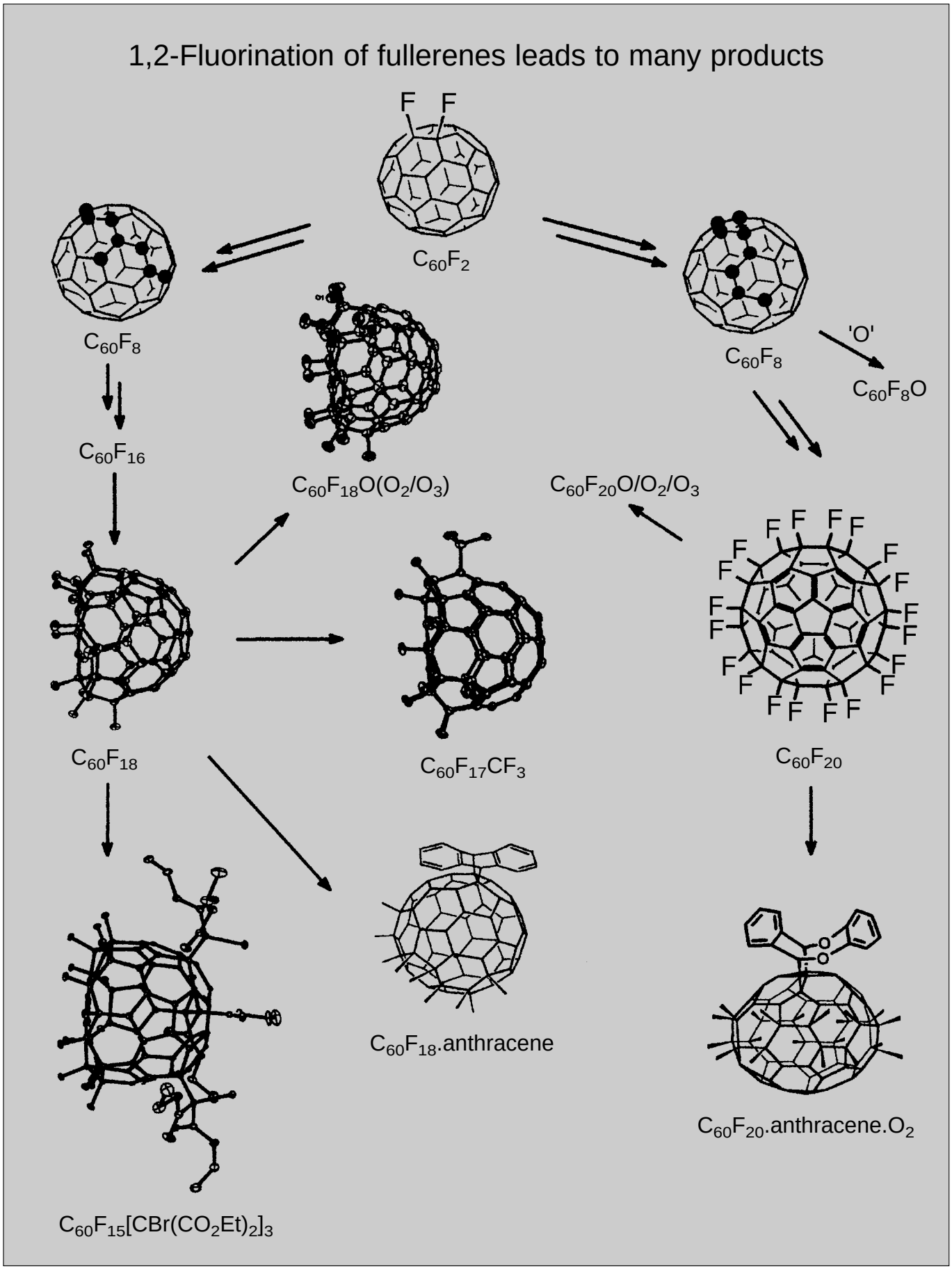

0947-6539/01/0719-4074 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 19

Fluorinated Fullerenes

Roger Taylor*[a]

Abstract: Recent developments in fluorination of fullerenes coupled with HPLC separation have permitted the isolation and subsequent structural characterisation of many derivatives, a number of which have novel and unexpected structures. The good solubility of fluorofullerenes, high reactivity towards nucleophiles and enhanced dienophilicity of the unsubstituted part of the cage, as a result of electron withdrawal by the fluorines, makes fluorofullerenes promising synthons. In particular that may have enhanced performance in donor–acceptor complexes with respect to bare fullerenes.

Keywords: annulenes · cycloaddition · fluorine · fullerenes · nucleophilic substitution

Introduction

Approximately 100 fluorofullerenes and derivatives have now been isolated and either partially or fully characterised. These include fluorinated [60]-, [70]-, [76]-, [78]-, [82]- and [84]fullerenes, fluorinated aza[60]fullerene, together with derivatives including epoxides, ethers (oxahomofullerenes), trifluoromethylfullerenes, cycloadducts, as well as aryl compounds and annulenes resulting from nucleophilic substitutions. The general properties and problems associated with fluorination are first described briefly.

Interest in fluorinating fullerenes arose initially from a belief that a material with properties analogous and possibly superior to Teflon could result from their total fluorination.[1] However, this overlooked the inability of the cage to flex significantly, hence twisting in order to avoid eclipsing interactions between adjacent C–F bonds cannot take place. These interactions preclude very high fluorination levels (i.e., $> C_{60}F_{48}$) and result in a calculated decrease in the C–F bond energy by 15% relative to a C–F bond in CF_4.[2]

[a] Dr. R. Taylor
School of Chemistry, Physics and Environmental Sciences
Sussex University, Brighton BN1 9QJ (UK)
Fax: (+44) 1273-677196
E-mail: r.taylor@sussex.ac.uk

Thus compared to Teflon, there is a reduced thermodynamic stability and a susceptibility to nucleophilic attack at the accessible carbon centres.[3] However, this reactivity combined with the good solubility of fluorofullerenes in many solvents (ca. 3 mg mL^{-1}—precise and relative values have yet to be determined) has changed the focus of interest in fluorofullerenes to one of product characterisation and derivatisation. The hydrophobic nature of fluorofullerenes causes them to be stable towards moisture unless a cosolvent is present.

Electron withdrawal is enhanced relative to the parent fullerenes as shown by: 1) increase in electron affinities by approximately 0.05 eV per added fluorine, the incremental effect decreasing at higher addition levels;[4, 5] 2) the reduction potential of $C_{60}F_{48}$ is 1.38 V more positive than for C_{60} (0.79 V with respect to the SCE compared to -0.59 under the same conditions; addition of a second electron causes loss of fluoride to give $C_{60}F_{47}^-$).[6] Thus fluorofullerenes have considerable potential as enhanced acceptors in donor–acceptor diads. The hitherto unavailability of the pure compounds in substantial amounts has resulted in a paucity of other comparative data, though the heats of formation of $C_{60}F_{48}$ and $C_{60}F_{36}$ (isomer mixture) have been determined (crystal, 298 K) as -7560 and -5360 kJ mol^{-1}, respectively.[7]

Fluorofullerene research is likely to expand once problems associated with production and purification of larger quantities can be overcome, and fluorine-decoupled ^{13}C NMR spectroscopy facilities become more widely available.

Eclipsing interactions are unimportant at lower addition levels, so that the combination of low steric requirements, product stability, and ease of ^{19}F NMR spectroscopic characterisation makes fluorination pre-eminent for determining the fundamental regiochemical properties of the fullerene cages. Thus in contrast to chloro- and bromofullerenes, EI mass spectrometry can be used for product identification; as is general for fullerene derivatives, the stability decreases the lower the addition level. HPLC separation of products is aided by both the high solubility of fluorofullerenes in toluene and the considerable difference in polarities of fluorofullerenes of fairly similar structure.

Two features dominate fullerene fluorination and are evident in the characterised derivatives. These are the attachment of fluorine pairs across 6,6-bonds, and the tendency to create structures with increased aromaticity relative to the fullerene precursor.

  0947-6539/01/0719-4075 $ 17.50+.50/0

Because it is difficult to see the locations of substituents in "three-dimensional" diagrams of polyaddended fullerenes, Schlegel diagrams are used extensively in this article.

Fluorinating Reagents

Only those fluorinating conditions which have led to isolable and characterisable derivative are described here.

Fluorine gas and xenon difluoride: Initial fluorination work involved the use of either F_2 or XeF_2 as fluorinating reagents and encountered a major problem.[8–11] Since no solvent stable to the reagents will dissolve fullerenes, fluorination has to be carried out under heterogeneous conditions, thereby precluding control over the extent of fluorination. Attempts to use short times of exposure to fluorine in order to reduce the fluorination level fail because of the close packing of the fullerene molecules. Hence fluorine attacks the outermost molecules, and extensively fluorinates these which expand away from the cluster (swelling is visible),[9, 10] thereby exposing the next layer. If therefore fluorination is stopped after a limited time, the product consists of a mixture of highly fluorinated and unfluorinated fullerenes.[12] A further consequence of the fullerene packing is that mixtures of C_{60} and C_{70} fluorinate much more rapidly than pure C_{60},[13, 14] due to the greater ease of penetration of the more open lattice of the mixture.[9] (Similar reasons cause *pure* C_{60} to dissolve only very slowly in hexane,[15] and C_{120} to dissolve much more slowly than when mixed with C_{60}.[16])

Thus for some time the only pure fluorinated fullerene that could be isolated was $C_{60}F_{48}$, the success being due to steric hindrance which drastically reduces the fluorination rate once 48 atoms have been added to the [60]fullerene cage. A high yield of this compound can be obtained by using severe fluorinating conditions, namely, fluorine at about 275 °C in either the presence[17] or absence of NaF.[18] Fluorination does continue above this level to produce traces of compounds up to $C_{60}F_{60}$ and beyond (necessarily involving in these latter cases, cage opening).[18] The cage-opening produces fluorinated fragments and evidence for their subsequent reactions is presented below.

Metal fluorides: Fluorination of fullerenes by metal fluorides was introduced by Dr. Olga Boltalina of Moscow University, and is carried out at high temperature (ca. 400 – 500 °C) under vacuum. The success of the method derives from the higher volatility of fluorofullerenes relative to the parent molecules; once fluorination reaches a certain level, the fluorofullerene is swept away from the fluorinating reagent and reaction stops. By selection of metal fluorides that evolve fluorine at different temperatures, it is possible to selectively (at least partially) reach a required fluorination level. At present this involves a somewhat serendipitous approach, nevertheless it has enabled major advances to be made recently in this field. Reagents that have proved to be particularly suitable include MnF_3, CeF_4 and K_2PtF_6.

In contrast to the formation of $C_{60}F_{48}$, it is not possible to produce exclusively a single product by this route, and extensive HPLC separation of the crude reaction mixture is then required. In this way fluorofullerenes ranging in quantity from 0.5 – 100 mg have been isolated.

Fluorinated [60]Fullerenes

Fullerene $C_{60}F_{48}$: This is a pure white solid, the structure of which was determined by two-dimesional ^{19}F NMR spectroscopy;[17, 18] the Schlegel diagram (Figure 1) shows both *R* and *S* forms of this chiral molecule. The structure was confirmed recently by single-crystal X-ray analysis (Figure 2), which reveals the indentation cause by the two groups of double bonds; these bonds are extremely short (1.30 Å) owing to the compression from the adjacent fluorines.[19]

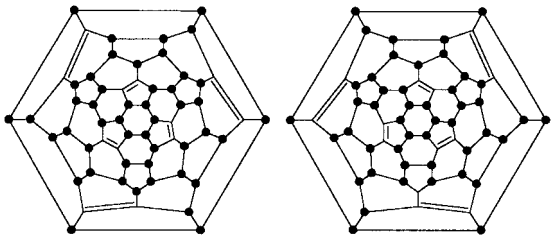

Figure 1. Schlegel diagrams for enantiomers of $C_{60}F_{48}$, ● = F.

Figure 2. Single-crystal X-ray structure for $C_{60}F_{48}$; black carbons are sp^3, grey carbons are sp^2.

$C_{60}F_{48}$ is potentially valuable as a highly concentrated source of fluorine that can be released on heating, for example, a maximum of 300 mL of F_2 from 1 g. It has been used to fluorinate aromatics[20] and, in preliminary experiments by using a Knudsen cell within a mass spectrometer, to produce fluorofullerenes of lower fluorine content such as $C_{60}F_2$.[4] This method has potential for further development through heating mixtures of $C_{60}F_{48}$ and C_{60}, obtained by precipitation from toluene. The latter technique may open up the lattice so that the problems outlined in the introduction can be overcome.

$C_{60}F_{48}$ forms coloured charge-transfer complexes with aromatic solvents, a greater bathochromic shift being observed the more electron-donating the aromatic, for example, a red solution in toluene.[18] Less highly fluorinated fullerenes generally give yellow solutions in toluene.

0947-6539/01/0719-4076 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 19

Fullerene $C_{60}F_{36}$: This fullerene was first observed together with $C_{60}F_{18}$ (both in the form of oxides) in the mass spectrum of a sample of mixed fluorofullerenes that had accidentally been treated with methanol.[21] It provided the first indication that fluorination and hydrogenation paralleled each other; $C_{60}H_{36}$ was the first fullerene compound to be prepared (accompanied by $C_{60}H_{18}$),[22] but the initial structural proposal was rejected subsequently in favour of a structure of T symmetry, predicted to be aromatic, since it should contain four planar aromatic hexagonal rings.[23] Unfortunately, $C_{60}H_{36}$ proved to be very susceptible to oxidation, which, together with the coupling multiplicities in the ^{1}H NMR spectrum, made determination of the structure impossible.

$C_{60}F_{36}$ (cream) is obtained by heating [60]fullerene with MnF_3 at 330 °C under vacuum, and separates (HPLC) into two isomers each giving three and twelve peaks of equal intensity in the ^{19}F NMR spectrum. The former is the predicted T isomer, whilst the latter could be one of a number of C_3 isomers.[24] Calculations[25] (for $C_{60}H_{36}$ but which are applicable to the fluoro analogues) limited the C_3 possibilities to two isomers, the correct one (also predicted to be the most stable) being identified by two-dimensional ^{19}F NMR spectroscopy.[26] Comparison of the ^{3}He NMR spectra for $C_{60}X_{36}$ (X = H, F) showed that the same isomers are obtained in both hydrogenation and fluorination.[26]

The Schlegel diagrams for the two isomers (Figure 3) show that each isomer is related to the other merely by means of 1,3-shifts of six fluorines (shown as open circles). Each isomer can be formed by contiguous addition of fluorine to the cage, whereas neither the other C_3 isomer, nor the D_3 isomer (predicted to be thermodynamically the most stable)[25] can be obtained in this way and, hence, are not formed.

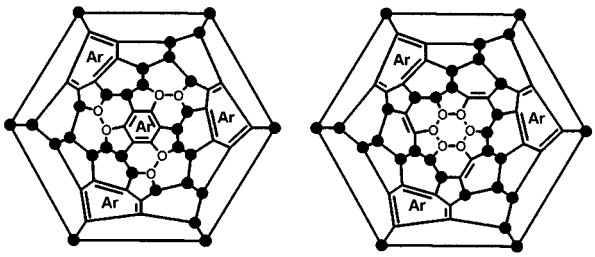

Figure 3. Schlegel diagrams for the T (left) and C_3 (right) isomers of $C_{60}F_{36}$; ●, ○ = F.

Both the T and C_3 isomers of $C_{60}F_{36}$ are highly aromatic, and contain four and three benzenoid hexagonal rings, respectively. This accounts for the ready cessation of fluorination at this addition level and the need to employ drastic conditions for $C_{60}F_{48}$ formation. The presence of the planar rings greatly distorts the cages as can be seen in their calculated structures (Figure 4).[27]

Fullerene $C_{60}F_{18}$: This lemon-yellow compound is obtained under the same conditions that produce $C_{60}F_{36}$ and is presumed, therefore, to be an intermediate—indeed the motif is found in the T isomer. It is more polar than $C_{60}F_{36}$ (longer HPLC retention time), and consequently less volatile.[28] A

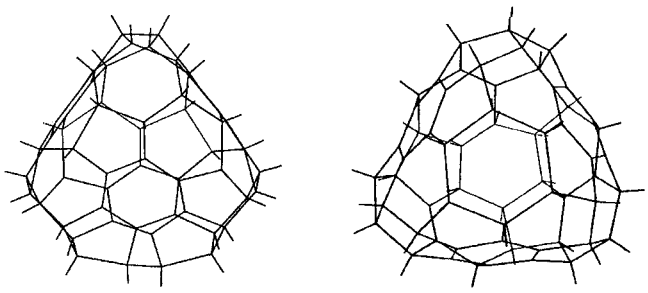

Figure 4. Calculated structures for the carbon cages of the T (left) and C_3 (right) isomers of $C_{60}F_{36}$.

higher yield is obtained by fluorination with K_2PtF_6 at 600 K.[29] Fullerene $C_{60}F_{18}$ (Figure 5) is isostructural with $C_{60}H_{18}$[30] (each gives a four line NMR spectrum having 1:2:2:1 intensity ratios)[29, 30] the structure being confirmed by single-crystal X-ray analysis, which proved the presence of the planar fully-delocalised hexagon (see Table 1).[31] The packing in toluene is shown in Figure 6.[31]

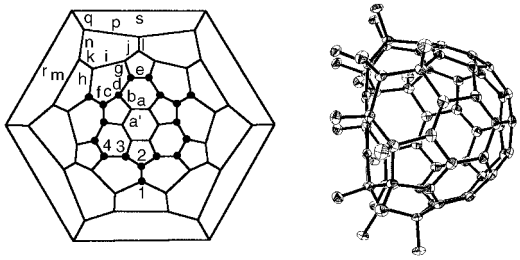

Figure 5. Schlegel diagram for $C_{60}F_{18}$ and single crystal X-ray structure.

Table 1. Bond lengths [Å] in $C_{60}F_{18}$ (for notations see Figure 5).

	C–C				C–F
a,a′	1.372	j	1.428	1	1.396
b	1.476	k	1.435	2	1.377
c	1.623	l	1.386	3	1.385
d	1.557	m	1.437	4	1.361
e	1.672	n	1.387		
f	1.558	p	1.436		
g	1.500	q	1.453		
h	1.524	r	1.387		
i	1.363	s	1.447		

Remarkable features evident from Table 1 are the following: 1) the bonds in the benzenoid ring are shorter than in benzene, attributed to compression arising from the effect of the adjacent fluorines, as seen also in hexafluorobenzene, though to a smaller effect; 2) the abnormally long and, therefore, weak C–C bond of 1.672 Å is very amenable to oxygen insertion to give the ether $C_{60}F_{18}O$ (described below). Oxygen similarly inserts into the next two longest bonds (1.623 and 1.557 Å), but not the 1.558 Å bond because the product is, according to calculations, less stable.

The combination of replaceable fluorines, a planar aromatic hexagon and a "normal" curved fullerene region makes $C_{60}F_{18}$ a potential precursor for the formation of a wide range of derivatives, especially donor–acceptor complexes, because of

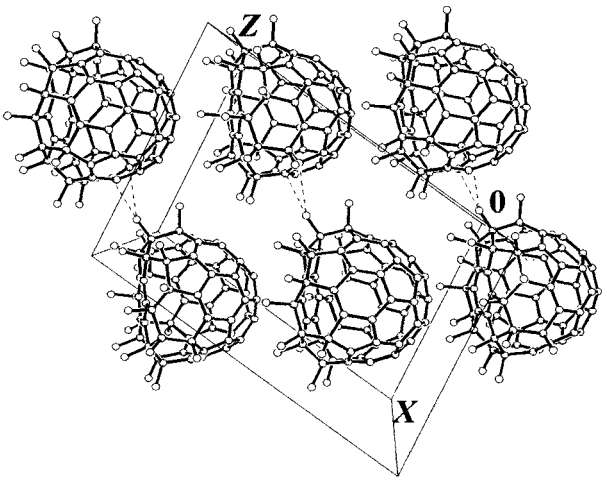

Figure 6. Packing of $C_{60}F_{18}$ in toluene.

the anticipated greater electron withdrawal by the fluorinated cage relative to that in [60]fullerene.

Fullerene $C_{60}F_{18}$ is evidently formed by a mechanism involving addition of pairs of fluorines across 6,6-bonds. Some early components in this process are described below; the penultimate step in this process is the formation of $C_{60}F_{16}$.

Fullerene $C_{60}F_{16}$: This is produced from fluorination of [60]fullerene with K_2PtF_6 at 465 °C. The ten-line ^{19}F NMR spectrum is consistent only with the structure shown in the Schlegel diagram (Figure 7).[32] The isolation of this compound arises from the presence of a benzenoid ring in the structure. This cannot be present in the $C_{60}F_{14}$ precursor, hence the high gain in stability upon addition of F_2 will be make isolation of $C_{60}F_{14}$ difficult; no evidence for its separate existence has been found.

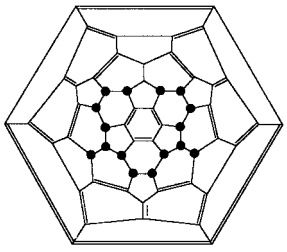

Figure 7. Schlegel diagram showing the structure of $C_{60}F_{16}$.

Fullerene $C_{60}F_2$: This compound (Figure 8) is formed in very low yield on fluorinating with K_2PtF_6 at 470 °C. The mass spectrum is poor due to the lower stability arising from the low substituent level. The compound has C_s symmetry (single line ^{19}F NMR spectrum at $\delta = -148.3$), consistent with it being the precursor for formation of all of the higher fluorinated [60]fullerenes.[33]

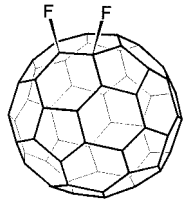

Figure 8. Structure of $C_{60}F_2$.

Fullerene $C_{60}F_{20}$: This remarkable compound is formed by fluorinating with either a mixture of MnF_3 and KF at 480 °C for 8 h, or Cs_2PbF_6 at 580 °C for 6 h. It is off-white and gives very pale lemon solutions in toluene; this indicates less charge transfer than in the case of $C_{60}F_{18}$, which gives a deeper yellow-green colour. It gives a single line in the ^{19}F NMR spectrum at $\delta = -132.8$.[34] The addition pathway for fluorination can occur by two routes, and either $C_{60}F_{18}$ or $C_{60}F_{20}$ can be produced. The former is aromatic and is therefore produced in larger quantity.[34]

Fullerene $C_{60}F_{20}$ (Figure 9) has been named 'Saturnene' in view of its unique structure comprising flattened poles (MM3 calculated distance between them of 6.29 Å) and an expanded equator (calculated sp^3C-sp^3C distance of 7.85 Å). It may be regarded as consisting of two dehydrocorannulene moieties held together by a $(CF)_{20}$ chain. A further unique aspect is the presence of two completely isolated conjugated regions. As in the case of $C_{60}F_{18}$ this compound should be useful for the formation of donor–acceptor complexes, an added feature here being the ability to add donors at either end of the molecule.

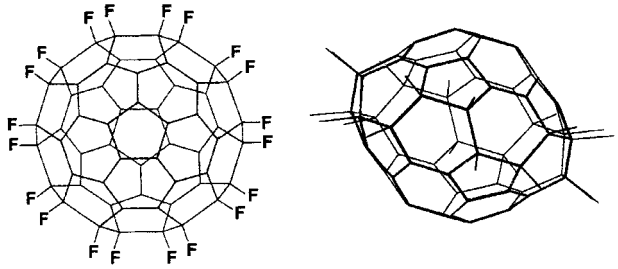

Figure 9. Polar view of $C_{60}F_{20}$ (left). The $C_{60}F_{20}$ cage (right: fluorines deleted for clarity).

Fluorinated [70]Fullerenes

Many fluorinated [70]fullerenes have been isolated by HPLC from fluorination of [70]fullerene with MnF_3 at 450 °C, and characterised by both mass spectrometry and ^{19}F NMR spectroscopy. Because of either coincidence of peaks or low sample quantity, successful analysis of the two-dimesional spectra to give the precise structures has not yet been possible. The products are composed of one isomer each of $C_{70}F_{34}$, $C_{70}F_{42}$ and $C_{70}F_{44}$, six isomers of $C_{70}F_{36}$, eight isomers of $C_{70}F_{38}$, and four isomers of $C_{70}F_{40}$. One isomer each of $C_{70}F_{36}$, $C_{70}F_{38}$ and $C_{70}F_{42}$ and two isomers of $C_{70}F_{40}$ have C_s or C_2 symmetry; the others are all C_1.[35]

Fluorinated Higher Fullerenes

Fullerenes $C_{76}F_{36}$, $C_{76}F_{38}$, $C_{76}F_{40}$, $C_{76}F_{42}$ and $C_{78}F_{42}$: Each of these components have been isolated in small quantities by HPLC from fluorination of [76]fullerene (containing a trace of [78]fullerene) with MnF_3 at 450–500 °C. $C_{76}F_{38}$ has C_1 symmetry and one of the $C_{76}F_{40}$ isomers has C_2 symmetry, but no further characterisation have been made with the quantities presently available.[36]

0947-6539/01/0719-4078 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 19

Fullerenes $C_{82}F_{44}$, $C_{84}F_{40}$ and $C_{84}F_{44}$: Each of these compounds (identified by mass spectrometry) have been isolated by HPLC from the fluorination of [84]fullerene (containing a trace of [82]fullerene) by MnF_3 at 470 °C.[37]

Fluorinated Aza[6]fullerene

Fullerene $C_{59}NF_{33}$: This is produced from fluorination of aza[60]fullerene by MnF_3 at 470 °C.[38] The molecular formula indicates a structure (Figure 10) that has a 10π-electron aromatic centre and, therefore, will be particularly stable. By contrast, hydrogenation gives $C_{59}NH_5$, which probably has a 6π-electron aromatic centre[38] (cf. $C_{59}NCl_5$),[39] the difference being attributable to the lower activation energy for fluorination. This can therefore overcome the loss of resonance energy on progressing beyond the five-addend stage.[38]

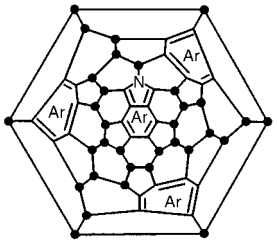

Figure 10. Schlegel diagram of conjectured aromatic structure for $C_{59}NF_{33}$.

Fluorotrimethylfluorofullerenes

Fullerenes $C_{60}F_{17}CF_3$ and $C_{60}F_{17}CF_2CF_3$: Various fluorotrimethylfluorofullerenes accompany the formation of $C_{60}F_{18}$. Since trifluoromethylation (giving uncharacterised products) can be accomplished by direct reaction with trifluoromethyl radicals,[40] the involvement of the latter seemed probable, since fluorination is accompanied by cage fragmentation[17, 20] giving fluoroalkyl species.

It is now known that a second route to fluoroalkylation is involved; the recent isolation of $C_{60}F_{17}CF_3$ indicates that insertion of CF_2 groups into C–F bonds occurs.[41] (Remarkably, $C_{60}F_{17}CF_3$ showed virtually no resonance for the CF_3 group in the ^{19}F NMR spectrum, which led to the belief originally that the compound isolated was the isomeric $C_{60}F_{18}CF_2$.[42]) The CF_2 group inserts into the two most accessible C–F bonds in the molecule in a 65:35 ratio to give the C_s and C_1 compounds, respectively, as shown in Figure 11; the latter component is a thus a chiral mixture. Figure 12 shows the single crystal X-ray structure of the main component.

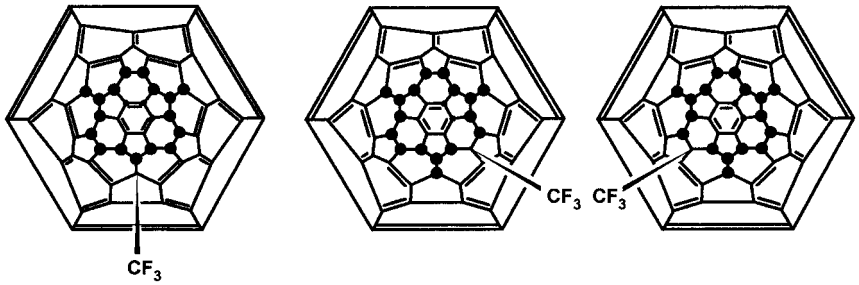

Figure 11. Schlegel diagrams of the isomers of $C_{60}F_{17}CF_3$.

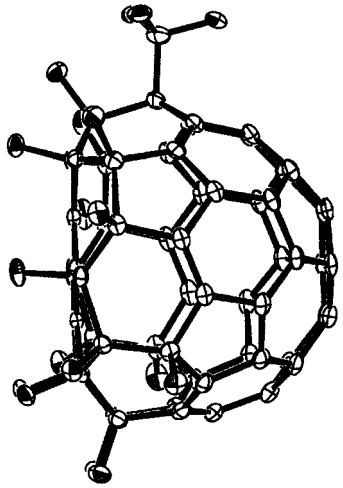

Figure 12. Single-crystal X-ray structure of the main (C_s) component of $C_{60}F_{17}CF_3$.

The insertion mechanism is confirmed by the isolation of the C_s-symmetric fullerene $C_{60}F_{17}C_2F_5$, which arises from further insertion of CF_2 into the existing CF_3 group.[41] Here only a single isomer is obtained, consistent with the lower steric hindrance that results from insertion into the C_s trifluoromethyl precursor.

In view of the greater electron-withdrawing power of trifluoroalkyl groups compared to fluorine, and possibly lower susceptibility to nucleophilic substitution, these groups may prove to be particularly important for enhancing the acceptor properties of fullerenes. Isolation of many other trifluoromethyl derivatives seems probable.

Fluorofullerene Oxides

The ready formation of numerous oxides is a feature observed early in studies of F_2-gas fluorination of fullerenes,[3, 10, 43] despite the anhydrous conditions employed, which indicated that reaction with oxygen traces occurred during the fluorination. However, the relative concentrations of these increased on reaction with methanol, hence it also seemed likely that these were epoxides that resulted from S_N2 nucleophilic substitution followed by elimination (Figure 13). [S_N2 (involving backside attack) could not apply, and S_N1 (involving fullerene cation formation) seemed improbable.[3, 43]]

Cations have since been observed[44] and their formation may be favoured when a greater number of sp^3-hybridised carbons that are less electron-withdrawing are present on the cage. However, the replacement mechanism is unimportant in the present context, it

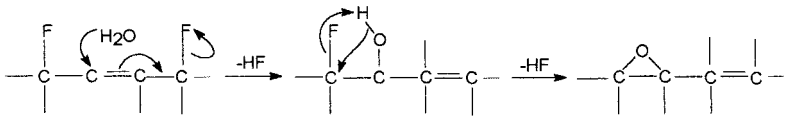

Figure 13. Conjectured mechanism of epoxide formation from fluorofullerenes.

being sufficient that the mass spectra of many isolated components are consistent with the following process [Eq. (1)]:[45]

$$C_{60}F_n \rightarrow C_{60}F_{n-1}OH \rightarrow C_{60}F_{n-2}O \quad (1)$$

Fullerene $C_{60}F_{18}O$: A [60]fullerene oxide, $C_{60}F_{18}O$, of C_s symmetry was isolated by HPLC from the product mixture obtained on producing $C_{60}F_{18}$. The ^{19}F NMR spectrum was consistent with either an epoxide or an ether, the former being assumed in view of the considerable evidence for the presence of epoxides (see above).[46] More recently, the single-crystal X-ray structure (Figure 14) showed the oxide to be an ether (oxahomofullerene),[47] which is the first such fullerene species to be isolated; homofullerenes and azahomofullerenes, the CR and NR_2 analogues, have been isolated previously.[48]

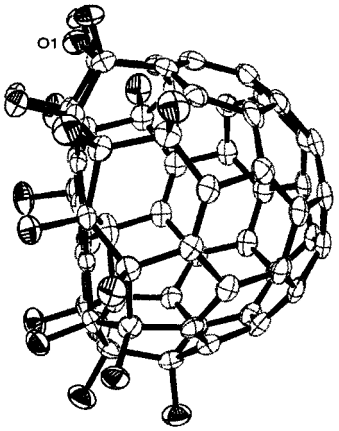

Figure 14. Single-crystal X-ray structure for the most abundant isomer of $C_{60}F_{18}O$.

To form this isomer, oxygen inserts into the longest (i.e., weakest) C–C bond in the molecule (see Table 1); insertion into the next longest bonds yields two further isomers.[49] The Schlegel diagrams for all three isomers are shown in Figure 15.

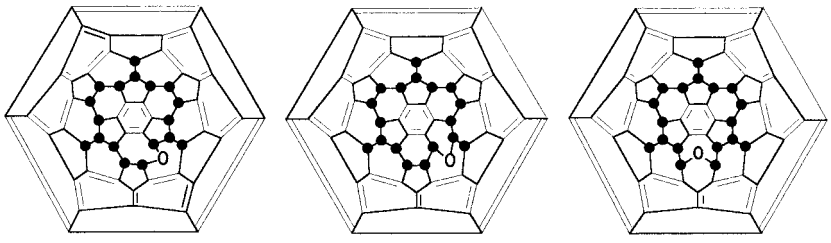

Figure 15. Schlegel diagrams for $C_{60}F_{18}O$ isomers of 44, 48 and 58 min retention times (motifs A, B and C, respectively).

Fullerene $C_{60}F_{18}O_2$: Seven isomers of the $C_{60}F_{18}O_2$ bis-ethers have also been isolated, and their one- and two-dimesional ^{19}F NMR spectra obtained.[50] In principle twenty-one isomers can be obtained by combinations of the motifs shown in Figure 15, and the heats of formation have been calculated.[50] The number of isomers possible for each motif combination are category are: 4 (A + A), 6 (A + B), 4 (B + B), 3 (A + C), 3 (B + C), 1 (C + C), twenty-one in all. Seven have been isolated, and four (Figure 16) positively characterised.

Other bis-oxides and some tris-oxides are produced, but in quantities for mass spectrometric characterisation only.

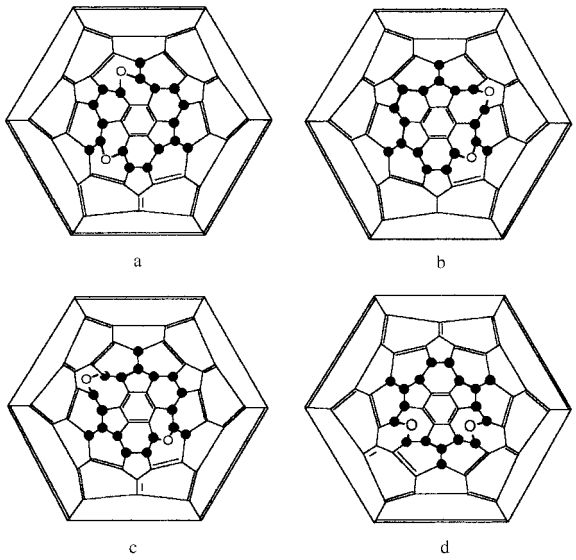

Figure 16. Schlegel diagrams of characterised bisoxahomo[60]fullerenes.

Fullerenes $C_{60}F_4O$, $C_{60}F_6O$ and $C_{60}F_8O$: These compounds have also been isolated from the product of fluorination of [60]fullerene with K_2PtF_6 under vacuum at 465 °C.[51] ^{19}F NMR spectra showed that both $C_{60}F_4O$ and $C_{60}F_8O$ have C_s-symmetrical structures, that $C_{60}F_6o$ has a structure intermediate between the other two and that the fluorines are arranged in linear arrays in each compound. This confirmed that fluorine addition to fullerenes is contiguous.

The structures were identified initially as epoxides, the combination of small sample size and unavailability of fluorine-decoupling rules out confirmation through the use of ^{13}C NMR spectroscopy. However, the subsequent discovery of oxygen insertion into C–C bonds of fluorofullerenes now makes it certain that these compounds are ethers, especially as the bond into which the insertion would occur corresponds to that which is most susceptible to cleavage in $C_{60}F_{18}$. Moreover, for the ether structures no precursor requir-

0947-6539/01/0719-4080 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 19

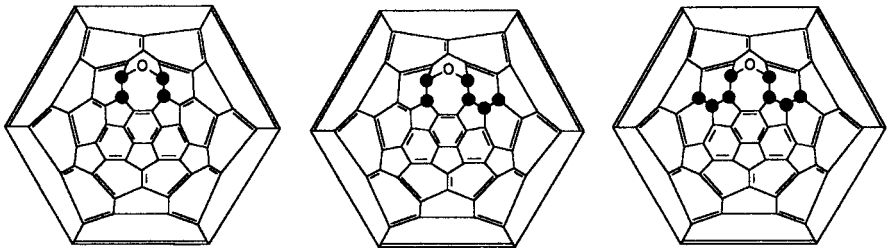

Figure 17. Schlegel diagrams of the fluorofullerene ethers, $C_{60}F_nO$: a) $n=4$, b) $n=6$, and c) $n=8$.

ing an additional two fluorines is required. The revised structures are given in Figure 17.[52]

Fullerenes $C_{60}F_{20}O$, $C_{60}F_{20}O_2$ and $C_{60}F_{20}O_3$: These compounds (which have slightly longer retention times) were isolated from the HPLC of $C_{60}F_{20}$, and characterised by mass spectrometry.[53] No structures could be deduced because of the small amounts of material, but $C_{60}F_{20}$ evidently forms oxides (presumably ethers) just as does $C_{60}F_{18}$.

Derivatives of Fluorofullerenes

This is the most recent area of fluorofullerene research, and is directed towards evaluating the fluorofullerenes as enhanced acceptors in donor–acceptor complexes. Given the limited amounts of material currently available, initial experiments have employed some known reactions of [60]fullerene to test their applicability to fluorofullerenes.

Derivatives of $C_{60}F_{18}$

Fullerene $C_{60}F_{15}Ph_3$ (triumphene): Halogenofullerenes are more powerful electrophilies than fullerenes, with fluorofullerenes being the most reactive. Substitution into aromatics is therefore feasible in the presence of Lewis acid catalysts, for example, the formation of $C_{60}Ph_5Cl$ from $C_{60}Cl_6$/benzene/$FeCl_3$.[54] This reaction illustrates the steric hindrance to the reaction, since only the most accessible chlorines are replaced. Likewise, $C_{60}F_{18}$ reacts with benzene/$FeCl_3$ to give the triphenylated compound $C_{60}F_{15}Ph_3$, the structure of which is indicated (^1H, ^{19}F NMR spectroscopy) to be that in Figure 18.[55] Only the three most accessible halogens are readily substituted, though preliminary evidence indicated that all *eighteen* fluorines can be replaced; $C_{60}Ph_{18}$ would probably qualify as being the most aromatic compound known. This reaction can in principle be used to make a large number of novel arylated fullerenes.

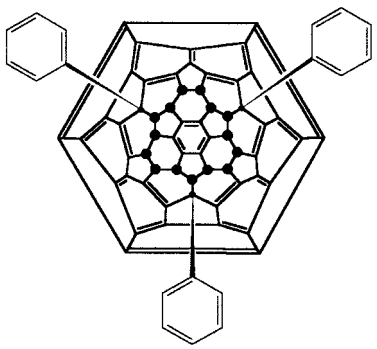

Figure 18. Schlegel diagram of the structure proposed for $C_{60}F_{15}Ph_3$.

[2+4] Cycloaddition with anthracene: Just as C_{60} and anthracene participate in [2+4] cycloaddition to give 1:1 complexes,[56] so similar complexes can be made from $C_{60}F_{18}$.[57] Addition can take place across four 6,6-bonds (a–d in Figure 19), with steric hindrance increasing the closer the bond is to the fluorines. Consequently, addition occurs most readily across bond a, to give a C_s-symmetry product. As in the case of the C_{60}/anthracene complexes, slow reversion to components occurs on standing at room temperature. Some oxidation of anthracene to anthraquinone accompanies the reaction.

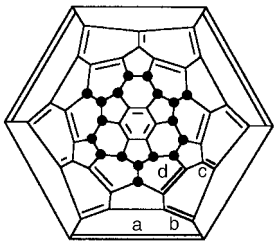

Figure 19. Positions available for cycloaddition in $C_{60}F_{18}$.

The adduct formed by addition across bond b is less stable and both readily reverts to components and rearranges to the C_s symmetry product. This is the first example of spontaneous migration of a cycloaddition across the surface of the fullerene cage.

1,3-Dipolar cycloaddition: The (Prato) reaction of [60]fullerene with sarcosine and formaldehyde involves the intermediate $CH_2{=}N^+Me{-}CH_2^-$, which participates in a [2+4] cycloaddition to give the product shown in Figure 20;[58] use of other aldehydes gives derivatives with a variety of substituents in the resulting heterocycle. The reaction is prone to give polyaddition.[59]

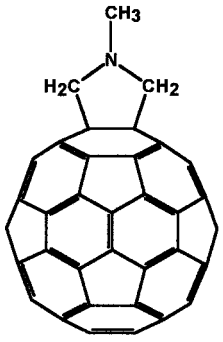

Figure 20. Product of the reaction of [60]fullerene with sarcosine and formaldehyde.

With $C_{60}F_{18}$, the reaction takes place across bonds a and b (see Figure 19) to give symmetrical and unsymmetrical monoadducts, respectively, together with a number of symmetrical and unsymmetrical bisadducts.[60]

The Bingel reaction: The reaction between fullerenes, diethyl bromomalonate and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU: a base) produces a [2+1] cycloadduct through the intermediate formation of the nucleophile $^-CBr(CO_2Et)_2$, which attacks the cage, followed by loss of Br^- to give the structure shown in Figure 21.[61]

  0947-6539/01/0719-4081 $ 17.50+.50/0

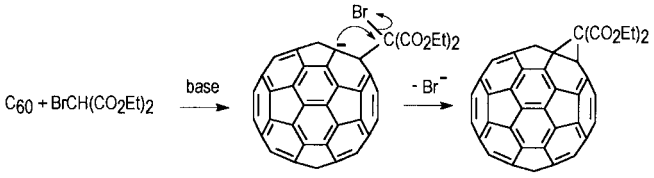

Figure 21. Normal product of the reaction of diethyl bromomalonate/DBU with C_{60}.

With $C_{60}F_{18}$ the reaction takes a different course with one, two or three of the most accessible fluorines being nucleophilically replaced. Moreover, because of its size, the incoming nucleophile occupies a δ-position relative to the departing fluorine, to give the products shown in Figure 22. The outstanding feature is that the trisubstituted product contains a fully delocalised 18π annulene belt, and this gives rise to an intense emerald green colour. The electrons in this belt are highly delocalised as shown by the bond lengths (single-crystal X-ray analysis) for the constituent bonds, which vary by only 0.013 Å.[62] It is anticipated that numerous of these annulenic fullerenes will become available in future.

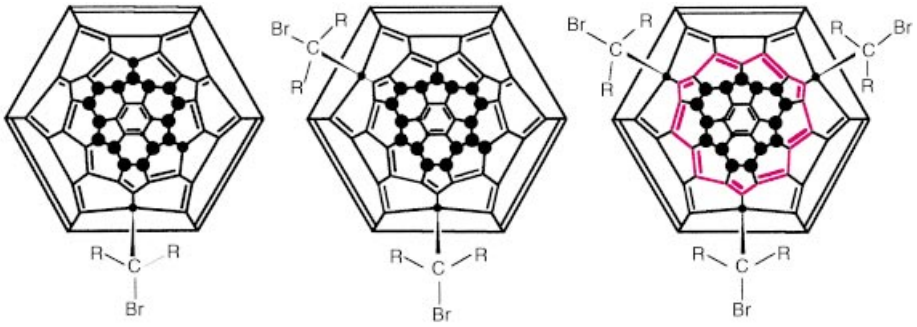

Figure 22. Mono-, di-, and trisubstitution products (R = CO_2Et) from the reaction of $C_{60}F_{18}$ with diethyl bromomalonate; the 18π annulene belt is in magenta.

Derivatives of $C_{60}F_{20}$

[2+4] Cycloaddition with anthracene: An unusual reaction takes place with anthracene, for a precedence for the reaction of 9,10-substituted anthracenes with C_{60} has been reported.[63] As in the reaction with $C_{60}F_{18}$, some oxidation to anthraquinone accompanies the reaction, but anthracene also undergoes oxygen addition to give an intermediate which then adds to the cage to give the product shown in Figure 23.[64]

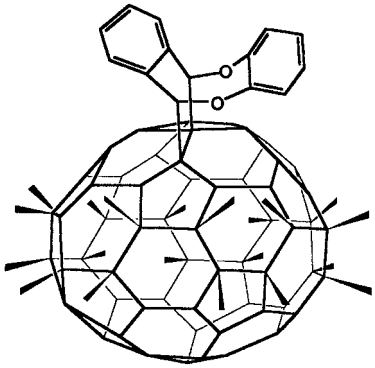

Figure 23. Product of the reaction of anthracene with $C_{60}F_{20}$.

Formation with respect to the alternative anthracene addition is favoured by the aryl ring attached to oxygens being constrained well away from the cage surface. The compound has no symmetry plane and therefore gives 20 × 1F signals in the ^{19}F NMR spectrum.

Conclusion

At one time it seemed that fluorination would not be a useful reaction of fullerenes due to the inability to control the reaction. The situation has changed dramatically such that there are now more fluorofullerenes known than for any other fullerene derivative involving a single addend type. The problems now centre on producing larger quantities of the crude products, and once this is solved one can anticipate rapid expansion of the field, with many hundreds (at least) of new compounds and derivatives being made. It is too much to expect that there will not be further surprises in this fascinating area.

Acknowledgement

I thank all of my collaborators, notably Ala'a Abdul-Sada, Anthony G. Avent, Peter Hitchcock and Xian-Wen Wei in relation to more recent studies, and John Holloway and Eric Hope (Leicester) together with John Langley (Southampton) for the earlier ones. I am especially grateful for the wonderful collaboration with Olga Boltalina and her group (Moscow) that has resulted in the important preparative breakthroughs in this field, and Joan Street (Southampton) for the excellent ^{19}F NMR spectra upon which so much has depended. The work described has been supported variously by the Royal Society, the Royal Society of Chemistry, INTAS (grant no. 97-30027), NATO, and the Russian "Fullerenes and Atomic Clusters" programme.

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162 – 164.
[2] B. I. Dunlap, D. W. Brenner, J. W. Mintmire, R. C. Mowrey, C. T. White, *J. Phys. Chem.* **1991**, *95*, 5763 – 5768.
[3] R. Taylor, J. H. Holloway, E. G. Hope, A. G. Avent, G. J. Langley, T. J. Dennis, J. P. Hare, H. W. Kroto, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1992**, 665 – 668.
[4] O. V. Boltalina, L. N. Sidorov, E. V. Sukhanova, I. D. Sorokin, *Chem. Phys. Lett.* **1994**, *230*, 567 – 570.
[5] R. Hettich, C. Jin, R. N. Compton, *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 263 – 267.
[6] F. Zhou, G. J. Van Berkel, B. T. Donovan, *J. Am. Chem. Soc.* **1994**, *116*, 5485 – 5486; N. Liu, H. Touhara, F. Okino, S. Kawasaki, *J. Electroanal. Soc.* **1996**, *143*, L214 – 217.
[7] T. S. Papina, V. P. Kolesov, V. A. Lukyanova, O. V. Boltalina, N. A. Galeva, L. N. Sidorov, *J. Chem. Thermodyn.* **1999**, *31*, 1328 – 1332; T. S. Papina, V. P. Kolesov, V. A. Lukyanova, O. V. Boltalina, A Ya. Lukonin, L. N. Sidorov, *J. Phys. Chem. B* **2000**, *104*, 5403 – 5405.
[8] H. Selig, C. Lifshitz, T. Peres, J. E. Fischer, A. R. McGhie, W. J. Romanov, J. P. McCaulay, A. B. Smith, *J. Am. Chem. Soc.* **1991**, *113*, 5475 – 5478.

[9] J. H. Holloway, E. G. Hope, R. Taylor, G. J. Langley, A. G. Avent, T. J. Dennis, J. P. Hare, H. W. Kroto, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1991**, 966–969.

[10] A. A. Tuinman, P. Mukherjee, J. L. Adcock, R. L. Hettich, R. N. Compton, *J. Phys. Chem.* **1992**, *96*, 7584–7589.

[11] K. Kniaz, J. E. Fischer, H. Selig, G. B. M. Vaughan, W. J. Romanov, D. M. Cox, S. K. Chowdhury, J. P. McCaulay, R. M. Strongin, A. B. Smith, *J. Am. Chem. Soc.* **1993**, *115*, 6060–6064.

[12] R. Taylor, G. J. Langley, J. H. Holloway, E. G. Hope, A. K. Brisdon, H. W. Kroto, D. R. M. Walton, *J. Chem. Soc. Perkin Trans. 2* **1995**, 181–187.

[13] Private communication from H. Selig to J. H. Holloway and R. Taylor.

[14] A. Hamwi, C. Fabre, P. Chaurand, S. Della-Negra, C. Ciot, D. Djurado, J. Dupois, A. Rassat, *Fullerene Sci. Technol.* **1993**, *1*, 499–535.

[15] R. Taylor, unpublished results.

[16] K. Komatsu, private communication.

[17] A. A. Gakh, A. A. Tuinman, J. L. Adcock, R. A. Sachleben, R. N. Compton, *J. Am. Chem. Soc.* **1994**, *116*, 819–820.

[18] O. V. Boltalina, L. N. Sidorov, V. F. Bagryantsev, V. A. Seredenko, A. S. Zapol'skii, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1996**, 2275–2278.

[19] S. I. Troyanov, P. A. Troshin, O. V. Boltalina, I. N. Ioffe, L. V. Sidorov, E. Kemnitz, *Angew. Chem.* **2001**, *113*, 2345–2347; *Angew. Chem. Int. Ed.* **2001**, *40*, 2285–2287.

[20] a) R. Taylor, unpublished work; b) A. A. Gakh, A. A. Tuinman, J. L. Adcock, R. N. Compton, *Tetrahedron Lett.* **1993**, *34*, 7167–7170.

[21] R. Taylor, G. J. Langley, A. K. Brisdon, J. H. Holloway, E. G. Hope, H. W. Kroto, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1993**, 875–878.

[22] H. Ajie, M. M. Alvarez, S. J. Anz, R. D. Beck, F. Diederich, K. Fostiropoulos, D. R. Huffman, W. Krätschmer, Y. Rubin, K. E. Schriver, D. Sensharma, R. L. Whetten, *J. Phys. Chem.* **1990**, *94*, 8630–8636.

[23] R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1667–1669; *Philos. Trans. R. Soc. London, A*, **1993**, *343*, 87–101; S. J. Austin, R. C. Batten, P. W. Fowler, D. B. Redmond, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1993**, 1383–1386.

[24] O. V. Boltalina, A. Ya. Borschevskii, L. N. Sidorov, J. M. Street, R. Taylor, *Chem. Commun.* **1996**, 529–530; O. V. Boltalina, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1998**, 649–654.

[25] B. W. Clare, D. W. Keppert, *J. Mol. Struct. (THEOCHEM)* **1994**, *315*, 71–77.

[26] O. V. Boltalina, M Bühl, A. Khong, M. Saunders, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1475–1479.

[27] S. Jenkins, M. I. Heggie, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2415–2419.

[28] V. Yu Markov, O. V. Boltalina, A. A. Gorjunkov, A. Yu Lukonin, L. N. Sidorov, G. Gigli, G. Balducci, R. Taylor, *Recent Adv. Chem. Phys. Fullerenes Relat. Mater. Proc. Symp.* **2000**, *10*, 109–120.

[29] O. V. Boltalina, V. Yu. Markov, R. Taylor, M. P. Waugh, *Chem. Commun.* **1996**, 2549–2550.

[30] A. D. M. Darwish, A. G. Avent, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Perkin Trans. 2* **1996**, 2051–2054.

[31] I. S. Neretin, K. A. Lyssenko, M. Yu. Antipin, Yu. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Yu. Lukonin, L. N. Sidorov, R. Taylor, *Angew. Chem.* **2000**, *112*, 3411–3414; *Angew Chem. Int. Ed.* **2000**, *39*, 3273–3276.

[32] A. G. Avent, O. V. Boltalina, A. Ya. Lukonin, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2*, **2000**, 1359–1361.

[33] O. V. Boltalina, A. Ya. Lukonin, J. M. Street, R. Taylor, *Chem. Commun.* **2000**, 1600–1602.

[34] O. V. Boltalina, P. A. Troshin, J. M. Street, R. Taylor, *Angew. Chem.* **2001**, *113*, 809–811; *Angew. Chem. Int. Ed.* **2001**, *40*, 787–790.

[35] R. Taylor, A. K. Abdul-Sada, O. V. Boltalina, J. M. Street, *J. Chem. Soc. Perkin Trans. 2* **2000**, 1013–1021.

[36] A. K. Abdul-Sada, A. V. Avakyan, O. V. Boltalina, Yu. Markov, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1999**, 2659–2666.

[37] O. V. Boltalina, A. K. Abdul-Sada, T. V. Avakyan, T. J. S. Dennis, V. Yu. Markov, R. Taylor, *J. Phys. Chem. B* **1999**, *103*, 8189–8191.

[38] O. V. Boltalina, T. Drewello, A. Hirsch, T. J. D. Jorgensen, V. Yu. Markov, U. Reuther, R. Taylor, *Recent Adv. Chem. Phys. Fullerenes Relat. Mater. Proc. Symp.* **1999**, *7*, 462–471.

[39] B. Nüber, A. Hirsch, *Chem. Commun.* **1998**, 405–406.

[40] Y. I. Lyakhovetsky, E. A. Shilova, B. L. Tumanskii, A. V. Usatov, E. A. Avetisyan, S. R. Sterlin, A. P. Pleshkova, Y. N. Novikov, Y. S. Nekrasov, R. Taylor, *Fullerene Sci. Technol.* **1999**, *7*, 263–288.

[41] O. V. Boltalina, P. B. Hitchcock, P. A. Troshin, J. M. 1Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2410–2414.

[42] A. G. Avent, O. V. Boltalina, A. Yu. Lukonin, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **2000**, 1–3.

[43] R. Taylor, G. J. Langley, J. H. Holloway, E. G. Hope, A. K. Brisdon, H. W. Kroto, D. R. M. Walton, *J. Chem. Soc. Perkin Trans. 2* **1993**, 181–187.

[44] A. G. Avent, P. R. Birkett, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Commun.* **1998**, 2153–2154; C. A. Reed, K.-C. Kim, R. D. Bolskar, L. J. Mieller, *Science* **2000**, *289*, 101–103.

[45] O. V. Boltalina, J. H. Holloway, E. G. Hope, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1998**, 1845–1850.

[46] A. G. Avent, O. V. Boltalina, P. W. Fowler, A. Ya. Lukonin, V. K. Pavlovich, J. B. Sandall, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1998**, 1319–1322.

[47] O. V. Boltalina, B. de La Vaissière, P. W. Fowler, P. B. Hitchcock, J. B. Sandall, P. A. Troshin, R. Taylor, *Chem. Commum.* **2000**, 1325–1326.

[48] T. Suzuki, Q. Li, K. C. Fhemani, F. Wudl, O. Almarsson, *Science* **1991**, *254*, 1186–1187; M. Prato, Q. Li, F. Wudl, V. Lucchini, *J. Am. Chem. Soc.* **1993**, *115*, 1148–1150.

[49] O. V. Boltalina, B. de La Vaissière, P. W. Fowler, A. Ya. Lukonin, A. K. Abdul-Sada, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2212–2216.

[50] O. V. Boltalina, B. de La Vaissière, A. Yu. Lukonin, P. W. Fowler, A. K. Abdul-Sada, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **2001**, 550–556.

[51] O. V. Boltalina, A. Ya. Lukonin, A. G. Avent, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **2000**, 683–686.

[52] A. G. Avent, O. V. Boltalina, A. Yu Lukonin, B. de La Vaissière, P. W. Fowler, J. M. Street, R. Taylor, *Recent Adv. Chem. Phys. Fullerenes Relat. Mater. Proc. Symp.* **2000**, *9*, 109–116.

[53] O. V. Boltalina, R. Taylor, unpublished results.

[54] A. G. Avent, P. R. Birkett, J. D. Crane, A. D. Darwish, G. J. Langley, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1994**, 1463–1465.

[55] O. V. Boltalina, J. M. Street, R. Taylor, *Chem. Commun.* **1998**, 1827–1828.

[56] K. Komatsu, Y. Murata, A. Miyabo, K. Takeuchi, T. S. M. Wan, *Fullerene Sci. Technol.* **1993**, *1*, 231; K. Komatsu, Y. Murata, N. Sugita, K. Takeuchi, T. S. M. Wan, *Tetrahedron Lett.* **1993**, *34*, 8473–8476; J. A. Schleuter, J. H. Seaman, S. Taha, H. Cohen, K. R. Lykke, H. H. Wang, J. M. Williams, *J. Chem. Soc. Chem. Commun.* **1993**, 972–974; F. Wudl, *Acc. Chem. Res.* **1992**, *25*, 157; M. Tsuda, T. Akayuki, T. Nogami, S. Kurono, M. Ohashi, *J. Chem. Soc. Chem. Commun.* **1993**, 1296–1298.

[57] A. G. Avent, O. V. Boltalina, J. M. Street, R. Taylor, X-W. Wei, *J. Chem. Soc. Perkin Trans. 2* **2001**, 994–997.

[58] M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.

[59] A. Hirsch, I. Lamparth, H. R. Karfunkel, *Angew. Chem.* **1994**, *106*, 453; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 437–438.

[60] X.-W. Wei, A. G. Avent, O. V. Boltalina, J. M. Street, R. Taylor, unpublished results.

[61] C. Bingel, *Chem. Ber.* **1993**, *126*, 1957–1959.

[62] X.-W. Wei, A. D. Darwish, O. V. Boltalina, P. B. Hitchcock, J. M. Street, R. Taylor, unpublished results.

[63] B. F. O'Donovan, D. Phil Thesis, University of Sussex, **1999**.

[64] X.-W. Wei, A. G. Avent, O. V. Boltalina, J. M. Street, R. Taylor, unpublished results.