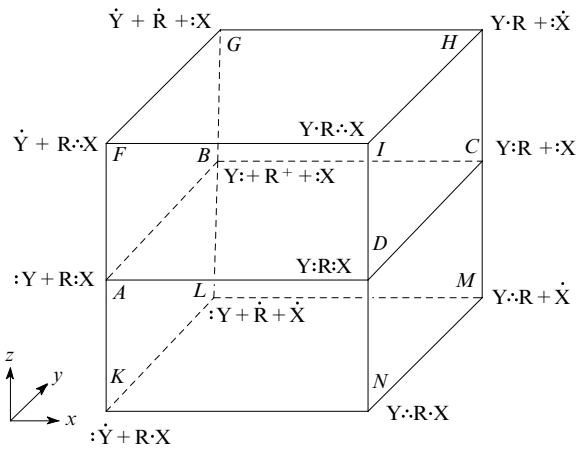
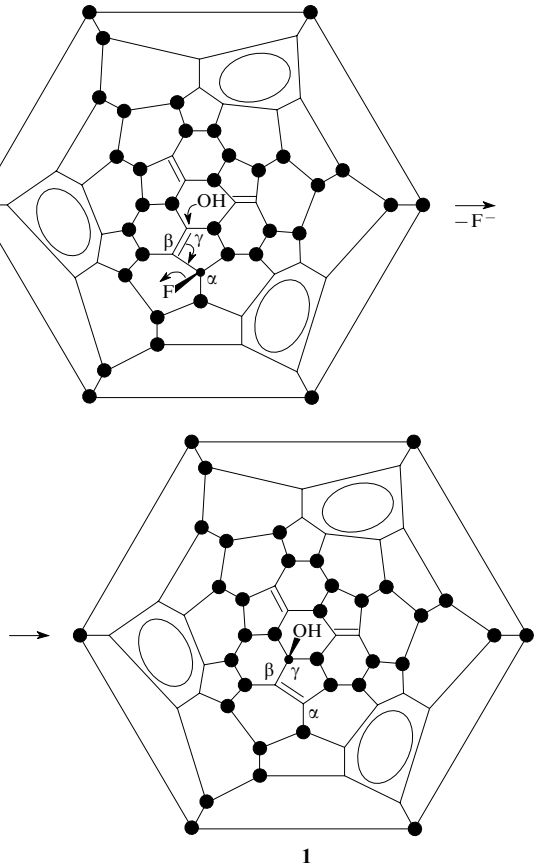


Figure 7. Three-dimensional reaction diagram for nucleophilic substitution reactions. See comments in the text.

The single-electron transfer from various donors to polyfluorofullerenes is rather well known (see Section III.1).[16, 18, 19, 21] These reactions are usually accompanied by complete or partial defluorination. Actually, it was found that hydrolysis of S_6- and D_3-$C_{60}F_{48}$ in aqueous acetone affords a complex mixture of products, including $C_{60}F_{42}O$, $C_{60}F_{40}O$, $C_{60}F_{38}O$, *etc.*[110] These data can be considered as evidence for the single-electron transfer mechanism in the case of hydrolysis of the strongest electron-withdrawing polyfluorofullerene, $C_{60}F_{48}$.

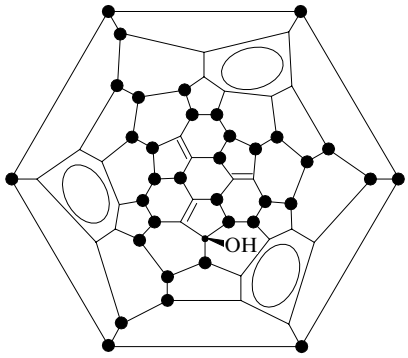
The C_{3v}-$C_{60}F_{18}$ and T-$C_{60}F_{36}$ compounds are stable with respect to hydrolysis. Hydrolysis of the C_3 and C_1 isomers of $C_{60}F_{36}$ proceeds without a loss of additional fluorine atoms.[109, 110] This would be impossible in the case of the single-electron transfer mechanism. Consequently, the nucleophilic substitution reactions of these substrates proceed by another pathway. A comparison of the structures of the T-$C_{60}F_{36}$ isomer, which withstands hydrolysis, and the hydrolysable isomers C_3-$C_{60}F_{36}$ and C_1-$C_{60}F_{36}$ (see Fig. 1 *c*–*e*) gives the answer to this question. In the T-$C_{60}F_{36}$ molecule, all double bonds adjacent to the fluorine atoms are involved in the aromatic benzenoid six-membered rings. This isomer contains only Ph–C(F)RR′-type fragments. In two other isomers, there are three isolated double bonds containing the C(F)RR′ fragment in the allylic position. It is known that nucleophiles can attack allyl halides both at the α- and γ-carbon atoms. The latter attack leads to the shift of the C=C double bond (the so-called S_N2' mechanism). The nucleophilic substitution in polyhalofullerenes should proceed by this mechanism.

Actually, dissolution of C_3-$C_{60}F_{36}$ in wet toluene affords C_1-$C_{60}F_{35}OH$ (**1**), which is consistent with the S_N2' mechanism.[109]



1

The isomers of hydroxypolyfluorofullerene C_1-$C_{60}F_{35}OH$, *viz.*, compounds **1** and **2** (Fig. 8), obtained upon hydrolysis of C_3- and C_1-$C_{60}F_{36}$, respectively, were isolated and characterised.[109] It was found that only the allylic fluorine atoms are replaced. On the contrary, the fluorine atoms that are surrounded only by other fluorine atoms or benzenoid rings remain intact.

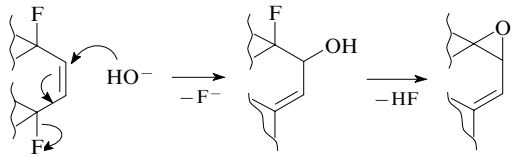


2

Figure 8. The Schlegel diagram of C_1-$C_{60}F_{35}OH$ (**2**).

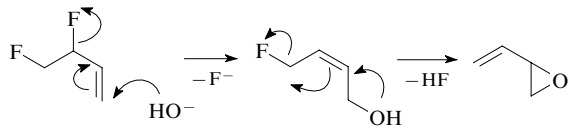
Compounds **1** and **2** easily undergo dehydrofluorination to give $C_{60}F_{34}O$. In this case, the oxygen atom is, apparently, involved in the epoxide ring. However, it should be borne in mind that some oxopolyfluorofullerenes generated as by-products in fluorination reactions of [60]fullerene, *viz.*, $C_{60}F_{2n}O$ ($n = 1-4$),[45] $C_{60}F_{18}O$[80] and $C_{60}F_{36}O$,[109] contain an oxygen atom as an intramolecular ether group.

It was hypothesised[36, 57] that epoxide is formed by elimination of HF from the adjacent OH and F groups. Therefore, the overall process of epoxide formation is described by reaction (1).



(1)

However, we are doubtful about this mechanism because the formation of the epoxide ring from halohydrins generally occurs by the S_N2 mechanism, which, as demonstrated above, is impossible in the case under consideration. Hence, the S_N2' mechanism described by reaction (2) seems to be more probable. Unfortunately, it is impossible to draw an unambiguous conclusion about the mechanism of this step because it is necessary to establish the structures of the resulting epoxides.



(2)

The further substitution of fluorine atoms can also occur. The $C_{60}F_{33}(O)OH$ and $C_{60}F_{32}O_2$ compounds were also detected among the hydrolysis products of the polyfluorofullerene $C_{60}F_{36}$.[118] The formation of these compounds is accompanied by migration of double bonds, which destabilises the molecule as a whole. Hence, the percentage of the latter compounds is low.

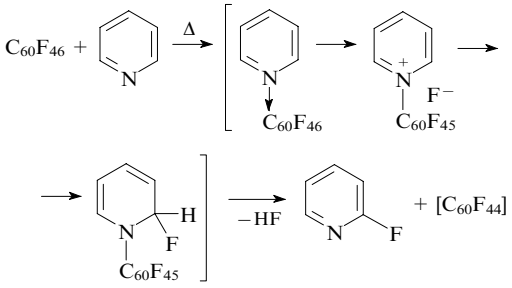
The analogous S_N2' mechanism of the substitution of fluorine atoms is observed for dissolution of D_3- and S_6-$C_{60}F_{48}$ in THF or acetone in the presence of water.[110] This treatment leads to the replacement of up to 12 halogen atoms. This is consistent with the presence of six double bonds, for which the S_N2' mechanism is possible. Subsequent elimination of HF gives fragments containing up to six epoxide rings.

Calculations of the formation energies of possible intermediates containing a hydroxy group demonstrated that the energy difference between these intermediates is small. Consequently, hydrolysis of $C_{60}F_{48}$ can afford complex mixtures of isomers.[110]

Thus, the nucleophilic substitution in polyfluorofullerenes occurs by the S_N2' mechanism or *via* the electron transfer and is possible only in the presence of the activated carbon–carbon double bond that is not involved in the aromatic ring and occupies the β position with respect to the leaving atom. Hence, the C_3- and C_1-$C_{60}F_{36}$ isomers containing three allylic fragments are much more reactive in nucleophilic substitution reactions than T-$C_{60}F_{36}$ in which the π-electron density is completely delocalised over the aromatic rings. It should also be noted that the double bonds containing several fluorine atoms in the nearest environment are more reactive. As a result, O-nucleophiles react more readily with higher polyfluorofullerenes than with lower polyfluorofullerenes, in particular, with $C_{60}F_{18}$, which are less reactive in these reactions.[109, 110]

b. Reactions with N-nucleophiles

The reactions of polyfluorofullerenes with N-nucleophiles are less studied than the reactions with O-nucleophiles. It is known that higher polyfluorofullerenes react readily with primary and secondary amines. For example, up to 55% of fluorine atoms are substituted in reactions of higher polyfluorofullerenes with Et_2NH during 1 h (^{19}F NMR spectroscopic data), and the percentage of the replaced fluorine atoms increases to 65% when the reaction time is increased to 12 h.[115] Pyridine also reacts slowly with higher polyfluorofullerenes $C_{60}F_{44}$–$C_{60}F_{46}$ with selective formation of 2-fluoropyridine.[107] To explain this fact, the authors suggested the mechanism involving the N addition followed by the migration of the fluorine atom.



This unexpected result may be of importance in the preparative chemistry of pyridine, because it is virtually impossible to synthesise 2-fluoropyridine by other methods. Besides, this is the first example of the use of higher polyfluorofullerenes as fluorinating agents for heterocyclic compounds.

c. Reactions with C-nucleophiles

Reactions with organometallic compounds. The formation of a new carbon–carbon bond is the most important reaction in synthetic chemistry of fullerenes. Hence, the reactions with C-nucleophiles attract the largest interest among nucleophilic substitution reactions of polyfluorofullerenes. Alkyl- and aryllithium compounds are known to be very reactive nucleophiles. In an early study on the chemical properties of polyfluorofullerenes,[115] it was demonstrated that these compounds react readily with typical C-nucleophiles, such as Grignard reagents and organolithium compounds. However, the products have not been isolated and analysed. Further detailed studies on the reaction of polyfluorofullerenes $C_{60}F_{44}$–$C_{60}F_{46}$ with alkyllithium reagents showed that this is one of the most efficient routes to polymethylated and polyphenylated [60]fullerenes with high degree of addition.[123]

Products with the compositions $C_{60}Me_n$ ($n = 2$–28) and $C_{60}Ph_n$ ($n = 2$–20) were synthesised by the reactions of a mixture of polyfluorofullerenes $C_{60}F_{44}$–$C_{60}F_{46}$ with an excess of MeLi and PhLi, respectively.[123] The formation of compounds with the number of methyl (phenyl) groups smaller than the number of fluorine atoms in the starting polyfluorofullerene is evidence for partial defluorination of the substrate in the course of the reaction. This suggests that the reactions of polyfluorofullerenes with organolithium compounds proceed by the single-electron transfer mechanism. This reaction pathway is also supported by the fact that a considerable amount of biphenyl was detected in the reaction with phenyllithium.[107] Fullerene methylation (or phenylation) products are orange (or brown), very readily soluble in nonpolar organic solvents, thermally stable at least up to 300 °C and storage-stable in air over a long period of time. It is of note that refluxing of polyfluorofullerenes in diethyl ether for 3 h is required to achieve the complete substitution of methyl groups for all fluorine atoms. At room temperature, mixed derivatives $C_{60}F_xMe_y$ are formed. The necessity of prolonged heating of the reaction mixture for the complete substitution of fluorine atoms is attributed to the fact that the electron-withdrawing properties of fullerene are decreased as the degree of substitution of methyl groups for the fluorine atoms increases and, as a consequence, to the incomplete reaction under milder conditions (*cf.* Ref. 115).

Arylation of $C_{60}F_{18}$. An alternative procedure for the introduction of aryl substituents into the fullerene cage is the Friedel–Crafts reaction. In this reaction, polyfluorofullerenes and aromatic compounds act as electrophiles and nucleophiles, respectively. In other words, the arylation reactions of polyfluorofullerenes belong to nucleophilic substitution reactions. Many arylated fullerenes, which are of practical interest, were synthesised by the reactions of fullerenes or polyhalofullerenes with aromatic compounds in the presence of Lewis acids. Arylfullerenes are soluble in organic solvents and storage-stable.

The Friedel–Crafts reaction with polyhalofullerenes was first described for polychlorofullerenes[2] (arylation of polychlorofullerenes is considered in detail in Section IV.1). Since alkyl fluorides are more reactive in the Friedel–Crafts reaction than analogous chlorides,[124] it can be expected that polyfluorofullerenes would also be involved in this reaction. Actually, it was found that the electrophilicity of polyhalofullerenes increases in the series Br < Cl < F.[125]

It can also be expected that of all polyfluorofullerenes the lower polyfluorofullerenes would be most reactive in the Friedel–Crafts reaction because fluorine atoms in these compounds are sterically more accessible. For example, $C_{60}F_{18}$ reacts with benzene in the presence of $FeCl_3$ at room temperature. On the contrary, attempts to replace fluorine atoms in higher polyfluorofullerenes $C_{60}F_{36}$ and $C_{60}F_{48}$ by phenyl groups using the Friedel–Crafts reaction failed.[112]

The trefoil-shaped triphenyl derivative $C_{60}F_{15}Ph_3$ (**3**), which was called triumphene (Fig. 9), was isolated from arylation products of polyfluorofullerene C_{3v}-$C_{60}F_{18}$ and completely characterised.[112]

Based on the ^{19}F NMR spectroscopic data, which are indicative of the C_{3v} symmetry of this molecule, evidence for the direct nucleophilic substitution of fluorine atoms according to the S_N1 mechanism was reported.[112] This mechanism is facilitated by the Friedel–Crafts catalyst. An increase in the reaction temperature results in the formation of $C_{60}Ph_{18}$, in which all fluorine atoms are replaced by phenyl groups. It was hypothesised[36, 112] that, in spite of presumable steric hindrance, the phenyl groups occupy the positions of fluorine atoms in the precursor. However, this is doubtful. The mass spectra of the reaction products show a low-intensity peak of

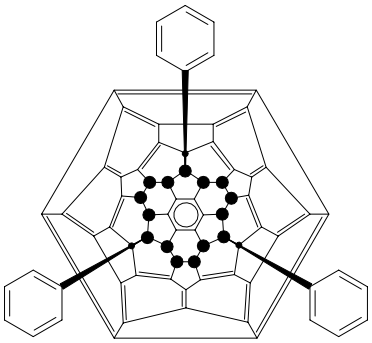


Figure 9. The Schlegel diagram of C_{3v}-$C_{60}F_{15}Ph_3$ (**3**).

the $C_{60}Ph_{19}^{+}$ ion. Apparently, this compound is formed as a result of further phenylation of the fullerene cage. This reaction is analogous to the well-known reaction of fullerene with benzene in the presence of $AlCl_3$.[93] In addition, $C_{60}F_{15}Ph_7$ and other phenylation products of polyfluorofullerene were detected in the reaction mixture.[112]

In studies of the reaction of polyfluorofullerene $C_{60}F_{18}$ with a wide range of aromatic compounds catalysed by $FeCl_3$, mono-, bis- and tris(aryl) derivatives **4**–**6** (Fig. 10) were detected.[112, 113] The results of these experiments are summarised in Table 3.

The degree of substitution of F atoms depends on the nature of the aromatic reagent. For example, the reactions of $C_{60}F_{18}$ with bulky arenes, such as naphthalene, biphenylene, pyrene or fluoranthene, yield monosubstituted compounds **4** as the major products. On the contrary, bis- (**5**) and(or) tris-substituted (**6**) products dominate in the reactions of $C_{60}F_{18}$ with smaller arenes, such as benzene, chloro- and 1,2-dichlorobenzenes, toluene, biphenyl, fluorene, *etc*. Some aromatic compounds do not give arylation products because of steric hindrance (for example, mesitylene), self-condensation side reactions[113] or low reactivity of the substrate (for example, trifluoromethylbenzene). Serious steric hindrance or self-condensation and chlorination of arenes in the presence of $FeCl_3$ as side reactions precluded synthesis of the substitution products of $C_{60}F_{18}$ with thiophene, perylene and azulene.

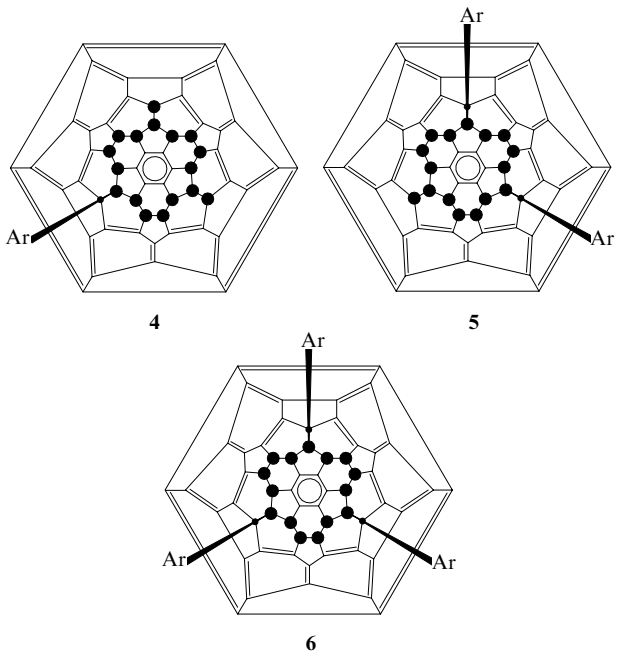


Figure 10. The Schlegel diagrams of electrophilic mono- (**4**), di- (**5**) and tri-substitution products (**6**) in $C_{60}F_{18}$ by different arenes (see Table 3).

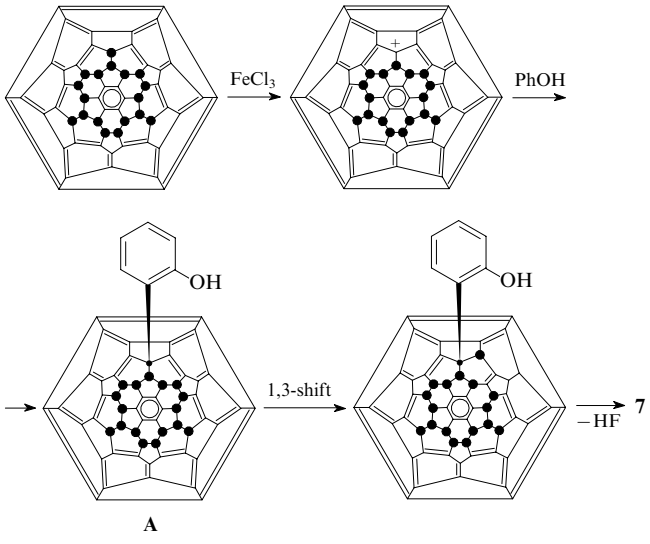
Table 3. Results of the replacement of fluorine atoms in $C_{60}F_{18}$ by different agents.

Arene	Product		
	4	**5**	**6**
Benzene	–	–	+
Chlorobenzene	–	–	+
1,2-Dichlorobenzene	–	–	+
Toluene [a]	+	+	+
Anisole	+	+	+
Diphenyl ether	+	+	+
Biphenylene	+	+	+
Naphthalene	+	+	+
Biphenyl	+	–	+
Fluorene [b]	+	–	+
Pyrene	+	–	–
Fluoranthene	+	+	–
Mesitylene	–	–	–
Perylene [b]	–	–	–
Coronene	–	–	–
Thiophene [c]	–	–	–
Azulene [b]	–	–	–
Trifluoromethylbenzene [c]	–	–	–

[a] The *para* isomer is generated as the major product, although fractions containing *ortho*- and *meta*-substitution products were isolated; [b] chlorination and(or) self-condensation of arene are side processes; [c] the reaction does not proceed.

The reactions of $C_{60}F_{18}$ with hydroxyl-containing aromatic compounds (phenol, hydroquinone and 2-naphthol) are not stopped after electrophilic defluoroarylation, but are accompanied by elimination of HF to give benzofuran derivatives of fullerene **7**, **8** and **9**, respectively (Fig. 11).[113, 125] The elimination of HF was described as a result of the direct attack of the OH group on the F atom, which becomes adjacent to the 2-hydroxyphenyl substituent after the 1,3-shift (Scheme 1). The possibility of the 1,3-migration of the fluorine atom was exemplified[63] by the transformations of isomers of $C_{60}F_{36}$.

Scheme 1



An alternative step of dehydrofluorination of the intermediate **A** involves the attack of the OH group on the adjacent

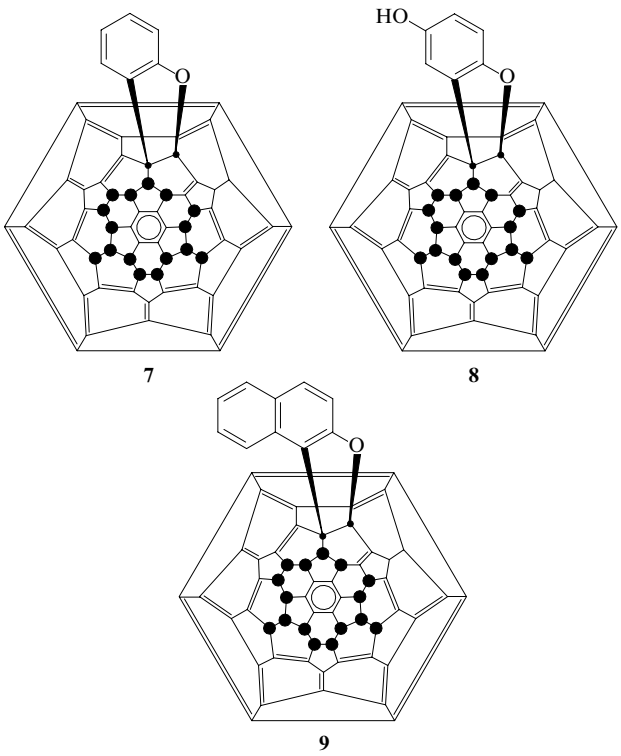
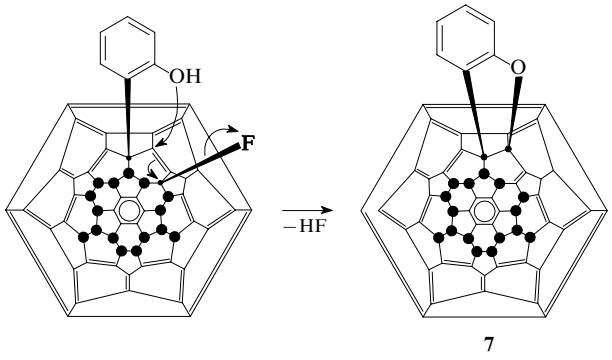


Figure 11. The Schlegel diagrams of compounds **7**–**9** prepared by the reactions of $C_{60}F_{18}$ with phenol, hydroquinone and 2-naphthol, respectively.

double bond accompanied by the migration of the electron pair and elimination of the fluorine atom (S_N2' reaction). Taking into account the discussion in Section III.2.a, the second pathway seems to be more probable.



The reaction of $C_{60}F_{18}$ with 2-naphthol affords naphtho[2,1-*b*]furano[*d*-1,2][60]fullerene as a by-product, which is formed as a result of complete defluorination of polyfluorofullerene.[125] The formation of this compound can be considered as evidence for the competitive single-electron transfer from naphthol to polyfluorofullerene. This process is not observed in the reaction of $C_{60}F_{18}$ with water, because water molecules are hard acids and non-polarisable nucleophiles and are rarely involved in electron transfer reactions. To the contrary, readily oxidisable 2-naphthol is much more prone to donate electrons to an appropriate acceptor.

The reaction of $C_{60}F_{18}$ with benzene in the presence of $SbCl_5$ afforded the expected $C_{60}F_{15}Ph_3$ product (**3**) along with two oxygen-containing derivatives.[114] One of these products is fluorooxyfullerene $C_{60}F_{14}OFPh_3$ (**10**) (Fig. 12); the second, a mixture of oxahomo derivatives (intramolecular ethers) $C_{60}F_{14}O_2Ph_3$.

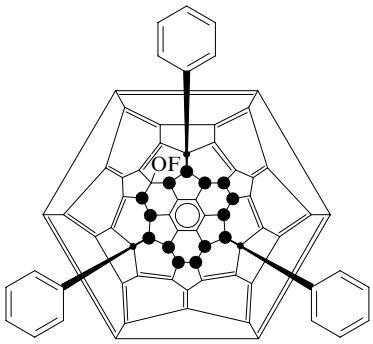


Figure 12. The Schlegel diagram of $C_{60}F_{14}OFPh_3$ (**10**).

Anomalous Bingel reaction. Since $C_{60}F_{18}$ can serve as a precursor for the formation of donor–acceptor dyads having stronger electron-withdrawing properties, attempts were made to involve this compound in reactions, which are generally used for the synthesis of analogous structures from C_{60}. The Bingel reaction is most often used for this purpose. This reaction involves the nucleophilic addition of the stabilised α-halocarbanion to the fullerene cage followed by the intramolecular substitution of the halogen atom to give methanofullerenes.[126, 127]

However, it appeared that the reaction of diethyl bromomalonate with $C_{60}F_{18}$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) proceeds by a mechanism different from the [2 + 1]-cycloaddition.[12] The reaction was found to give mono-, di- and trisubstitution products of diethyl bromomalonate groups for the fluorine atoms, *viz*., the compounds $C_{60}F_{18-n}[CBr(CO_2Et)_2]_n$ ($n = 1-3$) (Fig. 13). The degree of substitution can be regulated by the rate of addition of the base.[12, 128] Due to the presence of a leaving group (even a

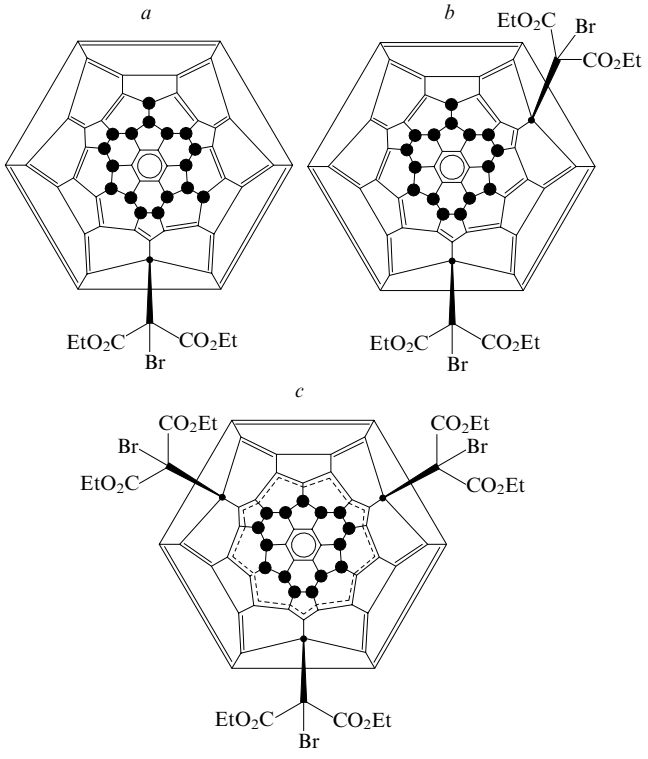
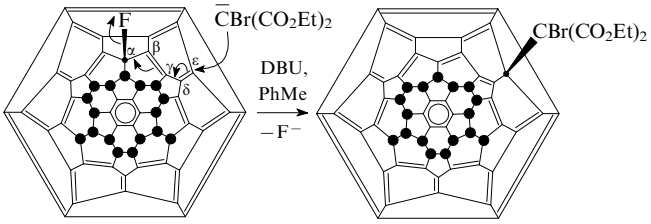


Figure 13. The Schlegel diagrams of $C_{60}F_{17}[CBr(CO_2Et)_2]$ (*a*), $C_{60}F_{16}[CBr(CO_2Et)_2]_2$ (*b*) and $C_{60}F_{15}[CBr(CO2Et)_2]_3$ (**11**) (*c*).

poor leaving group, such as the fluoride anion) in fullerene, after the addition of the diethyl bromomalonate carbanion to the polyfluorofullerene cage the reaction proceeds not as cyclopropanation. This follows a pathway analogous to the S_N2' reaction considered above in the discussion of the formation of epoxides from polyfluorofullerenes in the presence of atmospheric moisture (see Section III.2.a).[109, 110] The only difference is that the fluoride ion is eliminated as a result of the nucleophilic attack not on the γ-carbon atom, but on the more distant ε-carbon atom (to emphasise this fact, some authors used the notation S_N2'' mechanism, Scheme 2).[12, 14, 129]

Scheme 2



Apparently, the attack of the bulky nucleophiles $^-CBr(CO_2Et)_2$ on the γ-carbon atom (the S_N2' mechanism) is hindered due to steric effects caused by adjacent fluorine atoms. On the contrary, the attack on the ε-carbon atom (the S_N2'' mechanism) remote from fluorine atoms occurs without noticeable steric repulsions. As a result, one to three most sterically accessible fluorine atoms, which are adjacent to the double bond and are bound to carbon atoms bearing the largest positive charge are subjected to nucleophilic substitution in the $C_{60}F_{18}$ molecule. Semiempirical quantum chemical calculations by the AM1 and PM3 methods demonstrated [128] that among the carbon atoms of the $C_{60}F_{18}$ cage, the carbon atoms that lose fluorine atoms bear the largest positive charge. Of the fluorine atoms in the $C_{60}F_{18}$ molecule, the largest negative charges are accumulated on the leaving atoms.[128] Therefore, the reaction involves the successive replacement of three fluorine atoms and finally gives the trisubstituted product, which is not prone to further reactions.

The structure of the C_{3v}-symmetrical trisubstituted derivative $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ (**11**) established by X-ray diffraction deserves special attention.[12] This compound is characterised by the presence of the equatorial [18]annulene belt (see Fig. 13 *c*). Since all double bonds involved in the belt are in *trans* configurations, this fragment is called [18]trannulene according to the term proposed in the early theoretical study.[130] An analysis of the C–C bond lengths in the [18]trannulene fragment in $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ shows that these bonds are substantially equalised (the maximum difference is 0.018 Å) and vary from 1.392 to 1.410 Å. By contrast, these bonds in the starting $C_{60}F_{18}$ vary in a wider range (from 1.368 to 1.528 Å, *i.e.*, the difference is as large as 0.160 Å).[39]

It should be noted that π-electron delocalisation in the [18]trannulene fragment resulting in the equalisation of the bond lengths can be explained as a result of the formation of a single aromatic π-system. However, commonly known aromatic systems are annulenes, in which C=C bonds are either in *cis* (for example, benzene), or *cis*,*trans* configurations (for example, [18]annulene). These conformations are more favourable because the π orbitals involved in aromatic conjugation are perpendicular to the plane of the annulene ring. Nevertheless, the possibility of the existence of aromatic systems, which are additionally stabilised due to overlap of the π orbitals lying in the [*n*]annulene plane, has theoretically been predicted earlier.[131, 132] In particular, it was theoretically demonstrated [130] that aromatic stabilisation can be achieved by fixing the *trans* configuration of the [*n*]annulene ring (*i.e.*, the formation of [*n*]trannulene) upon its involvement in the molecular cage. The calculated geometry, energy and magnetic properties indicate that [*n*]trannulenes obey the Hückel rule, *e.g.*, $(4n+2)$ π-electron systems are aromatic, whereas $4n$ π-electron systems are antiaromatic. Therefore, due to the rigid fullerene cage and the arrangement of the addends in the $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ molecule, [18]annulene adopts the *trans* configuration, which satisfies the Hückel rule, resulting in aromatic conjugation. The aromaticity of the [18]trannulene fragment in the $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ molecule leads to a slight bond-length alternation in this ring,[12, 23] gives rise to the diamagnetic ring current induced by the external magnetic field [133] and leads to an increase in chemical stability of the $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ molecule compared to the starting polyfluorofullerene $C_{60}F_{18}$.[23, 110] Analogous [18]trannulene structural fragments were found in the fullerene derivatives D_{3d}-$C_{60}Cl_{30}$,[99] S_6-$C_{60}[CMe(CO_2Et)_2]_6$ and S_6-$C_{60}[CMe.(CO_2Bu^t)_2]_6$ synthesised more recently.[134] The mono- and disubstituted products $C_{60}F_{18-n}[CBr(CO_2Et)_2]_n$ (n = 1 or 2), unlike trisubstituted compound **11**, do not contain the [18]trannulene belt because of the presence of $C(sp^3)$ atoms disrupting the equatorial π-conjugation system (see Fig. 13 *a*,*b*).

Turning back to the discussion of the Bingel reaction mechanism, it should be noted that the formation of the [18]trannulene fragment is one of the factors responsible for the regiochemistry of nucleophilic substitution in $C_{60}F_{18}$. Actually, one of the three most activated fluorine atoms can be subjected to the nucleophilic displacement through the attack of a nucleophilic species both on the ε- and γ-carbon atoms (see Scheme 2). However, the formation of the aromatic [18]trannulene fragment is possible only upon the addition of a nucleophile at the ε-carbon atom, resulting in additional thermodynamic and kinetic stabilisation of the fullerene. After the formation of $C_{60}F_{15}[CBr(CO_2Et)_2]_3$, the fluorine atoms that remain in the molecule are separated from double bonds by aromatic π-systems of the benzenoid and [18]trannulene rings, which prevents further nucleophilic substitution.

The nucleophilic displacement of three fluorine atoms in the C_1- and C_s-$C_{60}F_{18}O$ isomers by $^-CBr(CO_2Et)_2$ anions afforded the corresponding [18]trannulenes, *viz.*, C_1- and C_s-$C_{60}F_{15}O[CBr(CO_2Et)_2]_3$, and these products were characterised.[129] These results demonstrate that the presence of the oxygen atom in the molecule results in neither steric nor electronic effects hindering the formation of trannulenes.

The reactions of $C_{60}F_{18}$ with a large number of malonates $HCX(CO_2R)_2$, with different ester [R = Me, Et, $PhCH_2$ or 3,5-$(MeO)_2C_6H_3CH_2$] and acceptor groups [X = F, Cl, Br, CN, CO_2Et, NO_2, $P(O)(OMe)_2$, SO_2CH_2Ph ot $C(O)CH_2$. $.CH_2Ph$], were studied to elucidate the influence of the nature of substituents and the size of the $^-CX(CO_2R)_2$ carbanion on the possibility of the synthesis of trannulenes.[14, 23, 129]

Almost all known malonates [except for oxomalonate $HC(C(O)CH_2CH_2Ph)(CO_2Et)_2$] were found to be involved in nucleophilic substitution reactions with $C_{60}F_{18}$. The inactivity of the oxomalonate under these conditions was attributed to the keto–enol tautomerism of the reagent.[14] The anions derived from fluoro- and cyanomalonates do not form trannulenes; instead, they give mono- or disubstituted products, *viz.*, $C_{60}F_{17}[CF(CO_2Et)_2]$, $C_{60}F_{17}[C(CN)(CO_2Et)_2]$ and $C_{60}F_{16}.[C(CN)(CO_2Et)_2]_2$, in low yields. Based on the differences in the ^{19}F NMR spectra of the fullerene derivatives $C_{60}F_{17}[C(CN)(CO_2Et)_2]$ and $C_{60}F_{17}[CBr(CO_2Et)_2]$, it was concluded [128] that cyanomalonate reacts at the γ position, *i.e.*, by the S_N2' mechanism.[14] However, it should be noted that the determination of the structure of $C_{60}F_{17}[C(CN)(CO_2Et)_2]$ only from ^{19}F NMR spectroscopic data is insufficiently reliable.

The reactions of $C_{60}F_{18}$ with $HC(SO_2CH_2Ph)(CO_2Et)_2$ and $HC[PO(OMe)_2](CO_2Et)_2$ afford trannulene-containing products in low yields.[14] The reaction of phosphorus-containing malonate is accompanied by dephosphonylation giving rise to $C_{60}F_{15}[CH(CO_2Et)_2]_3$. This is confirmed by the absence of signals in the ^{31}P NMR spectrum and resonances of the methoxy groups in the ^1H NMR spectra of the isolated product. Since potassium fluoride is known to induce dephosphonylation of tertiary phosphonates,[135] dephosphonylation of the trannulene belt is apparently initiated by fluoride anions generated in the reaction.[14]

Good yields of the corresponding trannulenes ($\sim$30%) were achieved in the reactions of $C_{60}F_{18}$ with $HCBr(CO_2R)_2$, where R = CH_2Ph [129] or $CH_2C_6H_3(OMe)_2$-3,5,[23] or with $HCX(CO_2Et)_2$, where X = Cl,[129] Br,[12, 128] CO_2Et or NO_2.[14] It should be noted that an increase in the bulk of the ester group leads to a decrease in the degree of substitution in $C_{60}F_{18}$. This can be overcome by increasing the malonate-to-fullerene ratio or introducing a bridge into malonate, resulting in an increase in the distance between the bulky substituent and the carbanionic centre.[23]

A series of trannulenes were synthesised by the reactions of $C_{60}F_{18}$ with methanetricarboxylates containing various photoactive functional groups.[22, 23] Methanetricarboxylates serve as an attractive alternative to halo- and nitromalonates. The advantages of the latter compounds are low pK_a, high nucleophilicity of anions, the absence of the keto–enol tautomerism, a rather large steric demands and stability. To achieve the efficient formation of trannulenes from $C_{60}F_{18}$, CH-acids should meet these requirements.

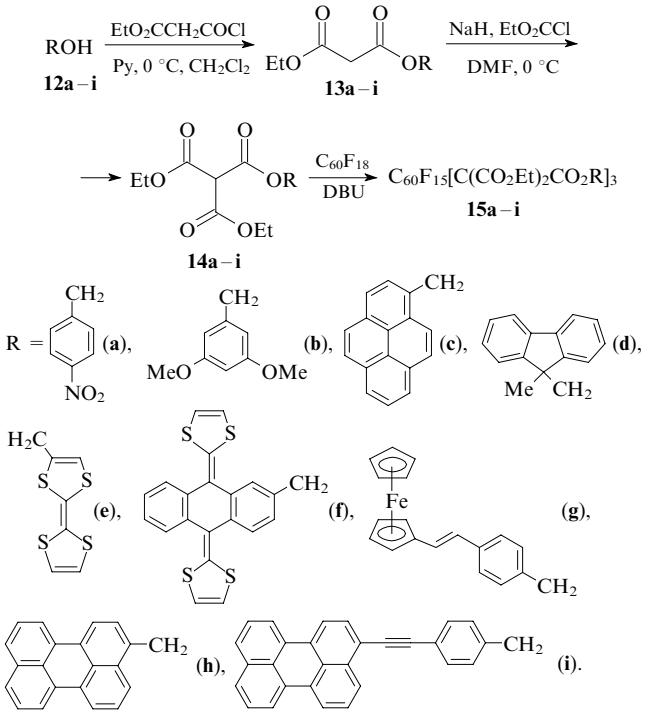
The starting methanetricarboxylates can easily be synthesised from the corresponding alcohols (Scheme 3). Commercially available alcohols **12a–i** containing photoactive fragments were used. Treatment of these alcohols with ethyl malonyl chloride afforded the corresponding malonates **13a–i**, which were deprotonated and coupled with ethyl chloroformate to form methanetricarboxylates **14a–i**. Trannulenes **15a–i** were synthesised from methanetricarboxylates **14a–i** and $C_{60}F_{18}$.

The results of the above studies demonstrate that the larger the bulk of the substituent shielding the nucleophilic carbanionic centre, the larger the amount of methanetricarboxylate **14** required for the synthesis of trannulene. Attempts to use perylene ester **14h** for the synthesis of trannulene **15h** failed in spite of a variation of the reaction conditions over a wide range. In all cases, bis-adduct **16** was obtained as the major product due to the size of the perylene fragment (Scheme 4).

The steric barrier was overcome by removing the bulky fragment from the reaction centre after the introduction of the phenylacetylene bridge between the perylene moiety and the methanetricarboxylate group. For example, the reaction of ester **14i** with $C_{60}F_{18}$ in the presence of a base produces trannulene **15i** in 31% yield.

All compounds **15** are emerald-green, which is typical of fullerene trannulenes [12, 23, 129, 134] due to intense absorption of the [18]trannulene fragment at 610–670 nm. In addition, the presence of this fragment leads to an increase in electron-withdrawing properties of the molecule, which is manifested in a substantial increase in the first potential of single-electron reversible reduction (from -0.005 to -0.10 V, CH_2Cl_2, SCE) [14, 22, 111] compared to that for $C_{60}F_{18}$ (-0.33 V, CH_2Cl_2, SCE).[108] To summarise, fullerene trannulenes have better chromophoric properties, more efficiently stabilise the negative charge compared to traditional fullerene derivatives prepared by the Bingel reaction and retain low reorganisation energy for transition into the charge-separated state due to the rigid fullerene cage. Based on this fact, it was suggested that

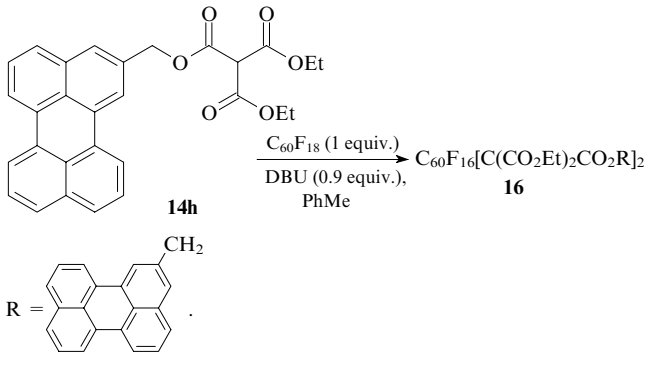
Scheme 3



Compound	**14** : $C_{60}F_{18}$: DBU ratio	Yield of **15** (%)
a	1.0 : 1.0 : 1.0	41
b	1.6 : 1.0 : 1.3	34
c	1.6 : 1.0 : 1.3	28
d	1.6 : 1.0 : 1.3	33
e	1.5 : 1.0 : 1.0	28
f	1.8 : 1.0 : 1.7	26
g	1.6 : 1.0 : 1.3	28
h	2.0 : 1.0 : 1.7	traces
i	1.6 : 1.0 : 1.3	31

trannulene derivatives of $C_{60}F_{18}$ are promising molecular 'building blocks' for the design of components of single-electron devices, molecular switches and sensors.[14, 22, 23, 136] In particular, studies of single-electron transfer in the tetrathiafulvalene–trannulene dyad demonstrated that these molecules can accumulate energy of photoexcitation in the long-lived (870 ns) charge-separated state.[22] However, it should be borne in mind that the use of fullerene trannulenes as electron-withdrawing building blocks is sometimes complicated by considerable activation barriers to the transition into the charge-separated state.[111]

Scheme 4



In conclusion of this section, it should be noted that the anomalous Bingel reaction (synthesis of trannulenes) can be accompanied by the formation of classical cyclopropanation products. For example, the reaction of $C_{60}F_{18}$ with diethyl bromomalonate generated *in situ* (from diethyl malonate and CBr_4) in the presence of DBU affords the usual cyclopropanation product C_1-$C_{60}F_{18}C(CO_2Et)_2$ in low yield.[128] It was hypothesised that the classical Bingel reaction proceeds as a result of the attack of the carbanion on the fluorine-free fullerene hemisphere. In addition, the $C_{60}F_{16}C(CO_2Et)_2$ adduct, which was generated as a result of a loss of two fluorine atoms upon cyclopropanation, was detected. The formation of this compound was attributed to defluorination of $C_{60}F_{18}$ with a base.

3. Cycloaddition to lower polyfluoro[60]fullerenes

The development of efficient methods for the synthesis and isolation of lower polyfluorofullerenes in the individual state allowed investigation of a number of cycloaddition reactions, which are widely used for functionalisation of C_{60}.[137] On the one hand, the presence of a large number of the attached fluorine atoms in polyfluorofullerene molecules leads to a strong increase in the electron affinity of these compounds compared to C_{60} and, consequently, to an increase in their electron-withdrawing properties. On the other hand, the presence of large fluorine-free fragments of the fullerene cage in lower polyfluorofullerenes allows the cycloaddition reactions to proceed without substantial steric hindrance, which is unlikely in the case of higher polyfluorofullerenes. Therefore, lower polyfluorofullerenes would be expected to be involved in cycloaddition reactions analogously to C_{60}. Due to lower symmetry of polyfluorofullerenes, a larger number of isomeric products can be formed. In addition, the reactions with electron-donating reagents can be accompanied by competitive complete or partial defluorination of substrates.

a. [2 + 3]-Cycloaddition (the Prato reaction)

One of the most widely used methods for the fullerene cage functionalisation is based on the Prato reaction (annulation of the pyrrolidine ring by the reaction of fullerene with azomethine ylides derived from α-amino acid esters and carbonyl compounds).[138]

The reaction of $C_{60}F_{18}$ with *N*-methylaminoacetic acid (sarcosine) and formaldehyde or benzaldehyde produced the corresponding fulleropyrrolidines, which were isolated and partially characterised by ^1H and ^{19}F NMR spectroscopy.[139] It should be noted that, unlike the anomalous Bingel reaction,[128] the Prato reaction with $C_{60}F_{18}$ proceeds by a traditional pathway, no products of substitution or elimination of fluorine atoms being detected. Cycloaddition to the $C_{60}F_{18}$ molecule at the fluorine-free fullerene hemisphere affords mono- and bis-adducts.

To interpret the structures of the resulting cycloadducts, it is necessary to consider possible cycloaddition patterns of azomethine ylide at C=C double bonds to form the pyrrolidine fragment. It is reasonable to exclude the double bonds involved in the benzenoid ring and the [5,6] bonds from consideration because the cycloaddition at these types of bonds reduces stabilisation due to aromatic conjugation and leads to an increase in strains in the fullerene cage. Consequently, the formation of a monoadduct can occur at one of four non-equivalent bonds, *a*, *b*, *c* or *d* (Fig. 14).

Two products prepared by annulation of the pyrrolidine ring to the $C_{60}F_{18}$ molecule (at the *a* and *c* bonds) should have C_s symmetry, whereas two other annulation products (the addition at the *b* and *d* bonds) are non-symmetrical. It is reasonable to suggest that steric hindrance does not allow the reaction to proceed at the *d* bond. Hence, the formation of three isomeric monoadducts would be expected; the bis-addition would be expected to give five symmetrical and eight non-symmetrical bis-adducts.

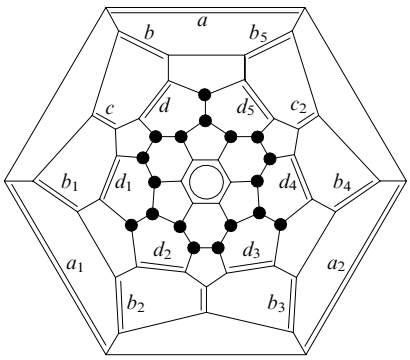
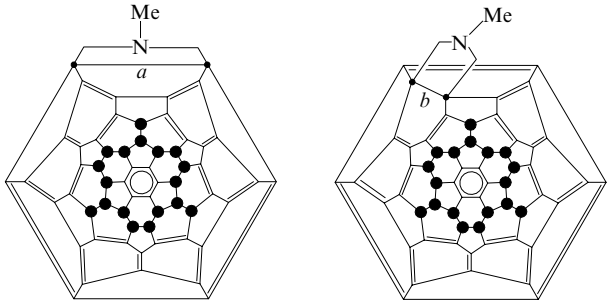


Figure 14. Possible cycloaddition sites in the $C_{60}F_{18}$ molecule.

Two monoadducts of three possible adducts were found experimentally (Fig. 15).[139] This reaction affords C_s-symmetrical monoadduct **17** as the major product as a result of the cycloaddition at the *a* bond most remote from the fluorine atoms. Non-symmetrical cycloadduct **18**, which is formed with the involvement of the *b* bond, is the minor product. The C_s-symmetrical cycloaddition product at the *c* bond was not detected in the reaction mixture. Apparently, the addition to this bond close to the flattened fragment of $C_{60}F_{18}$ leads to an increase in steric hindrance in the fullerene cage.



17 **18**

Figure 15. The Schlegel diagrams of the $C_{60}F_{18}(C_3H_7N)$ monoadducts.

Polycycloaddition products were also found, three C_s-symmetrical and four non-symmetrical bis-adducts being isolated. As in the case of monoadducts, the addition of azomethine ylide occurs predominantly at the *a* bond, whereas the addition products at the *c* and *d* bonds are absent. In other words, all bis-adducts are formed as a result of different cycloaddition patterns at the *a* and *b* bonds. For example, annulation of the pyrrolidine fragment at two *a* bonds (Fig. 16 *a*) was proposed[139] for one of the C_s-symmetrical isomers, *viz*., compound **19**. However, it should be noted that in this case the pyrrolidine rings are bound to one six-membered ring resulting in destabilisation of this isomer due to repulsion between these rings. Hence, it cannot be ruled out that C_s-symmetrical bis-adduct **19** is formed as a result of cycloaddition at the b_1, b_4 or *b*, b_1 bonds (see Fig. 16 *b*). Unfortunately, no ^{13}C NMR spectroscopic data were reported.[139]

The Prato reaction of $C_{60}F_{18}$ with sarcosine and benzaldehyde proceeds analogously to give a complex mixture of isomeric adducts.[139] Six major products and four minor

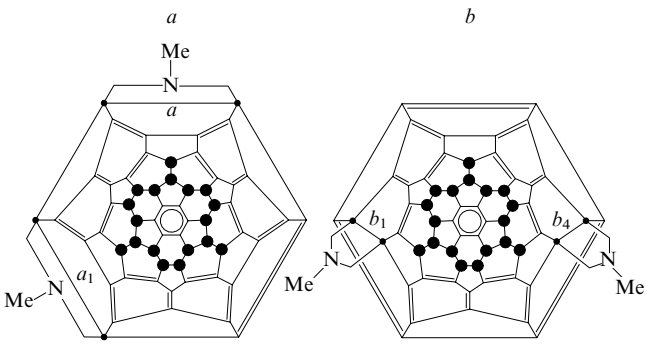


Figure 16. The Schlegel diagrams of two possible C_s-bis-adducts $C_{60}F_{18}(C_3H_7N)_2$ (**19**) (see the discussion in the text).

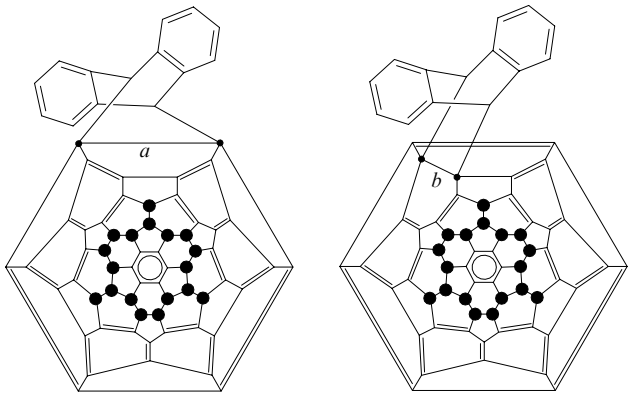


Figure 17. The Schlegel diagrams of monocycloadducts formed in the the Diels – Alder reaction of $C_{60}F_{18}$ with anthracene.

products were identified. These products were isolated in amounts insufficient for the structure elucidation.

Monoadduct **17** produced by the reaction of $C_{60}F_{18}$ with sarcosine and formaldehyde was unexpectedly detected in the reactions with other aldehydes.[139] This can be attributed to either the presence of an impurity of formaldehyde in sarcosine or the *in situ* formation of formaldehyde as a result of oxidation of sarcosine catalysed by fluorofullerene. The latter is evidenced by the fact that the major product (monoadduct) of the reaction of $C_{60}F_{18}$ with sarcosine and benzaldehyde is formed by refluxing a toluene solution of $C_{60}F_{18}$ with sarcosine in the absence of benzaldehyde in the reaction mixture! This result is attributed to the presence of traces of benzaldehyde in toluene (0.05%, HPLC data), the amount of which increases due to oxidation of toluene under the reaction conditions.

To summarize, the Prato reaction of lower polyfluorofullerenes is not accompanied by defluorination and produces complex isomeric mixtures of mono- and bis-adducts. The cycloaddition occurs predominantly at the sterically most accessible and fluorine-free fragment of the fullerene cage.

b. [2 + 4]-Cycloaddition reactions

Electron-deficient fullerene and its derivatives can be involved in the Diels – Alder reaction.[140 – 142] Polyfluorofullerenes are no exception.[13, 70] For example, refluxing of a toluene solution of $C_{60}F_{18}$ with anthracene under argon produced monocycloadducts **20** and **21**, which were isolated and partially characterised (in a ratio of 3 : 2, the total yield was 40%, Fig. 17).[13] Anthraquinone was found among by-products. The latter compound was also detected in the reactions of anthracene with C_{60} and $C_{60}Cl_6$. Apparently, fullerene or its halogen derivatives either act as oxidants in these reactions or catalyse oxidation of anthracene.

In the electron ionisation mass spectra of **20** and **21**, the molecular ion peak is absent, but the spectra show ions corresponding to $C_{60}F_{18}$ and anthracene, which is evidence that thermodesorption is accompanied by the retro reaction. This process is also typical of cycloadducts of non-halogenated C_{60}.[142]

The structures of monocycloadducts **20** and **21** were proposed based on the analysis of ^{1}H and ^{19}F NMR spectroscopic data. In this case, as in the Prato reaction, defluorination products are not observed. The major C_s-symmetrical (**20**) and minor non-symmetrical (**21**) isomers are produced by cycloaddition at the *a* and *b* bonds, respectively (see Fig. 17). Quantum chemical calculations (by the semiempirical AM1 method) of the thermal effects of the Diels – Alder reactions of $C_{60}F_{18}$ with anthracene, butadiene or benzene confirmed that the cycloaddition at the *a* bond is more favourable and this adduct is more stable.[143] Cycloadducts **20** and **21** partially decompose on storage. For example, the degree of decomposition of major compound **20** after two weeks of storage at room temperature is 5.5%. Minor product **21** is much less stable. Virtually immediately after isolation of compound **21** from the reaction mixture, a considerable amount of anthracene was detected by ^{1}H NMR spectroscopy. Moreover, spontaneous isomerisation of minor product **21** was observed. As a result, compound **20** and a new cycloadduct were obtained. The ^{19}F NMR spectroscopic study demonstrated that the latter compound has C_s symmetry although it differs from major product **20**. Apparently, this product is generated by the retro Diels – Alder reaction followed by cycloaddition at the *c* bond.

Fullerene $C_{60}F_{20}$ is another promising substrate for cycloaddition reactions. Due to high D_{5d} symmetry of the $C_{60}F_{20}$ molecule, the monoadduct can be formed as a result of cycloaddition to one of two non-equivalent [6,6] bonds (see Fig. 1 *g*). Since the approach of the reagent to one of these bonds is sterically hindered, the only cycloadduct would be formed.

The [2 + 4]-cycloaddition reaction of anthracene with polyfluorofullerene $C_{60}F_{20}$ was demonstrated [70] to proceed only under illumination and in the presence of dissolved oxygen. Oxidised non-symmetrical cycloadduct **22** was obtained in a yield of $< 40\%$. The structure of this product was proposed based on ^{1}H and ^{19}F NMR spectra (Fig. 18). The 'normal' C_s-symmetrical cycloadduct of anthracene and $C_{60}F_{20}$ was detected as an impurity.

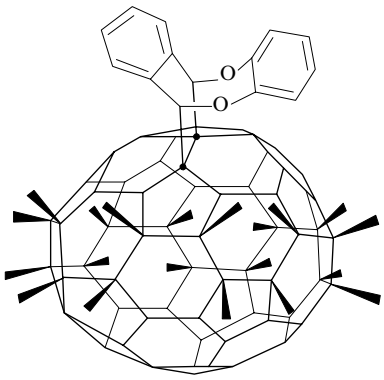
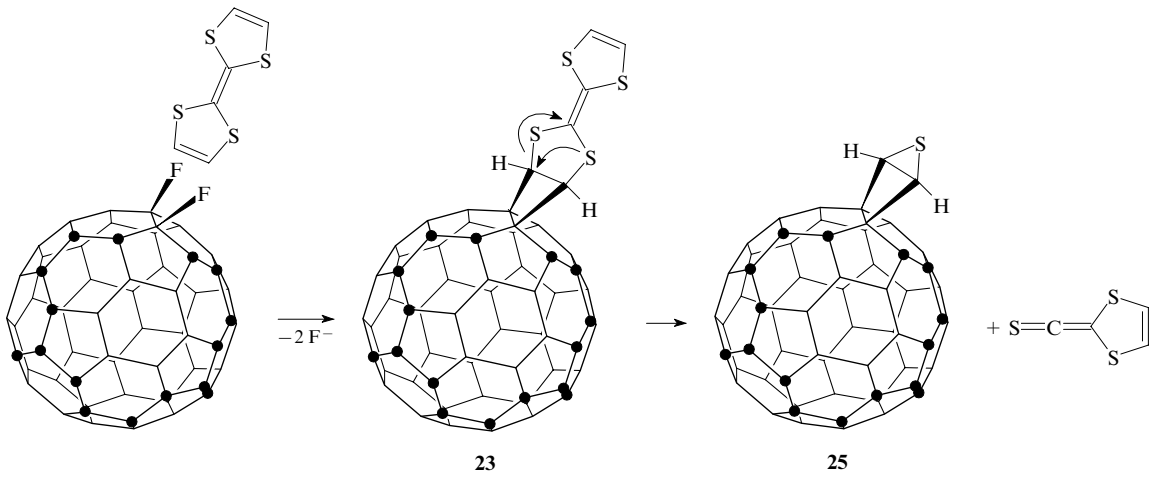


Figure 18. Structure of cycloadduct **22** (for clarity, the C – F bonds are represented as stereobonds).

Scheme 5



23 **25**

4. Miscellaneous reactions

a. Unusual cycloaddition reactions

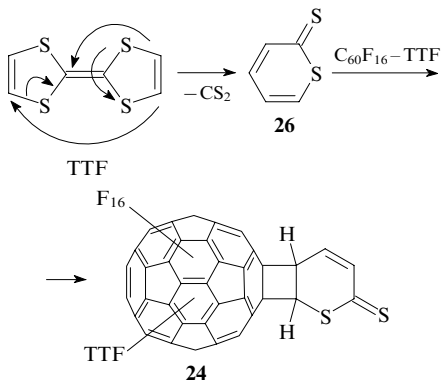
The use of tetrathiafulvalene (TTF) as an electron donor plays an important role in studies on the photoinduced electron transfer involving fullerene. Attempts to perform the reaction of $C_{60}F_{18}$ with tetrathiafulvalene led to the discovery of the previously unknown cycloaddition reaction.[15] Concentration of a solution of $C_{60}F_{18}$ and tetrathiafulvalene in toluene afforded products **23** and **24**. The non-symmetrical [$C_{60}F_{16}$ – tetrathiafulvalene] adduct (**23**) was obtained as the major product (Scheme 5).

Apparently, this reaction involves at least two steps. Initially, $C_{60}F_{18}$ undergoes partial defluorination due to the redox reaction of $C_{60}F_{18}$ with tetrathiafulvalene. Indeed, dehalogenation of $C_{60}Cl_6$, $C_{60}Br_6$ or $C_{60}Br_8$ with tetrathiafulvalene has been documented earlier,[144] although the reaction products were not isolated and characterised. Intermediate polyfluorofullerene $C_{60}F_{16}$ exhibits high reactivity with respect to tetrathiafulvalene and gives the [2 + 2]-cycloaddition product.

Storage of product **23** leads to its rearrangement to form two compounds with identical molecular masses. The unstable minor adduct was not studied in detail. Major adduct **25**, which is formed upon elimination of the thioketene fragment from derivative **23**, is a new type of fullerene derivatives, *viz*., thiirano[2,3-*a*]cyclobuta[*c*-1,2]fullerene.

The structure of compound **24** was determined by ^{1}H NMR spectroscopy and electron ionisation mass spectrometry. In this bis-adduct, unsaturated dithiolactone **26** generated from tetrathiafulvalene by elimination of CS_2 serves as the second addend (Scheme 6).

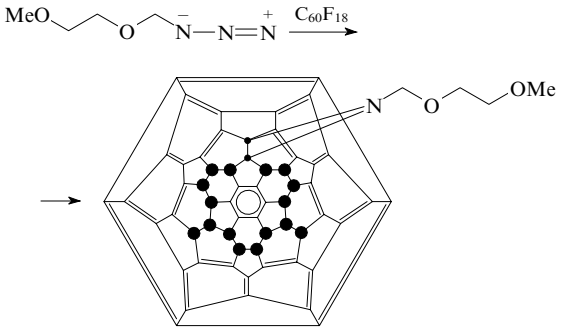
Scheme 6



26 **24**

TTF is tetrathiafulvalene.

An analogous replacement of two fluorine atoms is also observed in the reaction of $C_{60}F_{18}$ with 2-methoxyethoxymethyl azide.[145] The reactions of non-modified C_{60} with azides (in particular, with 2-methoxyethoxymethyl azide) generally produce open-cage fulleroid adducts, *viz*., azahomofullerenes, upon the [2 + 3]-cycloaddition of the azide followed by extrusion of N_2 (see, for example, Ref. 146). As in many above-considered examples, the use of polyfluorofullerenes as the substrate substantially changes the reaction pathway because of the ease of a loss of fluorine atoms giving rise to aziridinopolyfluorofullerene $C_{60}F_{16}N(CH_2OCH_2CH_2OMe)$.



b. Radical reactions

Fullerenes are readily involved in radical addition reactions.[25] In particular, the reactions of C_{60} with molecular fluorine [1, 11, 43] and with radical species generated *in situ* by decomposition of peroxides,[147] alkyl and perfluoroalkyl iodides,[6, 148] metal trifluoroacetates,[149] *etc*. were documented.

Polyfluorofullerenes are also involved in radical addition reactions but they are less reactive than fullerene. As mentioned above, fluorination of C_{60} with molecular fluorine proceeds by a radical mechanism. Evidently, fluorination of lower polyfluorofullerenes by fluorine also proceeds by a radical mechanism. The transformation of $C_{60}F_{36}$ into $C_{60}F_{48}$ is an example of such reactions.[64] As was discussed in Section II.1.a, further fluorination occurs under more drastic conditions due to steric strains and is accompanied by decomposition of the fullerene cage.[11, 58]

The formation of the mixed compounds $C_{60}F_x(R^F)_y$ (R^F = CF_3 or C_2F_5), which were detected in the reaction of C_{60} with high oxidation state metal fluorides, is yet another interesting example.[45, 82, 150] The 1,9- and 1,7-$C_{60}FCF_3$, C_1-$C_{60}F_5CF_3$,[150, 151] C_1-$C_{60}F_7CF_3$ (see Refs 45, 46 and 150) and C_s-$C_{60}F_{17}C_2F_5$ isomers and three isomers of $C_{60}F_{17}CF_3$, *viz*., one C_s-symmetrical isomer (65% of the total amount) and a pair of C_1 enantiomers (35%),[82, 152] were isolated from these reaction mixtures by HPLC. The structures of the compounds

were proposed based on ^{19}F NMR spectroscopic data and results of quantum chemical calculations. It should be noted that $C_{60}F_{17}CF_3$ has initially been considered [152] as the difluoromethanofullerene derivative $C_{60}F_{18}CF_2$. However, more recent X-ray diffraction study demonstrated [82] that this compound is an analogue of $C_{60}F_{18}$, with the only difference that one of the sterically most accessible fluorine atoms is replaced by the CF_3 group.

In a number of studies,[36, 82, 152] it was hypothesised that mixed fluoro- and perfluoroalkyl derivatives are generated through the insertion of the difluorocarbene $:CF_2$ into polyfluorofullerene at C–F bonds. The origin of difluorocarbene is attributed to thermal destruction of polyfluorofullerenes. This reaction can proceed analogously to the insertion of methylene into the C_{60} molecule upon hydrogenation [153] with the only difference that the methylene group is inserted at the double bond of fullerene, whereas difluoromethylene is inserted at the C–F bond. However, it should be noted that the more probable pathway of the formation of perfluoroalkylated fullerene derivatives involves the addition of the $^{\bullet}CF_3$ or $^{\bullet}C_2F_5$ radicals that are generated upon thermal destruction of polyfluorofullerenes to fullerene or its fluorination products. Actually, these radicals were detected upon decomposition of polyfluorofullerenes.[8, 58, 154, 155] Convincing evidence for the formation of mixed derivatives in the reaction of [60]fullerene with $^{\bullet}CF_3$ was reported.[67] It was demonstrated that the independent generation of the $^{\bullet}CF_3$ radicals at the moment of fluorination of fullerene with K_2PtF_6 gives rise predominantly to mixed fluoro and CF_3 derivatives of fullerene with the compositions $C_{60}F_{18-n}(CF_3)_n$ and $C_{60}F_{20-m}(CF_3)_m$ (n = 1–5, m = 1–6).

IV. Reactions of polychloro[60]fullerenes

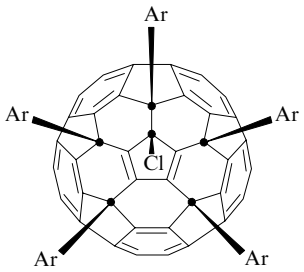
Until recently, $C_{60}Cl_6$ has been the only polychlorofullerene that was available in preparative amounts in high purity form.[89] Because of this, the reactions of polychlorofullerenes were studied in most detail for this compound. Higher chlorides, for example, $C_{60}Cl_{24}$,[100] $C_{60}Cl_{28}$ (Ref. 74) and two isomers of $C_{60}Cl_{30}$, were synthesised and isolated in the individual state.[99] This will help in studying their reactivity in detail and synthesising new derivatives of the fullerene series.

1. Arylation of polychlorofullerenes

Polychlorofullerenes readily enter the Friedel–Crafts reaction.[2] For example, ^1H and ^{13}C NMR spectroscopic studies demonstrated that stirring of a benzene solution of $C_{60}Cl_n$ with catalytic amounts of $AlCl_3$ at room temperature for 2 h leads to the formation of polyphenylfullerenes (according to mass-spectrometric data, up to 22 phenyl groups are attached).

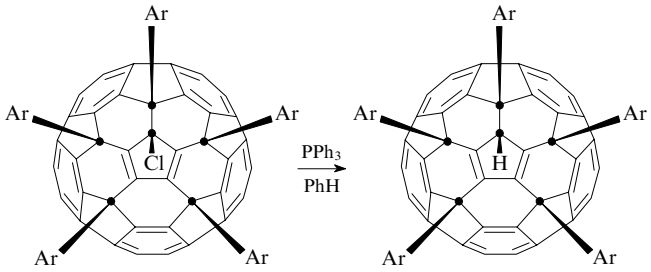
$$C_{60}Cl_n \xrightarrow[AlCl_3]{PhH} C_{60}Ph_m$$

The Friedel–Crafts reaction of fullerene $C_{60}Cl_6$ with various aromatic substrates was studied in detail.[156–158] The reactions of $C_{60}Cl_6$ with arenes in the presence of $FeCl_3$ were demonstrated to give the corresponding C_s-symmetrical aryl derivatives $C_{60}Ar_5Cl$ in yields ranging from 48% (Ar is thienyl) to 63% (Ar = 4-FC_6H_4). The reaction with toluene proceeds both at the *para* and *ortho* positions. The reactions with anisole and fluorobenzene gave exclusively *para*-substituted products, which were isolated and completely characterised.[157] The replacement of chlorine atoms by aryl groups at the same positions as those occupied by chlorine atoms in $C_{60}Cl_6$, indicates that the reaction proceeds through the cationic fullerene intermediate.



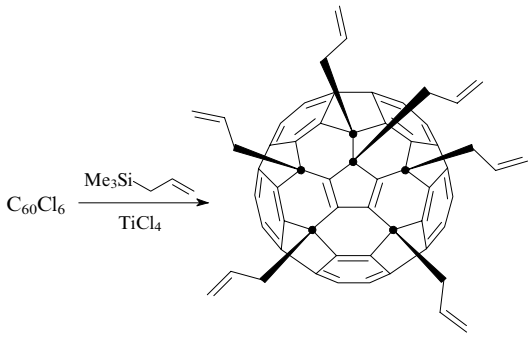
Ar = XC_6H_4 (X = H, Me, MeO, Bu^t, F, Me_3Si), thienyl.

In a more recent detailed study [158] of the reaction of $C_{60}Cl_6$ with fluorobenzene in the presence of $FeCl_3$, the major product $[C_{60}(4\text{-}FC_6H_4)_5Cl]$ was detected along with two C_s-symmetrical isomers of 1,4-$(4\text{-}FC_6H_4)_2C_{60}$, one non-symmetrical isomer of $C_{60}(4\text{-}FC_6H_4)_4$ and a small amount of $C_{60}(4\text{-}FC_6H_4)_4H_2$. The following scheme was proposed for the explanation of the formation of the latter compound. Initially, two chlorine atoms are replaced by a hydrogen atom, which is most likely generated from the solvent. The resulting intermediate enters the Friedel–Crafts reaction with fluorobenzene.[159] The substitution of hydrogen for chlorine atoms was also observed in the reaction of $C_{60}Ar_5Cl$ with triphenylphosphine.[157]



Ar = 4-FC_6H_4.

The steric hindrance in $C_{60}Cl_6$, which is the presently known bulkiest electrophile, plays an important role. For example, no reaction occurs with sterically hindered mesitylene.[158] At the same time, reagents with lower steric demands can replace all six chlorine atoms. For example, the reaction of $C_{60}Cl_6$ with an excess of allyltrimethylsilane in the presence of $TiCl_4$ produces hexaallylfullerene $C_{60}(CH_2CH{=}CH_2)_6$ in good yield.[160]



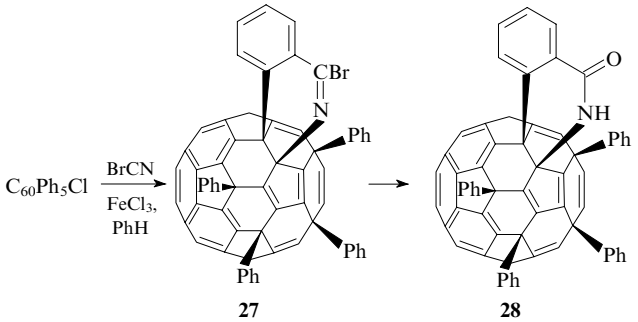
In this case, the steric factors are less significant, which facilitates the complete replacement of chlorine atoms. The pentasubstituted compound $C_{60}(CH_2CH{=}CH_2)_5Cl$ was isolated as a minor reaction product.

A comparative study of the geometry and electronic structures of the compounds $C_{60}Cl_6$, $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$ by quantum chemical calculations (the AM1 method) demonstrated that the nature of functional groups has no noticeable effect on the bond lengths in the fullerene cage (the difference in the lengths of the analogous C–C bonds is at most 0.01 Å).[161] For these derivatives, the addition of functional groups leads to a loss of the icosahedral (I_h) symmetry, cleavage of five carbon–carbon double bonds and the appearance of the isolated cyclopentadienyl fragment. The C–C bonds involving sp^3-hybridised carbon atoms (1.50–1.55 Å) are longer than those in C_{60}. The ^{1}H NMR spectroscopic study revealed free rotation of the phenyl groups at room temperature. This is consistent with the results of calculations by the AM1 method, according to which there is a large number of conformations in a narrow energy range. Therefore, the molecules $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$ are 'pseudo-C_s-symmetrical'.[156]

Calculations of the Mulliken charges illustrated the almost neutral character of chlorine atoms relative to the fullerene cage in $C_{60}Cl_6$ and a weak donor character of the phenyl groups in $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$. Each phenyl group in these compounds donates, on the average, 0.038 (in $C_{60}Ph_5Cl$) and 0.02 electrons (in $C_{60}Ph_5H$) to the carbon cage. The hydrogen atom bound directly to the fullerene cage acts as a strong donor (+0.217 e) and the chlorine atom, as a weak acceptor (−0.044 e). Unlike $C_{60}Ph_5H$, in which the negative charge is almost uniformly distributed over the functionalised fragment, the total charge in $C_{60}Ph_5Cl$ (0.150 e) donated by the addends is mainly redistributed to the intact part of the cage (−0.143 e).

Due to a combination of the aryl substituents and the reactive chlorine atom in the molecules $C_{60}Ar_5Cl$, the latter can be used as the starting compounds for further functionalisation.[162,163] For example, a new pathway of spontaneous oxidation of $C_{60}Ph_5X$ (X = H or Cl) to the benzofuran derivative of C_{60}, in which the oxygen atom forms a bridge between the carbon cage and one of the benzene rings, was found (see Section IV.2).[163]

The treatment of $C_{60}Ph_5Cl$ with cyanogen bromide allows the annulation of the quinoline fragment onto the fullerene cage.[162] The reaction is accompanied by a loss of the chlorine atom and the formation of the bromine-substituted CN bridge between the carbon cage and the *ortho* position of the adjacent benzene ring to form 1-bromoisoquinoline derivative **27**.

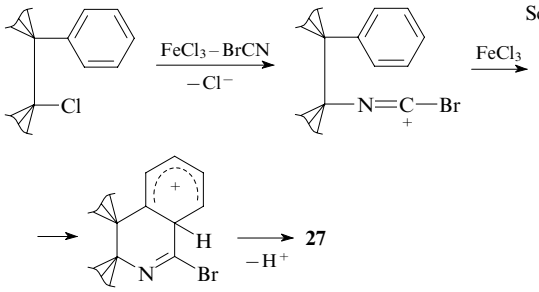


27 **28**

The structure of this derivative was confirmed by the synthesis of amide **28** by the nucleophilic substitution of a hydroxy group for the bromine atom.[162] Like the other amides, compound **28** is poorly soluble and crystallises from benzene as orange-red plates.

The proposed[162] mechanism of the formation of compound **27** (Scheme 7) is based on the experimental facts that the reaction does not proceed in the absence of $FeCl_3$ and that $C_{60}(4\text{-}FC_6H_4)_5Cl$ does not undergo this transformation. The dependence of the process on the presence of a strong Lewis acid is indicative of the involvement of a carbocationic intermediate in this reaction. In this case, the intermediate

Scheme 7



can be generated in the reaction of $FeCl_3$ with either $C_{60}Ph_5Cl$ or BrCN.

It should be noted that if the complex of BrCN with iron(III) chloride were an intermediate of this reaction, an electrophile would be formed and the latter would attack the phenyl group in $C_{60}Ph_5Cl$ predominantly at the most accessible *para* or (taking into account the electron-withdrawing character of the fullerene substituent) *meta* position. However, the absence of these products in the reaction mixture suggests that the transformation of $C_{60}Ph_5Cl$ into product **27** proceeds by a different mechanism involving the formation of the $C_{60}Ph_5^+$ cation.

Due to considerable steric hindrance, the $C_{60}Ph_5^+$ cation cannot react with the phenyl group of another $C_{60}Ph_5Cl$ molecule, but can react with the small BrCN molecule at the nitrogen atom. Then the electrophilic attack of the resulting iminium cation on the adjacent phenyl group occurs. The strong electron-withdrawing properties of fullerene hinder the electrophilic substitution in the aryl moiety bound to the fullerene cage. Nevertheless, high electrophilicity of the bromoiminium cation and the intramolecular character of the reaction (the entropy factor) do make this cyclisation possible.[164] In $C_{60}(4\text{-}FC_6H_4)_5Cl$, the electronegative fluorine atom is in the *meta* position to the site of attack and has a negative inductive effect, which makes the electrophilic attack even more difficult. In combination with the electron-withdrawing effect of the fullerene cage, this is sufficient for deactivation of the benzene ring even toward the intramolecular attack by the iminium electrophile.

2. Nucleophilic substitution reactions

Polychlorofullerenes are sensitive to hydrolysis and readily react with nucleophiles.[2] For example, the reaction of a mixture of polychlorofullerenes with excess KOH under reflux in methanol produced polymethoxyfullerenes, the most substituted product containing 26 methoxy groups (mass spectrometric data).[2]

$$C_{60}Cl_n \xrightarrow[\Delta]{MeOH,\ KOH} C_{60}(OMe)_m$$

This reaction proceeds simultaneously with partial hydroxylation of the substrate.

The reaction of a benzene solution of $C_{60}Cl_6$ with sodium alkoxide in the corresponding alcohol ROH (R = Me, Et) produces $C_{60}(OR)_5Cl$ in moderate yields (15%–20%).[165] The reaction proceeds rather rapidly under reflux, but several days are required for its completion at room temperature. The reaction of $C_{60}Cl_6$ with EtO^- yields 1,4-$(EtO)_2C_{60}$ as a by-product. Therefore, the substitution reaction is competitive with elimination of chlorine atoms. When $C_{60}Cl_6$ is heated with an alcohol in the absence of alkoxide ions, which are stronger nucleophiles, dechlorination becomes the main reaction. For example, the reaction of a benzene solution of $C_{60}Cl_6$ with methanol or isopropyl alcohol under reflux for 140 h produces 1,4-$(MeO)_2C_{60}$ or 1,4-$(Pr^iO)_2C_{60}$ in 11%–30% yields.[165] The

reaction of $C_{60}Cl_6$ with secondary aliphatic amines gives 1,4-diaminofullerenes (in 5% – 20% yields) and an inseparable mixture of tetra- and hexaaminofullerenes.[166]

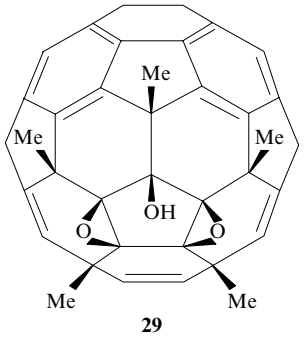
The reaction of $C_{60}Cl_6$ with an excess of methyllithium in a THF – cumene mixture at room temperature affords a complex mixture of products.[167] The completely alkylated derivative $C_{60}Me_6$ and chloropentamethylfullerene $C_{60}Me_5Cl$ are among the major reaction products. Since the arrangement of the addends typical of $C_{60}Cl_6$ is retained in these compounds, it was hypothesised that the reaction involves the frontal replacement of chlorine atoms by nucleophilic species. However, as mentioned above, we are doubtful about this mechanism.

As discussed above, the reactions of higher polyfluorofullerenes with nucleophiles proceed by the S_N2' mechanism. This mechanism is also possible for the transformation of $C_{60}Me_5Cl$ into $C_{60}Me_6$. However, it is inconsistent with the retention of the arrangement of the addends upon the transformation of $C_{60}Cl_6$ into $C_{60}Me_5Cl$, since it is known that alkyllithium compounds are involved in exchange reactions with alkyl halides rather than give coupling products. Presumably, the transformation of $C_{60}Cl_6$ into $C_{60}Me_5Cl$ involves the halogen – metal exchange step:

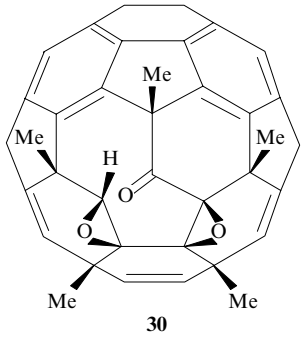
$$RX + R'Li \longrightarrow RLi + R'X.$$

This process was found to partly proceed in the reaction of phenyllithium with polyfluorofullerenes,[107] as evidenced by the presence of a certain amount of fluorobenzene as one of by-products. It is also known [168 – 173] that alkali metal fullerides smoothly react with alkyl halides to form the corresponding alkylfullerenes.

The compound $C_{60}Me_5Cl$ readily undergoes hydrolysis and oxidation.[165, 167, 174, 175] In the presence of atmospheric oxygen, epoxides with the compositions $C_{60}Me_5(O)OH$, $C_{60}Me_5O_2OH$ and $C_{60}Me_5O_3H$ were obtained. The X-ray diffraction study showed that the hydroxy group in the molecule $C_{60}Me_5O_2OH$ (**29**) occupies the position of the chlorine atom in the molecule $C_{60}Me_5Cl$, and two oxygen atoms form epoxide functions attached at the double bonds of the butadiene fragment in the five-membered ring.[174]



29

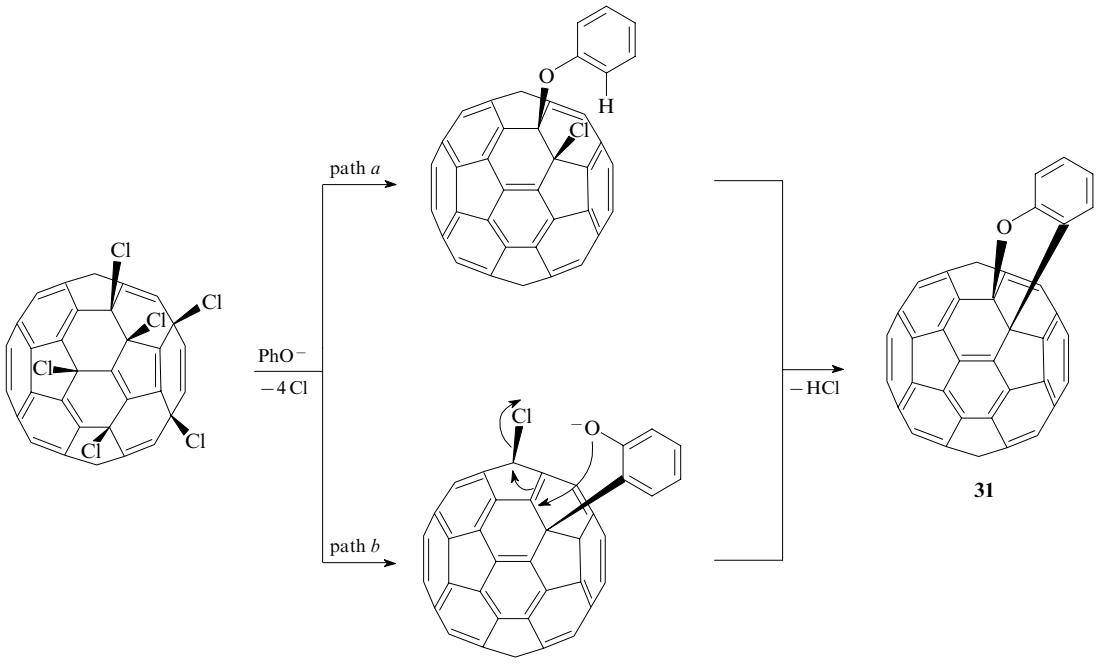


30

The compound $C_{60}Me_5O_3H$ (**30**) isomeric to bis(epoxy)fullerenol **29** is bis-epoxy ketone containing the open-cage fullerene, and compounds **29** and **30** undergo interconversions through the 1,3-tautomeric shift of the hydrogen atom of the hydroxy group.[175] It should be noted that the compounds $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$ containing a truncated pentagonal pyramidal fragment undergo oxidation too. The high reactivity of this fragment is apparently attributed to a high π-electron density on the double bonds.[176] The tendency of these oxygen-containing compounds to undergo decarbonylation during thermolysis, which can lead to an opening of the fullerene cage, is an important but, unfortunately, poorly studied characteristic feature of such compounds.[158, 167, 174]

The reactions of $C_{60}Cl_6$ with phenols (PhOH, 4-FC_6H_4OH or 4-$MeOC_6H_4OH$) and aniline in the presence of water and KOH represent an unusual example of the nucleophilic displacement of chlorine atoms followed by cyclisation.[177] The reactions with phenol or its substituted analogues produce benzofuran derivatives **31** (Scheme 8), while aniline gives indolofullerene. It should be noted that, although the reaction can lead to the nucleophilic displacement of several chlorine atoms by phenoxy or anilino groups, only one of these groups undergoes cyclisation to give a heterocyclic (benzofuran or indole) functional group. Other chlorine atoms are either eliminated or are subjected to the nucleophilic substitution without the ring formation. It was demonstrated that thiophene, being a weak nucleophile, does not react, and the

Scheme 8



31

reaction rate increases in the series PhOH < 4-FC_6H_4OH < 4-$MeOC_6H_4OH$ < $PhNH_2$ in accordance with an increase in the nucleophilicity of the reagent.

It was hypothesised [177] that a derivative with a chlorine atom bound to the fullerene cage in the *ortho* position with respect to the arene group, is formed as an intermediate in this reaction, and cyclisation occurs as a result of a loss of the *ortho*-hydrogen atom of the aromatic ring and the chlorine atom (see Scheme 8, path *a*).[177] In our opinion, it is more probable that this reaction involves the initial nucleophilic attack on the polychlorofullerene cage by the *ortho*-carbon atom of the phenoxide ion followed by the substitution of the phenoxide for the chlorine atom (see Scheme 8, path *b*) according to one of the above-considered nucleophilic substitution mechanisms.

V. Reactions of polybromo[60]fullerenes

Unlike reactions of polyfluoro and polychloro derivatives of fullerenes, chemical transformations of polybromofullerenes have not been adequately studied because the use of the latter as synthons is limited by their poor solubility and instability in most of organic solvents.[89] For example, dissolution of $C_{60}Br_6$ in chloroform, dichloromethane, 1,2-dichlorobenzene, carbon disulfide or cyclohexane is accompanied by its complete decomposition into C_{60} and Br_2.[103, 144] Disproportionation of $C_{60}Br_6$ giving rise to C_{60} and $C_{60}Br_8$ upon dissolution in organic solvents was also documented.[5, 103] Decomposition of $C_{60}Br_8$ to the starting fullerene and molecular bromine occurs upon heating in organic solvents to 70–80 °C, whereas $C_{60}Br_{24}$ does not decompose even upon prolonged refluxing in 1,2-dichlorobenzene (180 °C).[103] Therefore, thermal stability of polybromofullerenes in organic solvents increases in the series $C_{60}Br_6$ < $C_{60}Br_8$ < $C_{60}Br_{24}$, which is consistent with the thermogravimetric data for crystalline polybromofullerenes.[102] Thermal decomposition of polybromofullerenes under an inert atmosphere or under vacuum leads to molecular bromine and C_{60} fullerene. In the presence of oxygen, this process is accompanied by the formation of fullerene oxides, which, under these conditions, are readily involved in the cycloaddition reaction to form difullerenofuran derivatives.[178] It should be noted that thermolysis of polybromofullerenes in the presence of oxygen affords rather easily fullerene oxides. On the contrary, C_{60} fullerene is involved in these reactions only in the presence of strong oxidising agents, *e.g.*, ozone or peroxides, or as a result of photochemical or electrochemical reactions.[179, 180]

Like other halogen derivatives of fullerenes, polybromofullerenes enter the Friedel–Crafts reaction with arenes catalysed by $AlBr_3$ or similar Lewis acids.[2, 181] The reactions of $C_{60}Br_{24}$ with benzene, toluene or fluorobenzene in the presence of $AlBr_3$ produce polyarene derivatives $C_{60}Ar_n$ ($n = 2–16$; Ar = Ph, MeC_6H_4 or FC_6H_4).[181] In the presence of organic electron donors of the tetrathiafulvalene series, $C_{60}Br_6$ and $C_{60}Br_8$ undergo debromination accompanied by the formation of C_{60} and the donor radical cation.[144]

The reaction of polybromofullerene $C_{60}Br_{24}$ with methanolic KOH produces a complex mixture of polymethoxyfullerenes $C_{60}(OMe)_n$ ($n = 2–26$).[181] The treatment of polybromofullerenes with aqueous alkalis or aqueous dioxane leads to their complete hydrolysis to form fullerenols with complex composition.[182] In the case of aqueous dioxane, the substitution of bromine atoms in fullerenes $C_{60}Br_8$ and $C_{60}Br_{24}$ is the main reaction giving rise to compounds of compositions similar to $C_{60}(OH)_{10}$ and $C_{60}(OH)_{26}$, respectively. In reactions with aqueous alkalis, the nucleophilic substitution of bromine atoms is accompanied by the additional attachment of hydroxy groups to the fullerene cage to give fullerenols containing a large number of hydroxy groups, whatever the composition of the starting polybromofullerene. An elemental analysis demonstrated that alkali metal fullerenolates are present among the products obtained by alkaline hydrolysis of polybromofullerenes. This fact accounts for higher solubility of these fullerenols in water compared to fullerenols prepared according to other procedures. It should be noted that pH of aqueous solutions of alkali metal fullerenolates is close to neutral, which is typical of salts of strong acids. This is apparently due to the strong electronegative nature of the fullerene cage functionalised by a large number of electron-withdrawing hydroxy groups.

It was demonstrated that polybromofullerenes react with silver trifluoroacetate upon heating in aromatic hydrocarbons.[182] In the case of $C_{60}Br_8$ and $C_{60}Br_{24}$, the compounds with the compositions $C_{60}(CF_3COO)_{2-3}(OH)_{6-5}$ and $C_{60}(CF_3COO)_{2-4}(OH)_{6-7}$ were obtained as the major products. It can be seen that the compositions of the resulting compounds do not correlate with the number of the replaced bromine atoms. The formation of hydroxy derivatives was attributed to high sensitivity of the intermediates to atmospheric moisture. However, the products do not undergo further hydrolysis in the presence of HCl. Analogously, phosphorylation of $C_{60}Br_{24}$ and $C_{60}Br_6$ in THF by $(EtO)_2$-POLi leads to the addition of up to six diethoxyphosphoryl groups $PO(OEt)_2$ to the fullerene cage.[181]

The selective substitution of bromine atoms in polybromofullerenes is exemplified by the reactions of $C_{60}Br_{24}$ with $SbCl_5$ (or with $KICl_4$) at 140–150 °C [74, 100] and with XeF_2 in liquid anhydrous HF at room temperature.[50] In both cases, the T_h-$C_{60}Cl_{24}$ and T_h-$C_{60}F_{24}$ compounds isostructural to the starting polybromofullerene were obtained as the major products. Polychlorofullerenes, in turn, can be transformed into T_h-$C_{60}Br_{24}$ by the reactions with liquid bromine.[73] In earlier studies,[71, 183] attempts have also been made to replace bromine and chlorine atoms by fluorine; however, individual compounds have not been obtained.

It should be noted that, according to quantum chemical calculations, fullerene T_h-$C_{60}F_{24}$ is thermodynamically unstable and can undergo disproportionation to $C_{60}F_{18}$ and $C_{60}F_{36}$. Apparently, that is why this compound was not isolated from products of high-temperature syntheses of polyfluorofullerenes under thermodynamic control.[34, 183] However, T_h-$C_{60}F_{24}$ can be synthesised by the reaction of $C_{60}Br_{24}$ with XeF_2 under mild conditions, which is evidence for its kinetic stability to further rearrangements. Unfortunately, the mechanism of this reaction remains unknown and it can only be hypothesised that the reaction involves the concerted Br–F exchange at the sp^3-carbon atom or(and) a sequence of addition and elimination reactions.[50] It cannot be ruled out that the reaction of $C_{60}Br_{24}$ with XeF_2 is of the radical cation nature, analogously to that assumed for fluorination of bromopentafluorobenzene C_6F_5Br or bromotetrafluorobenzenes C_6F_4HBr with xenon difluoride in liquid HF.[184, 185] The reaction of benzene derivatives with XeF_2 is not accompanied by debromination, which is apparently associated with a higher C–Br bond energy in these compounds. In the case of polybromofullerenes, in which the bromine atoms are bound to tertiary carbon atoms and cause steric strain in the cage, the C–Br bond energy is substantially lower, resulting in elimination of bromine atoms. Nevertheless, mixed compounds with the composition $C_{60}F_{25}Br$ were detected among the reaction products of $C_{60}Br_{24}$ with XeF_2. Therefore, under these conditions, not only the substitution of fluorine for bromine atoms, but also the addition of fluorine atoms to the fullerene cage is observed.

* * *

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