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Novel formation of a fluorinated aziridino[60]fullerene

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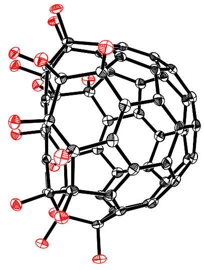
Abstract—Reaction of $MEMN_3$ (methoxyethoxymethylazide) with $C_{60}F_{18}$ results in replacement of two fluorines by the $>NCH_2OCH_2CH_2OMe$ function giving a C_s symmetrical aziridinofluorofullerene, $C_{60}F_{16}NCH_2OCH_2CH_2OMe$.

$C_{60}F_{18}$ **1**[1] is a fullerene unique in undergoing more types of reaction than any other: η^6 co-ordination at the flat fully aromatic face, electrophilic aromatic substitution, cycloadditions on the curved face, nucleophilic substitution of peripheral fluorines under Bingel conditions, elimination–substitution to give a $C_{60}F_{16}$ derivative, oxygen insertion into both FC–CF and CF bonds, and $:CF_2$ insertion into C–F bonds.[2] We now report another novel reaction of **1**.



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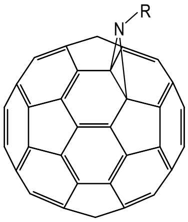

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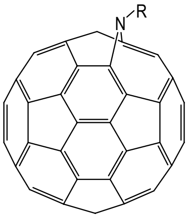

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Reactions of fullerenes with N-containing precursors lead either to addition across a 6:6 π-bond (giving epiminofullerenes (aziridinofullerenes **2**)), or insertion into a 6:5 σ-bond to give azahomofullerenes **3**. The latter are the main products from reactions of fullerenes with azides (especially $MEMN_3$) followed by N_2 extrusion,[3] whilst the former dominate in reactions with nitrenes (obtained from various precursors).[4–7] Reactions with azides have led to open cage[8] and hetero-fullerenes.[9]

In extending our studies of $C_{60}F_{18}$ chemistry we hoped to make fluorinated azahomofullerene derivatives, and hence fluorinated open-cage fullerenes and fluorinated heterofullerenes. Pure $C_{60}F_{18}$ (17 mg, 14.5%) was obtained by heating a mixture of [60]fullerene (80 mg), MnF_3 (270 mg) and K_2NiF_6 (160 mg) at 510 °C for 1 h, extraction of the cooled mixture by toluene and separation by HPLC (high pressure liquid chromatography). A toluene solution of $C_{60}F_{18}$ (10 mg, 9.42×10^{-6} mol) was heated with $MEMN_3$ (6.3 mg, 4.71×10^{-5} mol) under reflux for 6 h. The filtered product was separated by HPLC (250 × 10 mm Cosmosil Buckyprep column, toluene flow rate of 4.7 mL min^{-1}). Peaks were eluted at 2.3, 2.9, 4.4, 12.3 (**4**), 21.3 (**5**) and 38.4 min. The last was recovered $C_{60}F_{18}$ whilst the first three peaks were non-fullerene by-products. Yields of **4** and **5** were ca. 2 and 3 mg, respectively.

Component 5. *Mass spectra*: The MALDI-TOF spectrum (negative mode) showed the parent ion at 1127 amu ($C_{60}F_{16}NMEM$) with a fragment ion at 1108 amu (loss of F). The EI spectrum (70 eV) showed the $C_{60}F_{16}$ fragment ion at 1024 amu.

^1H NMR (400 MHz, $CDCl_3$) δ 5.59 (2H, s, CH_2), 3.93 (2H, t, *J* 4.7 Hz, CH_2), 3.63 (2H, t, *J* 4.7 Hz, CH_2) and 3.42 (3H, s, Me).

^{19}F NMR (376 MHz, $CDCl_3$, Fig. 1) δ −130.64 (2F, d, *J* 14 Hz), −136.02 (2F, s), −136.60 (2F, s), −138.30 (2F, s), −142.68 (2F, d, *J* 26 Hz), −143.38 (2F, s), −144.22 (2F, d, *J* 26 Hz), −158.25 (2F, m, and 7 and 18 Hz). The

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Keywords: Fluorofullerenes; Cycloaddition; Methoxyethoxymethylazide; Aziridinofullerenes.

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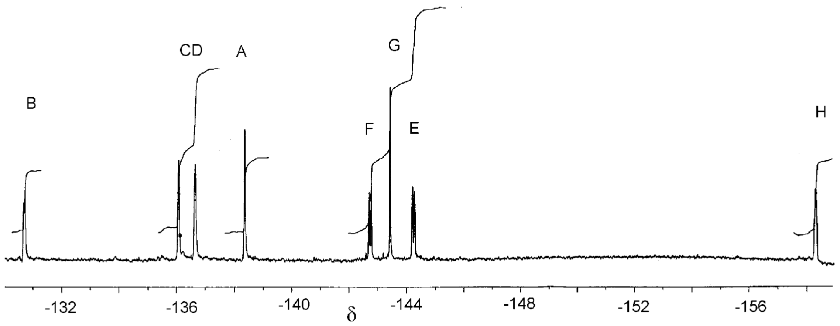

Figure 1. ^{19}F NMR spectrum for **5**.

2D spectrum (Fig. 2), established the fluorine connectivities: A–C (*m,p* across the benzenoid ring); A–D, B–F (both 1,4 conj.); A–E, B–H, C–G, C–H, D–F, D–H, E–F (all 1,2); B–C, B–D, C–D (all 1,3).

The C_s structure (Fig. 3) is readily deduced from these data. We can be certain that addition of N rather than insertion (which would give an azahomofullerene) has taken place, because the latter would require a structure possessing 18 fluorines instead of 16. Addition or insertion into the curved nonfluorinated part of the cage can also be discounted, since again the product would retain 18 fluorines.

Further confirmation of the structure is provided by comparison of the ^{19}F NMR chemical shifts for corresponding fluorines for $C_{60}F_{16}$ and the derivative **5** (Table 1).[10] Whereas peaks B, C, D, F, G, H for **5** are upfield from those for $C_{60}F_{16}$ by an average of only 1.35 ppm, peaks A and E are upfield by 10.5 and 7.1 ppm, respectively. There is thus a severe electronic disturbance next to A and near to E, which locates the addition site. This also further eliminates the possibility of insertion into either of the 6:5 bonds straddling the symmetry plane (which would give a C_s product) since the disturbance would be too far away from A and E to have any significant effect.

Thus the azide group has replaced two fluorines. We reported recently an analogous replacement of the same fluorines by a tetrathiofulvalenyl (TTF) group,[11] and in both cases the normal addition pathway is diverted by the facile loss of two fluorines. Note that the (two) peaks corresponding to **A** in the (unsymmetrical) TTF derivative were also shifted upfield by >10 ppm. The conjectured mechanism (Fig. 4) parallels that proposed for the formation of the TTF derivative. Although strong C–F

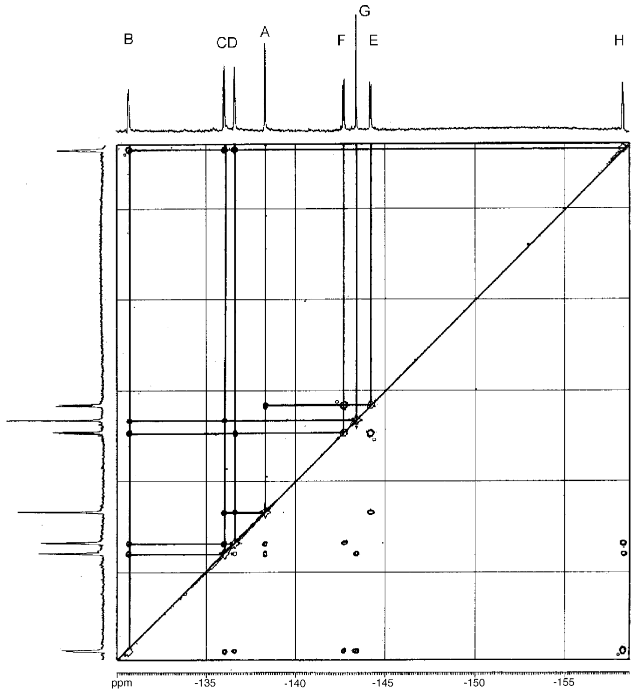

Figure 2. 2D COSY ^{19}F NMR spectrum for **5**.

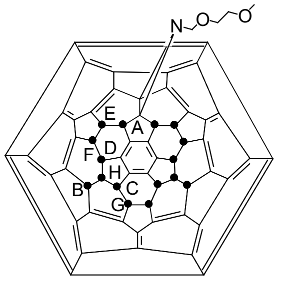

Figure 3. Schlegel diagram for **5** (● = F), fluorine positions as in Figure 1.

Table 1. Fluorine chemical shifts (ppm) for $C_{60}F_{16}$ and **5**

Position	$C_{60}F_{16}$	**5**	δ ($C_{60}F_{16}$-**5**)
A	−127.8	−138.3	*10.5*
B	−128.5	−130.6	2.1
C	−135.2	−136.0	0.8
D	−136.0	−136.6	0.6
E	−137.1	−144.2	*7.1*
F	−140.8	−142.7	1.9
G	−142.2	−143.7	1.5
H	−157.0	−158.2	1.2

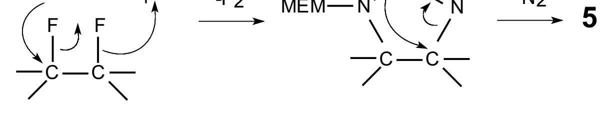

Figure 4. Conjectured mechanism for the formation of **5**.

bonds are broken, the energy loss is compensated by C–N and F–F bond formation, N_2 elimination, and by the reduction of eclipsing interactions of the adjacent C–F bonds through cycloaddition. Fullerene C–F bonds are also broken in the formation of trannulenes, where the energy deficiency arising from C–C bond formation is compensated by increase in aromaticity of the products.[12]

This result provides the first example of the formation of a fluorinated aziridino[60]fullerene, and provides a route for the formation of derivatives for electron-transfer studies.

Component 4. This is also a $C_{60}F_{16}$ derivative. The EI MS shows a parent ion at 1164 amu with fragment ions at 1149 amu (M-Me), and 1024 amu ($C_{60}F_{16}$), whilst the MALDI-TOF spectrum shows a parent ion at 1164 amu (fragment ions at 1132 and 1024 amu). The addend evidently contains oxygen and a methyl group, but the ^{1}H NMR spectrum shows no MEM moiety, whilst the ^{19}F NMR spectrum indicates a compound with slight asymmetry. Further studies on larger samples will be needed to solve the structure.

Acknowledgements

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