Formation and characterisation of $C_{60}F_8O$, $C_{60}F_6O$ and $C_{60}F_4O$; the sequential pathway for addition to fullerenes

Olga V. Boltalina,[a] Andrei Yu. Lukonin,[a] Anthony G. Avent,[b] Joan M. Street[c] and Roger Taylor[b]

[a] *The Chemistry Laboratory, CPES School, University of Sussex, Brighton, UK BN1 9QJ*
[b] *Chemistry Department, Moscow State University, Moscow 119899, Russia*
[c] *Chemistry Department, The University, Southampton, UK SO17 1BJ*

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$C_{60}F_8O$, $C_{60}F_6O$ and $C_{60}F_4O$, obtained from the reaction of [60]fullerene with K_2PtF_6 at 465 °C, have the lowest fluorine contents of any fluorofullerene yet isolated; the addend motifs in each are subsets of that found in $C_{60}F_{18}$ and indicate how polyaddition levels are created in fullerenes.

Fluorofullerenes are potentially the most important of the halogenofullerene synthons because of their higher solubility and reactivity. Control of fluorination has however proved to be very difficult, and only $C_{60}F_{48}$ has been obtained by fluorine gas fluorination.[1] More recently, the species $C_{60}F_{36}$[2] and $C_{60}F_{18}$[3] were obtained from fluorination with metal fluorides. Preparation of fluorofullerenes of lower fluorine content is desirable.

The understanding of the addition patterns in fullerenes is still in its infancy; in particular, the pathways that lead to high addition levels have not been identified. Cycloadditions, the most explored fullerene reactions, give eight bis addends (nine for unsymmetrical addends), of which the *cis*-1 and *trans*-1[4] are disfavoured sterically and statistically, respectively. Other additions comprise mainly: (i) those involving bulky reagents *e.g* chlorination, bromination, and alkylation; (ii) hydrogenation and fluorination, which give similar patterns to each other, but different from those in (i) due to the absence of significant steric hindrance. Determination of the addition patterns in these latter two reactions is thus of particular importance for evaluating electronic and structural effects upon the addition pathways.

Following our recent discovery of the selective arylation of $C_{60}F_{18}$,[5] we scaled up the preparation of the latter. Purification by HPLC produced many by-products which were not seen in the previous small-scale preparation.[6] These include $C_{60}F_4O$, $C_{60}F_6O$ and $C_{60}F_8O$, which now provide important information concerning the manner in which polyaddition levels are attained in derivatised fullerenes. In previous work involving fluorination of [60]fullerene with fluorine gas, many oxide species were detected amongst numerous others in the EI mass spectrum of the raw product.[7] The ion intensities for species $C_{60}F_nO$ ($n = 2$–10) were quite significant in some batches, but it was unclear whether these represented actual compounds or merely fragmentation ions. The present work indicates that these were indeed actual compounds and this has implications for the future large scale preparation and isolation of fluorofullerenes, as described below.

Experimental

[60]Fullerene (240 mg) was fluorinated with K_2PtF_6 (575 mg) at 465 K under moderately high vacuum (*ca.* 0.01 bar) as described previously[3] to give crude $C_{60}F_{18}$ (300 mg). The material was partially pre-purified by vacuum sublimation, and the sublimate (280 mg) was dissolved in toluene (*ca.* 25 ml) and then filtered through a 15 mm plug of paper tissue that had been compacted into a Pasteur pipette; this filtration technique avoided solvent evaporation and hence reaction of the fluorofullerene with condensed moisture. The filtrate was purified by HPLC using a 10 mm × 25 cm Cosmosil Buckyprep column, with toluene elution at 4.7 ml min^{-1} (≡1 ml min^{-1} for a 4.6 mm column). This yielded numerous components, the characterisation of which will require considerable further work which we hope to undertake subsequently. However, we were able to separate, each in *ca.* 1 mg quantities at the given elution times, $C_{60}F_4O$ (16 min), $C_{60}F_6O$ (24.5 min), $C_{60}F_8O$ (35 min), and $C_{60}F_{18}O$ (45 min, which is consistent with that found previously).[8] The isolated $C_{60}F_8O$ was virtually pure, but the other two derivatives contained minor by-products, as shown by the spectra (below). Because of the particular importance of these derivatives, and the ease with which fluorofullerenes undergo nucleophilic substitution, we did not risk losing them at this stage by attempting removal of the by-products by repeated recycling.

Results and discussion

The elution order

It is notable that the elution order differs from that normally observed with fluorofullerenes (and other fullerene derivatives), since the *least* addended compound elutes first. This implies that substantial differences in polarities result from the significant difference in fluorine contents between the compounds. By contrast, methylated fullerenes of low but differing methyl contents elute in the ‘normal’ order,[9] but these derivatives are likely to have rather similar polarities to one another.

The EI mass spectra (70 eV)

The mass spectrum for $C_{60}F_8O$ [Fig. 1(a)] shows the parent ion at 888 amu, together with fragmentation ions due to loss of 2 × F_2. The spectrum for $C_{60}F_6O$ [Fig. 1(b)] shows the parent ion at 850 amu (with fragmentation loss of 3 × F_2) together with species of 938 and 1162 amu arising from traces of $C_{60}F_8OCF_2$ and $C_{60}F_{18}(CF_2)_2$ (the latter giving a $C_{60}F_{17}$ fragmentation ion at 1043 amu, due to loss of C_2F_5). These species produce additional lines in the ^{19}F NMR spectrum (below). The spectrum for $C_{60}F_4O$ [Fig. 1(c)] shows the parent ion at 812 amu and fragmentation loss of 2 × F_2. Both spectra 1(b) and 1(c) show the fragmentation peak for $C_{60}O$ (736 amu), behaviour found pre-

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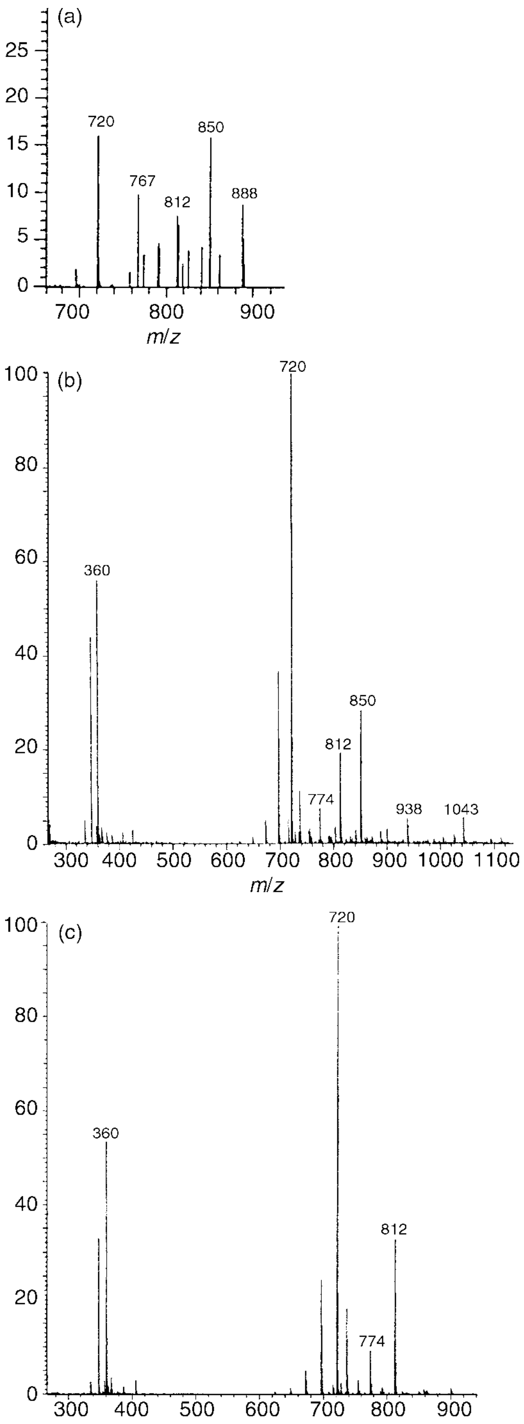

Fig. 1 EI mass spectra (70 eV) for (a) $C_{60}F_8O$, (b) $C_{60}F_6O$, and (c) $C_{60}F_4O$, respectively.

viously in the mass spectrum of a mixture of fluorofullerenes and their oxide derivatives.[10]

The IR spectra (KBr)

The spectra for $C_{60}F_8O$, $C_{60}F_6O$, $C_{60}F_4O$ [Figs. 2(a)–(c), respectively] show in the C–F stretching region, bands at 1260, 1168, 1132, 1098, 1085 and 1066 cm^{-1} ($C_{60}F_8O$), 1146, 1122, 1090, 1067, 1051 and 945 cm^{-1} ($C_{60}F_6O$), and 1147, 1106, 1064, 1025 and 940 cm^{-1} ($C_{60}F_4O$). In general the spectra show more lines as the structures become more complex, with that for $C_{60}F_8O$ most resembling that for $C_{60}F_{18}O$ and $C_{60}F_{18}$.

The ^{19}F NMR spectra (either 339 and 376 MHz)

$C_{60}F_8O$. The spectrum (Fig. 3) consists of four lines of equal intensity, δ_F −77.69 (2 F, d, 20 Hz), −134.21 (2 F, t, 20 Hz), −144.36, (2 F, t, 20 Hz) and −148.21 (2 F, d, 20 Hz). This very simple pattern shows that the molecule has C_S symmetry and contains two groups of four fluorines which are adjacent in a 'linear' array, and the two arrays are not in contact. The far downfield pair must be those nearest to the oxygen. Previously, we found that for $C_{60}F_{18}O$, in which the epoxide oxygen was one carbon removed from these nearest fluorines, the peaks for these appeared downfield at −94.6 ppm.[7] In the present case the substantially greater downfield shift shows that the epoxide must be *adjacent* to the downfield fluorines. Only one structure [Fig. 6(a)] fits the data, and in this the epoxide is replaced by the two fluorines from which it must be derived (through nucleophilic substitution by water and subsequent HF elimination).[10] The identification of the peaks 1–4 in the spectrum are shown on the Schlegel diagram [Fig. 6(a)]. The motif of this compound is a subset of that in $C_{60}F_{18}$.

$C_{60}F_6O$. The spectrum [Fig. 4(a)] consists of six lines of equal intensity at δ_F −74.46 (dd, 4 and 20 Hz), −82.55 (d, 8.6 Hz), −133.14 (m), −143.58 (m), −145.80 (m), and −149.25 (6.5 Hz). The 2D COSY spectrum [Fig. 4(b)] shows that these comprise two groups, one of two fluorines, the other of four fluorines. Two of the fluorines (one from each group) are well downfield and the positions in the spectrum show that they are each directly adjacent to the oxygen. From the 2D spectrum the correspondence between the peaks [Fig. 4(b)] and their positions is identified as shown in the Schlegel diagram, [Fig. 6(b)]. The motif for $C_{60}F_6O$ is thus a subset of that for $C_{60}F_8O$, and this is considered further below.

Other peaks due to impurities are evident in the spectrum, but these show no couplings to the six main peaks. They appear at δ_F *ca.* −63.2, −68.85, −68.96, −71.1, −130.4, −135.34, −136.24, −137.31 and −142.4. The latter could be due to CF_2 (known to appear in this region)[11] and indicated to be present by the mass spectrum, and the peak at −71.1 probably arises from a fluorine adjacent to oxygen (a second oxygenated species was indicated by the mass spectrum). The peaks at −63 and −69 ppm are indicative of the presence of a CF_3-containing species.[12]

$C_{60}F_4O$. The spectrum [Fig. 5(a)] consists of two main coupled peaks, δ_F −80.38 (2 F, d, 4 Hz), −148.36 (2 F, d, 4 Hz), see the expansion in Fig. 5(b). The downfield peak is in almost the same position as that for $C_{60}F_8O$, the same arguments locate its position, and only one structure is possible [Fig. 6(c)].

There are also sixteen minor peaks at δ_F −126.49, −131.77, −135.32, −137.40, −137.84, −143.48, −143.93, −147.10, −147.49, −149.20, −154.13, −155.19, −158.24, −162.58, −164.09, −164.39 and the integrals indicate that two are coincident giving eighteen overall. There are no downfield peaks so this compound is not an oxide. Since no other species was evident in the mass spectrum, the overall inference is that an unstable and unsymmetrical isomer of $C_{60}F_{18}$ may exist, but thus far we have been unable to isolate this minor species.

The resonance positions in each oxide

Notably, the resonances for the fluorines in the four-fluorine arm of $C_{60}F_6O$ (−74.5, −133.1, −143.6 and −145.8 ppm) are close to those in $C_{60}F_8O$ (−77.7, −134.2, −144.4 and −148.2 ppm). Similarly the resonances in the two-fluorine arm of $C_{60}F_6O$ (−82.6, −149.3 ppm) are almost identical to those found in $C_{60}F_4O$ (−80.4, −148.4 ppm). This provides compelling evidence for the structural similarity of the three compounds. Moreover, it is seen that as the number of less electron-withdrawing sp^3 carbons decreases from $C_{60}F_8O$ to $C_{60}F_4O$, so there is a gradual downfield shift of the resonances (an average of 1.7 ppm between the 4 F arms of $C_{60}F_8O$ and $C_{60}F_6O$, and 1.5 ppm between the 2 F arms of $C_{60}F_6O$ and $C_{60}F_4O$). This further confirms the structural assignments.

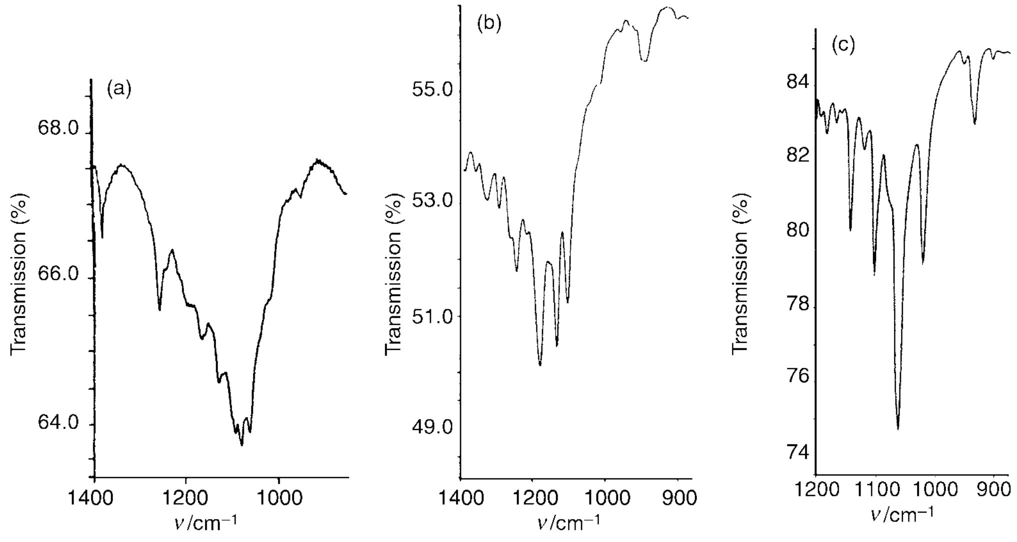

Fig. 2 IR spectra (KBr) for (a) $C_{60}F_8O$, (b) $C_{60}F_6O$, and (c) $C_{60}F_4O$, respectively.

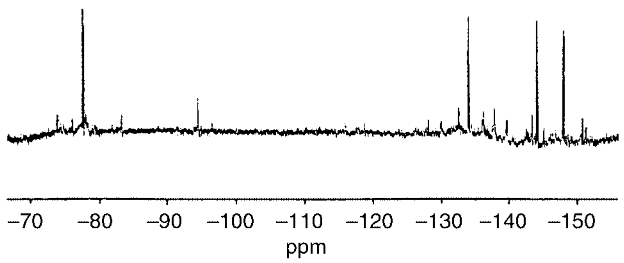

Fig. 3 ^{19}F NMR spectrum for $C_{60}F_8O$ (339 MHz).

The oxide motifs

The motif in $C_{60}F_4O$ is a subset of that in $C_{60}F_6O$, which is in turn a subset of the motif in $C_{60}F_8O$, and the motifs for all three appear in $C_{60}F_{18}$. This provides key information concerning the manner in which these addend patterns are built up:

(i) 1,2-Dihydro[60]fullerene gives mainly the 1,2,3,4-tetrahydro derivative on hydrogenation,[13,14] which we have argued is due to the partial aromatic nature of the fullerene.[13,15] 1,2-Addition increases the electron localisation in the addended hexagon, hence the π-density of the remaining double bonds, thereby directing addition to these.

(ii) We have conjectured that a consequence of (i) is that further addition gives either an 'S' or 'T' pattern;[15,16] these have been seen previously only in $C_{60}O_3$.[17]

The structure of $C_{60}F_4O$ shows the predicted 'T' pattern. Further addition according to the principle in (i) then gives the *motif* of $C_{60}F_6O$ and then that of $C_{60}F_8O$ (see below); the only alternative would place four fluorines and the epoxide in the same hexagon, which is sterically unfavourable. Further addition in this manner gives the $C_{60}F_{18}$ motif (with oxygen replaced by F_2), the subsequent additions being constrained to create a central fully-delocalised benzenoid ring.[16]

We now address the question of how the addition process is initiated. It seems unlikely that the products are produced from fluorination of any $C_{60}O$ impurity in the original C_{60} because the oxide would degrade at the reaction temperature. Nor, for the same reason, does it appear likely that the more highly fluorinated epoxides are formed by fluorination of the lower homologues. The most probable scenario is that a 'T' pattern $C_{60}F_6$ species is formed initially and that this then fluorinates stepwise as to give $C_{60}F_8$ and then $C_{60}F_{10}$. Subsequently nucleophilic substitution by adventitious water followed by elimination of HF from the adjacent OH and F gives the epoxide. Notably, in each molecule there are three less-hindered fluorines (more susceptible to OH attack) but only one is adjacent to a fluorine atom with three fluorine neighbours, and thus more readily removed (steric acceleration). Further work may show if this is a general mechanistic feature. We note too that the nucleophilic substitution cannot here proceed *via* addition–elimination[7] in view of the product structures; only direct substitution seems possible. In which case this constitutes the first evidence for such a process for a halogenofullerene occurring in the absence of a Lewis-acid catalyst (*cf. e.g.* ref. 5).

The implication of this work is that species $C_{60}F_nO$, (n = 10–16) could also exist, but we have not yet identified them in the HPLC eluents. Preliminary work indicates that the species of longer retention times are mainly isomers of $C_{60}F_{18}O_2$, and since these more highly fluorinated species are more

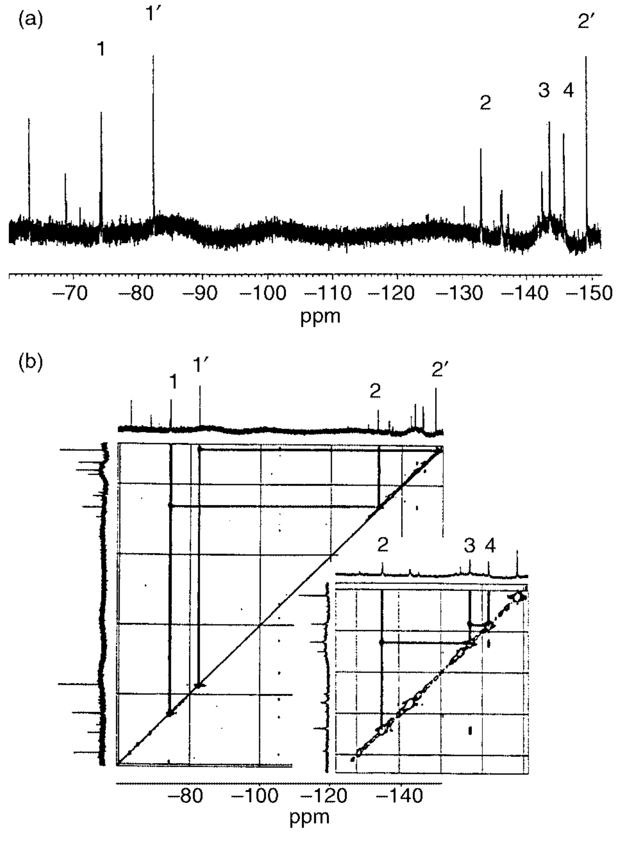

Fig. 4 (a) ^{19}F NMR spectrum for $C_{60}F_6O$ (376 MHz). (b) 2D COSY ^{19}F NMR spectrum for $C_{60}F_6O$; inset shows expansion of part of the spectrum.

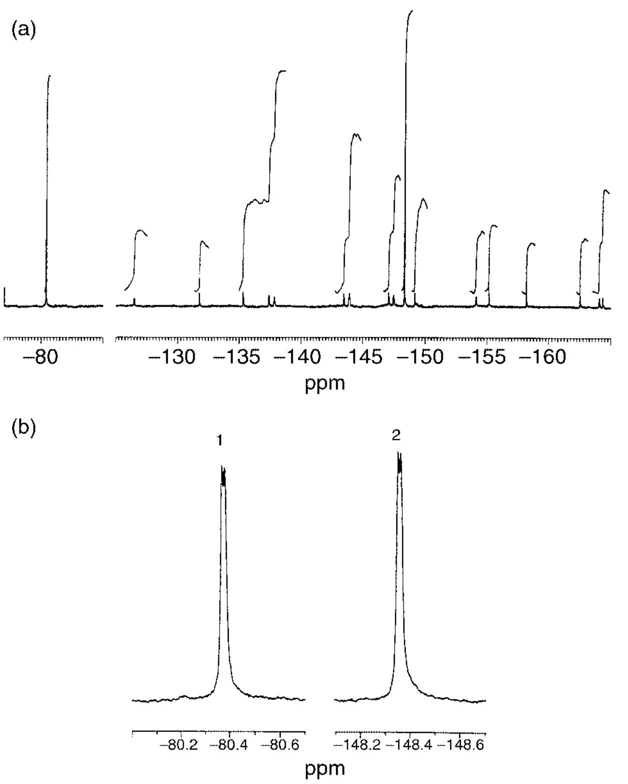

Fig. 5 (a) Overall ^{19}F NMR spectrum for $C_{60}F_4O$ (376 MHz). (b) Expansion of the −80 and −148 ppm region of the spectrum in Fig. 5(a), showing the coupling between the two main peaks.

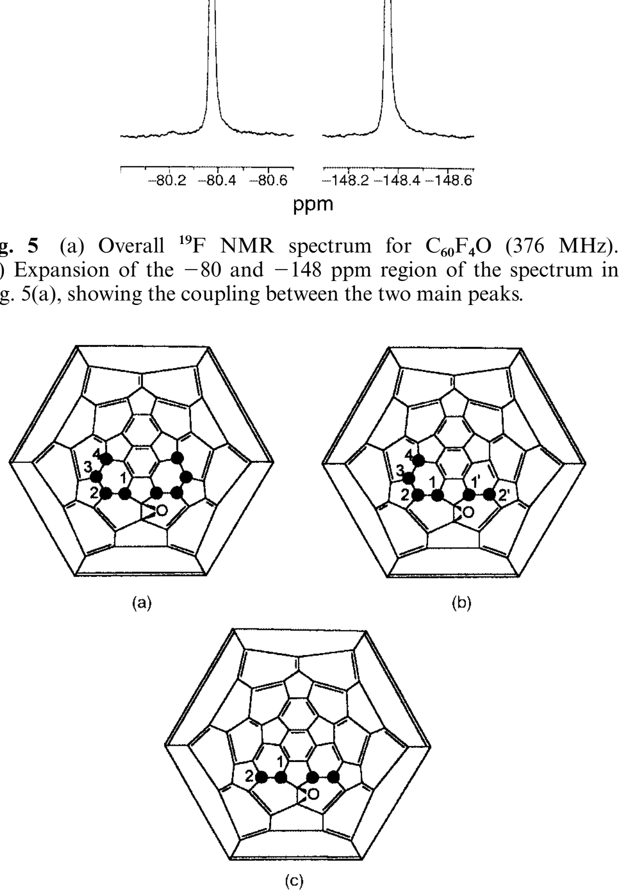

Fig. 6 Schlegel diagrams for (a) $C_{60}F_8O$, (b) $C_{60}F_6O$, and (c) $C_{60}F_8O$, respectively.

volatile, they may mask any other products during EI mass spectrometry. Further work in this area is continuing.

For large scale production of individual fluorofullerenes, the metal fluoride route will not be satisfactory because of the costs involved. However, as demonstrated here, this route does enable us to identify the HPLC retention times for given compounds, so that it may be possible ultimately to separate these from the complex mixture of products that are produced by fluorination with fluorine gas.

Footnote

A referee suggested that it would be valuable to see if the electronic absorption spectra of these compounds varies systematically in view of the incremental change in the cage structure. We plan therefore to produce larger quantities of these derivatives so that secondary purification may be undertaken, and hope to report these results along with details of other fluorofullerene epoxides currently being isolated.

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