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[60]- and [70]Fullerenes are trifluoromethylated across 5:6-bonds

Adam D. Darwish, Anthony G. Avent, Ala'a K. Abdul-Sada and Roger Taylor*
The Chemistry Laboratory, CPES School, University of Sussex, Brighton, UK BN1 9QJ.
E-mail: R.Taylor@sussex.ac.uk; Fax: 44 1273 677196; Tel: 44 1273 678602

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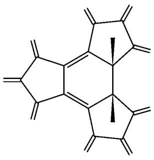
Trifluoromethylation of [60]- and [70]fullerenes occurs across both 6:6- and 5:6-bonds giving unsymmetrical tetramethyl adducts having four contiguous CF_3 groups; both fullerenes give bis adducts which do not involve 6:6-addition, and unsymmetrical hexa-adducts (with contiguous CF_3 groups) are also obtained from [60]fullerene,

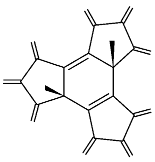
Fullerene additions have hitherto fallen into three main categories: (i) 1,2-cycloadditions across a 6:6-bond; (ii) 1,4-addition of bulky groups such as Br, Cl, R, Ar; (iii) 1,2-addition of small groups across a 6:6-bond;[1] tetra-addition of hydrogen and fluorine takes place across adjacent double bonds.[2] For some intermediate size addends, both 1,2- and 1,4-addition is believed to occur *e.g.* ref. 3. 1,2-Addition (**1**) is favoured by having no strain-increasing double bonds in pentagons;[4] for 1,4-addition (**2**) there is no adjacency hindrance but a double bond is located in a pentagon. 1,6-Addition (**3**) has generally been discounted because the addends are adjacent, and double bonds are located in *two* pentagons. Calculated heats of formation for hydrogenation are 776.1, 780.0 and 794.5 kcal mol^{-1} for **1**, **2**, and **3**, respectively;[5] 1,2-addition preference diminishes with increasing addend size.[6]

Trifluoromethylation, one of the first fullerene reactions to be investigated, readily adds of up to 22 CF_3 groups to [60]- and [70]fullerenes.[7–10] Perfluoroalkylation of [60]fullerene has also been studied.[11] Trifluoromethylfullerenes are stable to strong acids and bases,[8] aqueous solutions, temperatures beyond 270 °C, are very volatile[7,8] and soluble in organic solvents. Studies of the isolation and characterisation of derivatives are sparse, because numerous products are obtained (especially if the reactions are carried out in protic solvents), which are very difficult to separate by HPLC (high pressure liquid chromatography). Only $C_{60}F_{17}CF_2CF_3$, $C_{60}F_{17}CF_3$ (three isomers),[12] $C_{60}F_7CF_3$,[13] and $C_{60}(CF_3)_2$,[14] have been characterised.

We have trifluoromethylated [60]-, [70]-, [76]-, [78]- [84]- and aza[60]fullerene, under aprotic, and in some cases protic conditions. We report here novel [60]- and [70]fullerene results under the former conditions [pyrolysis of CF_3CO_2Ag/fullerene mixtures (6:1 w/w) at 300 °C and 0.05 mBar], a modification, to avoid work-up difficulties, of the Hiemeyer CF_3CO_2Na method.[10,15] Since the volatile trifluoromethylfullerenes were retained within the reaction mixture instead of being deposited in the reactor cold zone, some co-ordination to silver may occur. The solution from toluene sonication was filtered, and analysed. Some CF_3/H-containing species were also obtained indicating that either silver co-ordinated or radical species were also present, decomposed by the toluene during work-up.

Up to 20 and 12 CF_3 groups, were added to [60]- and [70]-fullerenes, respectively. HPLC separation on 250 × 10 mm Cosmosil columns [either 5 PYE (4 ml min^{-1}) or Buckyprep (4.7 ml min^{-1})] with consecutive elution by toluene or 1:1 toluene:heptane, as necessary) yielded very many derivatives; in this preliminary report we describe some unusual results.


(**1**)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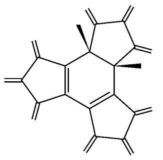
(**3**)

Each fullerene yielded a bis-trifluoromethyl derivative. Unusual behaviour was shown by the ^{19}F NMR spectrum (Fig. 1) of $C_{70}(CF_3)_2$ (978 amu, 5 PYE, 1:1 tol.:hept., 32.5 min), the two quartets (J 12 Hz) indicating the CF_3 groups to be adjacent. Instead of addition occurring across the (normally most reactive) 1,2-bond (see Fig. 2 for numbering), giving a C_s symmetry product, the ^{13}C NMR spectrum (*ca.* 64 sp^2 lines) showed the product to have C_1 symmetry. The only ('double') bond in [70]fullerene that could give a C_1 product is 7,21 and addition across this occurs (as a minor species) in very few reactions,[16,17] and is unlikely to be preferred to either 1,2- or 5,6-addition. A feasible explanation is that addition occurs across a 5:6-bond; the sole known example (benzyne cycloaddition across the 7,8-positions),[17] is driven by a unique equatorial bond structure.

Further evidence came from the ^{19}F NMR spectra for two isomers of $C_{70}(CF_3)_4$ **A**, 35 min and **B**, 49 min (5 PYE, 1:1 tol:hept.); Fig. 3a shows the mass spectrum for **A** (1116 amu). Each consisted of two quartets and two septets proving that they are unsymmetrical and contain a 'linear' sequence a→b→c→d of trifluoromethyl groups: **A**, δ −65.50 (sept, 12 Hz), −65.92 (sept, 14 Hz), −66.53 (q, 12 Hz), −68.78 (q, 15 Hz); **B**, δ −64.02 (sept, 12 Hz), −64.61 (sept, 13 Hz), −65.16 (q, 13 Hz), −67.42 (q, 12 Hz); Fig. 3b shows the spectrum for **B**. 6:6-Bond

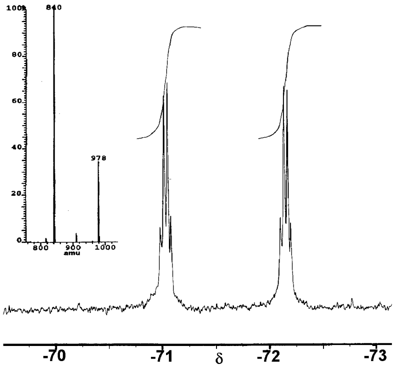

Fig. 1 ^{19}F NMR spectrum for $C_{70}(CF_3)_2$; inset shows the mass spectral peak of 978 amu.

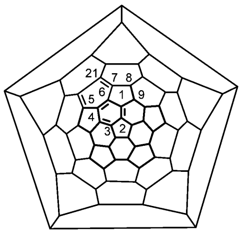

Fig. 2 Schlegel diagram for [70]fullerene with relevant numbering.

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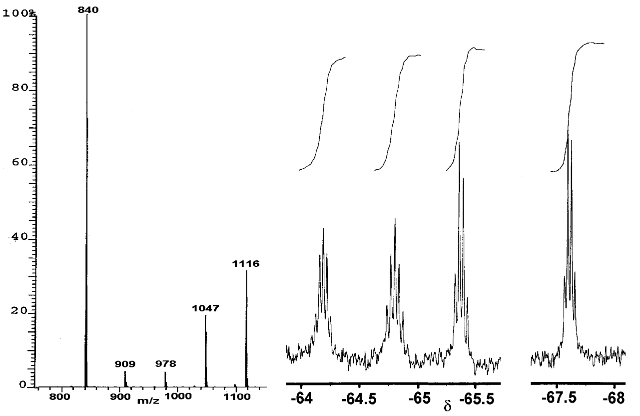

Fig. 3 (a) EI mass spectrum (70 eV) for $C_{70}(CF_3)_4$ (**A**); (b) ^{19}F NMR spectrum for $C_{70}(CF_3)_4$ (**B**).

addition to comply with this symmetry requires these to be either 1,2,5,6 or 5,6,7,21 adducts, whereas we could expect the (symmetrical) 1,2,3,4 adduct. Moreover, we have identified ten other unsymmetrical $C_{70}(CF_3)_4$ isomers, a number impossible if addition occurs across 6:6 bonds only. Addition across both 6:6- *and* 5:6-bonds is indicated, shown by the difference of the coupling constants for the a/b *vs.* c/d CF_3 groups in both tetra-adducts.

Additional evidence comes from $C_{60}(CF_3)_2$ (17.4 min retention time, Buckyprep 1:1 tol.:hept.) which gives a single ^{19}F NMR line at $\delta -69.32$ (*cf.* −69.5).[14] The sp^2 region of the ^{13}C NMR spectrum shows δ 148.78, 148.29, 147.52, 147.45 (1C) 147.27, 146.90, 146.88, 146.78, 145.73, 145.29, 144.23, 144.22, 144.10 (1C), 143.97, 143.87 (1C) 143.50, 143.37, 143.23, 143.15, 142.93, 142.88 142.62 (1C), 142.35, 141.63, 141.56, 141.45, 140.71, 138.75 (4C) *cf.* 27×2 C + 4×1 C required for either 1,4- or 1,6-addition; the slight shortfall is due to adjacent F coupling. 1,2-Addition requires 13×4 C + 3×2 C. 1,4-Addition is improbable because of evidence obtained for tetrakis addition:

(i) We have isolated an unsymmetrical $C_{60}(CF_3)_4$ isomer (**C**, 16.5 min retention time, Buckyprep 1:1 tol.:hept.) (996 amu, Fig. 4a) comprising four equal intensity peaks (two overlapping septets, resolved (50 °C) into δ_F −65.60 and −65.74) and two quartets at δ_F −68.17, −69.71, J 13.5 and 12 Hz respectively (Fig. 4b). Only a 'linear' positional sequence a→b→c→d as found for $C_{70}(CF_3)_4$ can account for these results (see Fig. 5).

(ii) We have isolated other unsymmetrical tetramethyl adducts, and two of these (**D**, **E**, 13.0 and 14.1 min, Buckyprep 1:1 tol.:hept.) show four quartets, (**D**: δ 67.88, 68.51, 68.63, 68.98; 12.5, 12.9, 12.6, 13.0 Hz, respectively; **E**: δ 67.93, 68.37, 69.40, 69.91; all 12.4 Hz). Each therefore has two isolated pairs of adjacent CF_3 groups. However, there can be only *one* unsymmetrical adduct (*trans*-2 isomer) if addition takes place only across 6:6-bonds. The other isomers therefore involve addition across at least one 5:6-bond.

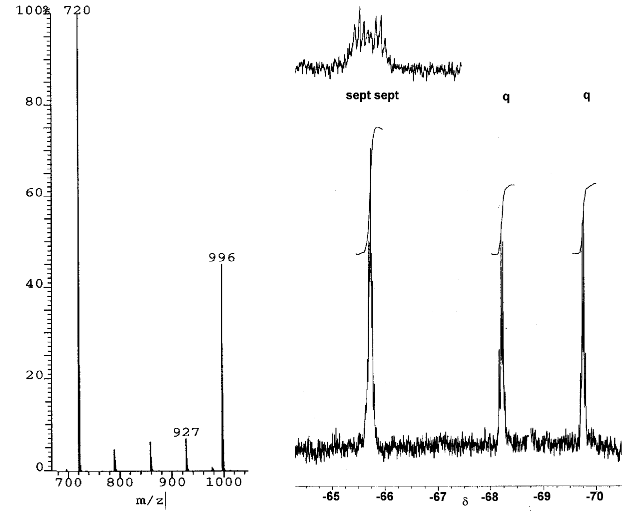

Fig. 4 (a) EI mass spectrum (70 eV); (b) ^{19}F NMR spectrum for unsymmetrical $C_{60}(CF_3)_4$, isomer **C**.

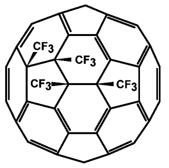

Fig. 5 Proposed structure of $C_{60}(CF_3)_4$ isomer **C**.

(iii) We have isolated some unsymmetrical hexa-adducts, two of which (**F**, **G**, 12.3 and 10.6 min, Buckyprep 1:1 tol.:hept.) show four septets and two quartets: **F**, δ 64.4 (sept), 65.47 (sept), 65.485 (sept), 66.5 (sept), 67.35 (q), 69.64 (q), all 12.9 ± 1.2 Hz; **G**, δ 63.5 (sept), 65.2 (sept), 65.61 (sept), 65.65 (sept), 67.7 (q), 68.4 (q), 12.4, 12.8, 12.7, 14.6, 14.5, 12.3 Hz, respectively. These data show that the CF_3 groups are contiguous, that the molecules have no symmetry and 5:6-addition must be involved.

A possible existence of a balance between kinetic and thermodynamic stability in this reaction, will be addressed later.

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