$C_{60}F_{20}$: "Saturnene", an Extraordinary Squashed Fullerene[**]

Olga V. Boltalina,* Vitaly Yu. Markov,
Pavel A. Troshin, Adam D. Darwish, Joan M. Street,
and Roger Taylor*

In our program of fluorinating fullerenes by metal fluorides under vacuum followed by HPLC separation of the products, we have isolated and in many cases fully characterized the following: $C_{60}F_2$,[1] $C_{60}F_{16}$,[2] $C_{60}F_{18}$,[3, 4] $C_{60}F_{36}$ (two isomers),[5] $C_{60}F_nO$ ($n = 4$, 6, 8),[6] $C_{60}F_{18}O$ (three isomers),[7, 8] $C_{60}F_{18}O_2$ (seven isomers),[9] $C_{60}F_{17}CF_2CF_3$,[10] $C_{60}F_{17}CF_3$ (two isomers),[10] forty-nine derivatives of [70]fullerene,[11] $C_{76}F_n$ ($n = 36$, 38, 40, 42, 44), $C_{78}F_n$ ($n = 38$, 42), $C_{82}F_{44}$, $C_{84}F_{40}$, and $C_{84}F_{44}$.[12] The success in this work is due to the high polarity of the fluorofullerenes, which results in the derivatives having significantly different retention times. Moreover, they have substantial solubility in both toluene and alkanes, which further facilitates the separations.

Many of these components have been formed through fluorination with K_2PtF_6 under vacuum at approximately 465 °C, the major product under these conditions being $C_{60}F_{18}$. During preparation of a larger amount of this material, we isolated many other components, including a number of ethers (oxahomofullerenes) and bis-ethers.[7–9] One of the latter was accompanied by a shoulder peak of 75 min retention time which gave a mass spectrum showing the presence of $C_{60}F_{20}$ with the typical $-n$F fragmentation pattern, but the amount was insufficient for further characterization.

Subsequently we have scaled-up the preparation through the use of an MnF_3/KF fluorinating mixture. Whereas fluorination of [60]fullerene with MnF_3 gives mainly $C_{60}F_{36}$,[5] addition of an equimolar amount of KF reduces the overall fluorinating ability and gives greater yields of products with lower fluorine content, including $C_{60}F_{18}$ and $C_{60}F_{20}$. The isolated amount of the latter (1–2 mg) was sufficient for spectroscopic study and we now report its extraordinary structure.

$C_{60}F_{20}$ is off-white and with toluene forms only very pale lemon solutions, in contrast to other fluorofullerenes which give deeper lemon-yellow solutions. It has unusual solubility behavior, in that the pure material is very reluctant to redissolve in toluene, but eventually does so. This behavior is reminiscent of the behavior of pure C_{60} towards, for example, hexane and may be attributed in both cases to close packing of the cages so that penetration of the lattice by the solvent is very slow.

The mass spectrum (Figure 1) shows the parent ion peak at 1100 amu, with a fragmentation pattern of regular loss of 20 F atoms (either singly or as pairs) down to C_{60}, showing the compound to be $C_{60}F_{20}$; the pattern is reminiscent of the behavior of $C_{60}F_{16}$[2] and $C_{60}F_{18}$[3] under EI conditions. The spectrum was duplicated precisely from a second sample.

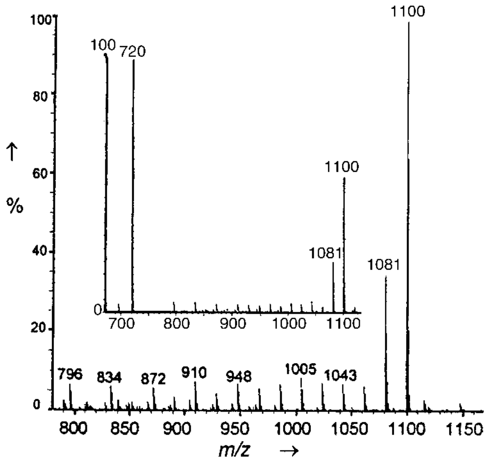

Figure 1. EI mass spectrum (70 eV) for $C_{60}F_{20}$ (inset shows full range).

The IR spectrum (KBr) (Figure 2) consists mainly of a single band at 1131 cm^{-1} in the C–F stretching region indicative of a highly symmetrical structure. Small shoulder peaks to the main band are at 1206, 1183, 1162, 1111, 1102,

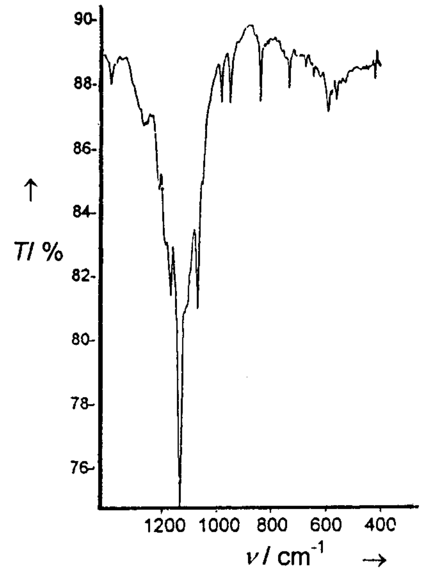

Figure 2. IR spectrum (KBr) of $C_{60}F_{20}$.

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[*] Dr. O. V. Boltalina, V. Yu. Markov, P. A. Troshin
Chemistry Department
Moscow State University
Moscow 119899 (Russia)
Fax: (+7) 095-9391240
E-mail: ovb@capital.ru

Dr. R. Taylor, Dr. A. D. Darwish
School of Chemistry, Physics & Environmental Sciences
Sussex University, BN1 9QJ (UK)
Fax: (+44) 1273-677-196
E-mail: R.Taylor@sussex.ac.uk

J. M. Street
Chemistry Department
The University
Southampton, SO17 1BJ (UK)

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1066, and 1047 cm^{-1}; other minor peaks occur at 981, 951, 839, and 732 cm^{-1}.

The most outstanding spectroscopic feature is the single line ^{19}F NMR spectrum (Figure 3) at $\delta = -132.8$. This is as notable as the single line ^{13}C NMR spectrum obtained for C_{60} itself,[13] and shows that all twenty fluorine atoms are equivalent.

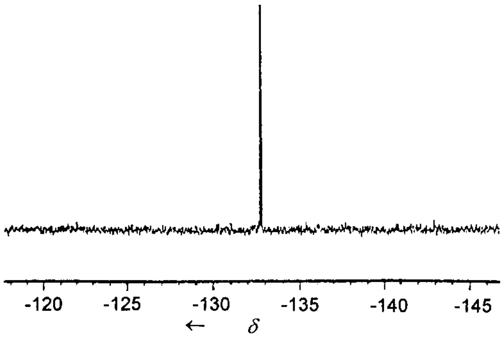


Figure 3. ^{19}F NMR spectrum (338.9 MHz) of $C_{60}F_{20}$.

The structure of the compound is shown in Figures 4a and 4b, and comprises two dehydrocorannulene caps held together by a $(CF)_{20}$ chain; isostructural $C_{60}H_{20}$ was first described theoretically by Keppert and Clare.[14] Figure 4c shows the structure as a Schlegel diagram.

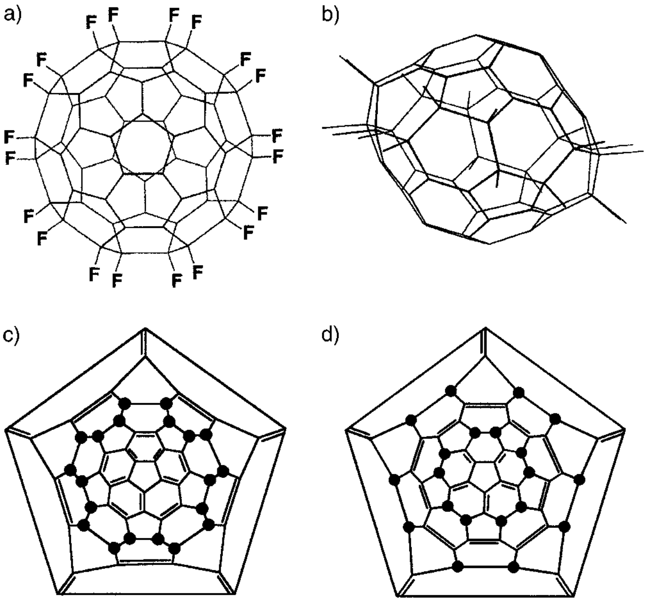
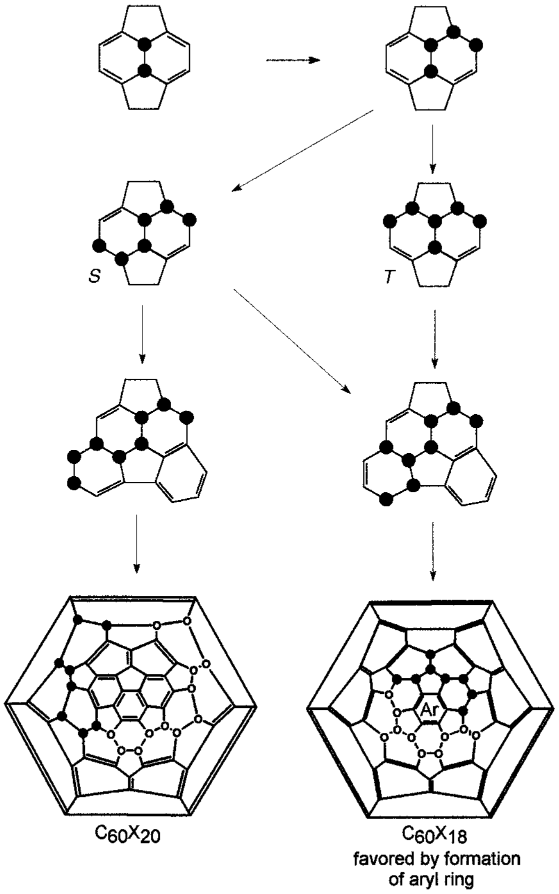


Figure 4. Structure of $C_{60}F_{20}$ (a) and its quite highly strained cage (b). c) $C_{60}F_{20}$ shown as a Schlegel diagram (● = F). d) The alternative structure for $C_{60}F_{20}$, ruled out by the mechanistic pathway.

The molecule is quite highly strained, the extent of cage distortion being shown by the distances (MM3) of 6.29 Å (between the polar caps) and 7.85 Å (between sp^3 carbon atoms on opposite sides of the equator) compared to 6.83 Å in [60]fullerene itself. Thus the flattened poles and expanded equator is reminiscent of a spinning planet (Figure 4b), and the name "saturnene" commends itself in particular.[15]

The calculated lengths (AM1) of the sp^3–sp^3 bonds are 1.69 (5:6 bond) and 1.58 Å (6:6 bond), the former being the longest is the most probable site (cf. [7]) for oxygen insertion. We have found mass spectrometric evidence for traces of the mono-, bis-, and trisoxides at 1116, 1132, and 1148 amu, respectively, in material tailing the main band. The length of the longest bond is the same as the longest bond in $C_{60}F_{18}$ (obs.: 1.672 Å;[4] calcd (AM1): 1.69 Å[7]).



Scheme 1. Mechanism of contiguous addition to [60]fullerene (X = F, H). Solid circles show the position of the addends in the precursor structure; open circles show the further addition sites giving the final structures (see text).

In deducing a mechanism for the formation of $C_{60}H_{18}$ we argued that at a given stage in the contiguous addition pathway, two options were presented, one of which would lead to $C_{60}H_{18}$, the other to $C_{60}H_{20}$ (Scheme 1).[16] Because of the strain present in the latter we suggested that its formation was less likely. The arguments apply equally to fluorination, and the fact that $C_{60}F_{20}$ is indeed formed under the same conditions that lead to $C_{60}F_{18}$, and moreover in about 5% relative yield is fully consistent with the mechanistic scenario. In Scheme 1, the initial contiguous addition to 1,2-difluoro[60]fullerene leads to 1,2,3,4-tetrafluoro[60]fullerene. The next stage can give either 1,2,3,4,9,10-hexafluoro[60]fullerene (*S* pattern) or 1,2,3,4,11,12-hexafluoro[60]fullerene (*T* pattern). Further addition to either of these can lead ultimately to $C_{60}F_{18}$ (the further addition sites are indicated by open circles in the Schlegel diagram (Scheme 1)) a process strongly favored by formation of the fully delocalized central aromatic ring. However, continuation of the zigzag addition to the *S* structure results only in the formation ultimately of $C_{60}F_{20}$.

There is only *one* possible alternative $C_{60}F_{20}$ structure that would give a single ^{19}F NMR line, and this has isolated pairs of fluorine atoms arranged as shown in Figure 4d. This can be ruled out because it cannot be formed by the contiguous addition mechanism which is now well established to apply in fluorination and also in hydrogenation.[2, 3, 5, 6, 17] Moreover it has ten double bonds in pentagons (a destabilizing feature),[18] whereas the structure in Figure 4a–c has none. This predicted instability is confirmed by the calculated heats of formation which are higher for the alternative structure by 80.2, 89.0, and 130.1 kcal mol^{-1} (AM1, PM3, MNDO, respectively). The alternative structure is ruled out further by the EI mass spectrometric fragmentation pattern of $C_{60}F_{20}O$, which yields $C_{58}F_{17}^{\bullet}$ and $CF_3CO^{\bullet}$. For elimination of the latter fragment, adjacency of three fluorine atoms is required.

An area of intensive current fullerene research concerns the construction of donor–acceptor derivatives likely to have photonic/photovoltaic applications, and this has been reviewed recently by Guldi.[19] In these, the fullerene derivative is the acceptor, and the need is for enhancement of the electron withdrawal by the cage, thereby retarding back-electron transfer for the cage to the donor. Unfortunately, most donors make the cage less electron withdrawing by changing the hybridization state of some of the cage carbon atoms. However, the presence of many fluorine atoms on the cage increases the electron withdrawal, as indicated by the electron affinities (eV) of 4.05 ($C_{60}F_{44/46}$),[20] about 3.48 ($C_{60}F_{36}$),[21] and 2.74 ($C_{60}F_2$)[22] compared to 2.65 for C_{60}.[23] The reduction potential of $C_{60}F_{48}$ is also 1.38 V more positive than the first reduction potential of C_{60}.[24] Electron withdrawal in $C_{60}F_{20}$ may be further aided by the strain such that the carbon atoms acquire greater s character. This is indicated by the downfield location of the ^{19}F NMR signal, relative to that for $C_{60}F_2$ ($\delta = -148.3$).[1] Since there are two faces on the molecule for attachment of addends, one can envisage polymeric structures in which the donors are bonded to two $C_{60}F_{20}$ molecules, and so on. The molecule may thus prove to be an important synthon for such applications, and with this in mind we are seeking to improve the yield so that electrochemistry and other relevant experiments can be performed.

Experimental Section

$C_{60}F_{20}$ was isolated from the products of heating mixtures (ground intimately in a dry box) in a glass reactor under reduced pressure (1×10^{-3} mmHg); the mixtures comprised either [60]fullerene (240 mg) and Cs_2PbF_6 with heating at 580 °C for 6 h, or [60]fullerene (60 mg) and an equimolar KF/MNF_3 mixture (420 mg) with heating at 480 °C for 8 h. The products were extracted with toluene, filtered with exclusion of moisture, and separated by HPLC using a 10 mm × 25 cm Cosmosil Buckyprep column with elution by toluene at 4.7 mL min^{-1}). The main component ($C_{60}F_{18}$) eluted at 37 min, and $C_{60}F_{20}$ eluted at 74 min. The material of this latter retention time and obtained by either preparative method was spectroscopically identical.

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