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Methylation of [76]fullerene and [84]fullerenes; the first oxahomo derivatives of a higher fullerene†

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Methylation of [76]fullerene by reaction with Al–Ni alloy/NaOH followed by quenching of the intermediate anions with methyl iodide gives a mixture of methylated and methylenated products together with oxide derivatives. The major derivatives are five isomers of $C_{76}Me_2$ (one of C_s symmetry due to 1,6-$C_{76}Me_2$) and $C_{76}(CH_2)_n$ (n = 2–4), together with corresponding mono-oxides. The single line ^1H NMR spectrum of mono-oxide $C_{76}Me_2O$ shows it is an oxahomofullerene (ether) the first example derived from [76]fullerene, oxygen being inserted between the CMe groups in 1,6-$C_{76}Me_2$giving a product of C_2 symmetry. The probable structures of the unsymmetrical dimethyl derivatives have been deduced from heats of formation calculated by AM1 and density functional methods. Bis-oxide $C_{76}Me_4O_2$ is the first bis oxahomo[76]fullerene to be isolated and gives two equal-intensity lines in the ^1H NMR spectrum showing that it must also have C_2 symmetry; probable structures are considered. Methylation of [84]fullerene takes place less readily and only four $C_{84}Me_2$ derivatives were isolated, two of them in quantities sufficient to show the symmetries as C_1, and either C_2 or C_s.

Introduction

Exploration of higher fullerene chemistry has been relatively sparse because of both the low availability of the starting materials, the extensive work required to purify them, and their lower reactivity compared to [60]- and [70]fullerenes. Studies of [76]fullerene include hydrogenation (between 46 and 50 hydrogen atoms are added),[1] fluorination (between 36 and 40 fluorine atoms are added),[2] reaction with phosphoryl radicals (which gave seven out of the possible nineteen $RC_{76}^{\bullet}$ radicals),[3] and photochemical silylation with disilirane which gave eight mono-adducts, four of which were shown to have C_1 symmetry.[4] Specific locations were proposed in osmylation (two enantiomers were resolved, addition being assumed to occur across either the 2,3- or 1,6-bonds),[5] [2 + 4]cycloadditions, which yielded C_2 and C_1isomers, believed to involve addition across the 1,6- and 2,3-bonds respectively, together with three other C_1 isomers;[6] and the Bingel reaction which gave a C_2 diastereoisomeric pair (also assumed to involve 1,6-addition), together with C_1 diastereoisomers (believed to involve addition across the 2,3- and 4,5-bonds).[7] (See Fig. 1 for numbering.)

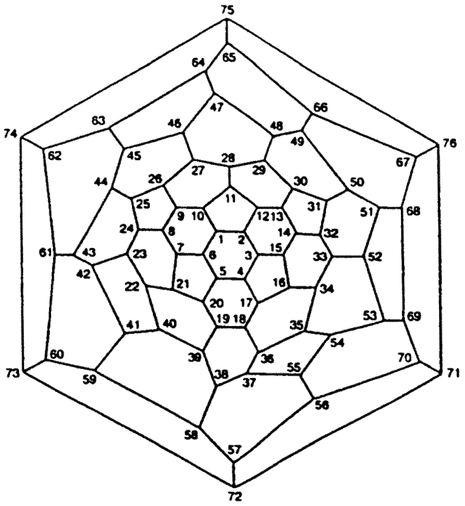

Fig. 1 Schlegel diagram for [76]fullerene, showing numbering.

Calculations of π-densities indicated a decreasing bond reactivity order of 14,15 (0.608) > 4,5 (0.603) > 1,6 (0.603) > 2,3 (0.598) > 29,30 (0.578) < 11,28 (0.576),[8] and notably the first four bonds collectively comprise a combination of the *T* and *S* addition patterns that relate to [60]fullerene addition.[9] However, the differences in π-densities are not large and the kinetic addition pathway that would lead to such locations may be over-ridden in polyaddition by thermodynamic effects. Thus for five-fold addition, the involvement of consecutive double bonds in a contiguous *S* pattern is calculated to be involved, *viz* 14,15 − 2,3 − 1,6 − 7,8 − 23,24.[10] Addition across the 4,5-bond is for example disfavoured in the polyaddition because it introduces severe eclipsing interactions.

Electrophilic alkylation is hindered by the electron-withdrawing properties of the cage, but can be circumvented either by reaction of the electrophile with the fullerene radical anion (produced both by reaction with alkali metals), or by nucleophilic substitution of a halogeno group by alkyl groups. The former method has been shown to give addition of up to 24 methyl groups to [60]fullerene, with (uncharacterised) $C_{60}Me_6$ and $C_{60}Me_8$ prominent.[11] More controlled addition can be obtained by initial electrochemical reduction, which has led to isolation of a mixture of 1,2- and 1,4-$C_{60}Me_2$,[12] and (uncharacterised) $C_{60}R_2$ (R = Et, n-Bu), $C_{60}Me_4$ and $C_{60}Me_6$.[13]

[60]Fullerene has also been alkylated by addition of nucleophilic alkyl groups from reagents MR (M = alkali metal), with quenching of the intermediate $C_{60}R_n^-$ either by electrophilic H or alkyl R′ to give either $C_{60}RH$ or $C_{60}RR'$;[14–17] the organocopper reagent MeMgBr/CuBr/Me_2S has been used in a related procedure.[18] Alkylation occurs by reacting fullerenes with ketones inside a mass spectrometer,[19] cyanoalkyl groups have been attached to [60]fullerene by reaction with azo(bisisobutyronitrile),[20] and monoalkylation can be effected by reaction of fullerenes with alkyl halides in the presence of Zn/DMF.[21]

Recently we have studied methylation of [60]- and [70]-fullerenes, involving both the parent fullerenes and chloro derivatives, methylation in the latter case being obtained *via* nucleophilic substitution. The regiochemistry differs according

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† Electronic supplementary information (ESI) available: HPLC separation data (Table S1) and calculated heats of formation (Table S2). See http://www.rsc.org/suppdata/ob/b3/b316163c/

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to the method used, and as well as methylated products some oxygenated derivatives were obtained, some of which were characterised as hydroxyepoxides and open-cage tautomers.[22] For methylation of [70]fullerene we used (i) reaction with lithium followed by quenching with MeI which gave $C_{70}Me_n$ ($n < 26$, $C_{70}Me_6$ being the most abundant species); the isolated $C_{70}Me_2$ consisted mainly of a 3.4 : 1 ratio of the 1,2- and 5,6-isomers, together with smaller amounts of five other unsymmetrical isomers; (ii) nucleophilic substitution of $C_{70}Cl_{10}$ by MeLi which gave $C_{70}Me_n$ ($n = 2, 4, 6, 8$); (iii) reduction with Al/Ni alloy/NaOH/DMSO/THF followed by reaction with MeI which gave $C_{70}Me_n$ ($n = 2, 4, 6, 8, 10$) together with $C_{70}Me_2H_2$.

Because the latter reaction appeared to give good control of addition, we have employed it in the investigation of the methylation of [76]fullerene and [84]fullerenes.

Experimental

The higher fullerenes (supplied in a crude mixture by Hoechst) were separated by HPLC (high pressure liquid chromatography) using a 250 × 20 mm Cosmosil Buckyprep column operated at a flow rate of 18 ml min^{-1}, to give [76]-, [78]-, and [84]fullerenes.

In a typical experiment, a suspension of [76]fullerene (4 mg, 0.0044 mmol), Al–Ni alloy (50 mg, 1.16 mmol) and NaOH pellets (300 mg 7.5 mmol) were placed in a Schlenk round-bottomed flask, which was evacuated and filled with argon three times. Distilled DMSO (5 ml) and THF (5 ml) were added, followed by degassed water (2 ml), the mixture being then stirred. As the NaOH dissolved the reduction took place rapidly with accompanying effervescence of hydrogen, and the solution turned deep brown; stirring under argon was continued overnight.

The solution of C_{76} anions was transferred (*via* a cannula) to another 25 ml Schlenk round-bottomed flask under argon, leaving a colourless aqueous caustic layer. Methyl iodide (300 ml, excess) was added to the anion solution and stirred overnight under argon. The resultant brown/black reaction mixture was extracted with toluene, washed with water, dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. The deep brown toluene solution of [76]fullerene derivatives was separated by HPLC using a 250 × 10 mm Cosmosil 5 PYE column with elution by toluene at 4 ml min^{-1}. The data are given in Table S1 †. The procedure was quadruplicated for [76]fullerene and duplicated for [84]fullerene.

Theoretical calculations

Formation energies of dimethyl[76]fullerenes were calculated using the semi-empirical AM1 Hamiltonian implemented in the program MOPAC[23] and the density functional code AIMPRO.[24]

The formation energy of the most stable isomer of $C_{76}(CH_3)_2$ calculated using AM1 is 1260.5 kcal mol^{-1}. Semi-empirical methods are known to be not very accurate in determining formation energies and different semi-empirical methods often give very different values for the same compound.[25–27] However, relative AM1 energies of isomers can be regarded as more reliable. Therefore we compare below relative energies of $C_{76}(CH_3)_2$ isomers.

We performed local density functional calculations with the AIMPRO code[24] in the supercell approach, using the carbon basis set optimised for graphite. We used a 30 × 30 × 30 a.u. cubic cell. The calculated energies are converged with respect to the cell size. This indicates that in the cell of this size there is no interaction between the fullerene molecules, and they can be regarded as isolated.

The formation energy of [76]fullerene relative to the standard state (graphite) was calculated as 683.0 kcal mol^{-1}, or 0.39 eV per carbon atom. There are no experimental data available at present on the formation energy of [76]fullerene. However, there have been experimental measurements of formation enthalpies of [60]-[26,28] and [70]fullerene,[27,29,30] and it has been predicted theoretically that formation energies of [70–84]fullerenes are rather close to each other and lie within the range 0.34–0.40 eV per atom, [31,32] larger fullerenes being more stable than small ones.

Therefore the formation energy per atom of [76]fullerene can be compared with the experimental standard formation enthalpy of gaseous [70]fullerene obtained as a sum of the formation enthalpy of crystalline [70]fullerene given by combustion calorimetry and its sublimation enthalpy at 298.15 K. Values, according to different sets of experimental data,[27,29,30] range from 0.38 to 0.41 eV per atom. Our DFT energy per carbon atom of [76]fullerne, 0.39 eV per atom, agrees with the experimental numbers and with theoretical estimates of 0.38 eV per atom by Hartree–Fock calculations[31] and 0.35 eV per atom by tight-binding molecular dynamics.[32]

The formation energy of the most stable isomer of $C_{76}(CH_3)_2$ given by DFT calculations is 615.55 kcal per mol. The energies of other isomers in Table S2 † are given relative to this number.

Results and discussion

(a) [76]Fullerene

The mass spectrum of the crude reaction product showed species containing up to *ca.* ten methyl or methylene groups present. However, the higher volatility of the higher addended fullerenes exaggerates their concentration and only insignificant amounts were isolated by HPLC. Some differences in product composition from each of the four runs were revealed (Table S1 †), but the two main eluents from each occurred at 9.7 and 11.2 min, the former being obtained in the greater amount. The minor components were obtained in quantities sufficient for mass spectrometric analysis only. The main features are:

1. In contrast to methylation of either [60]- or [70]fullerene, the main products have only a few methyl (2, 6) or methylene groups (2, 4) present (942, 1002, 940, 968 amu, respectively). This may reflect the lower reactivity of [76]fullerene.

2 Some species of the same mass, notably 940 amu [$C_{76}(CH_3)_2$], and 954 amu [$C_{76}\{CH_2)_3$] elute at different retention times, indicating them to be isomers

3. A number of oxides are produced, *viz.* $C_{76}(CH_2)_nO$, $n = 2$, 3, 4 (956, 970, 984 amu), $C_{76}Me_4O_2$ (1004 amu), and $C_{76}Me_2O$ (956 amu) and $C_{76}Me_2O_2$ (974 amu). This parallels the results obtained in the methylation of [60]- and [70]fullerenes.[22]

4. For a given addend level, the methylenated species tend to elute earlier.

5. For methylenated species such as $C_{76}(CH_2)_2$, although it is not possible to ascertain if there is a single ethylene bridge or two separate methylene ones attached to the cage, the former seems more likely since the methylenes are added in pairs.

A. Fractions eluting at 9.7 min. The relative intensities of the components of these fractions varied slightly with each experiment, and Fig. 2 shows a representative mass spectrum; the peak at 936 amu is due to a small amount of [78]fullerene present in the original [76]fullerene.

The ^1H NMR spectrum in the methyl region for the 9.7 min fraction from run 1 (Fig. 3) showed ten peaks at δ 2.996 (A), 2.962 (B), 2.927 (C), 2.805 (D), 2.789 (E), 2.697 (F), 2.621 (G), 2.559 (H), 2.537 (I) and 2.408 (J). The same peaks were obtained (but with different relative intensities) from the other runs (spectra not shown). Features of these spectra are as follows.

The equal intensity nOe coupled peaks A and G are due to an unsymmetrical dimethyl compound. Other equal intensity peak pairs (confirmed in a second sample) are D/E, F/I and H/J. The do not show nOe coupling but indicate unsymmetrical dimethyl

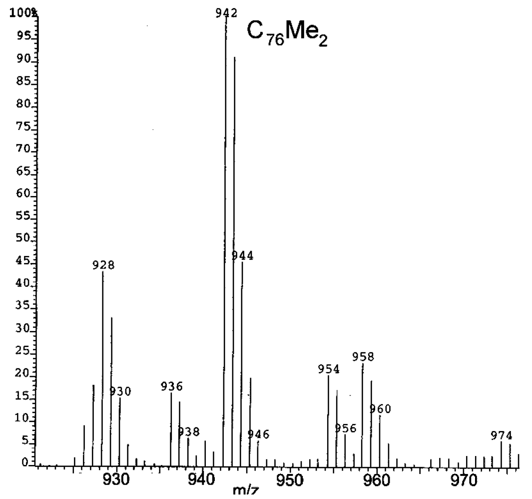

Fig. 2 EI mass spectrum (70 eV) of the 9.7 min HPLC eluent (see text).

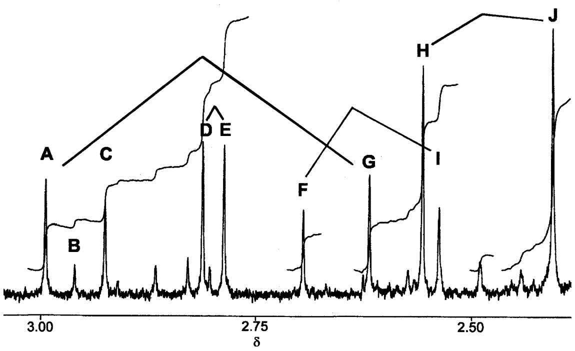

Fig. 3 ^{1}H NMR spectrum of 9.7 min HPLC eluent (run 1).

compounds with remote methyl groups. (Minor peaks present were shown not to be attached to a fullerene by the technique of T_i inversion recovery.) Thus overall there are four peak pairs indicative of the presence of unsymmetrical dimethyl derivatives, plus two unpaired peaks, (B and C); other evidence (below) indicates that peak B is due to an oxide.

One 9.7 min fraction was reprocessed using a 1 : 1 mixture of toluene : heptane, to give peaks eluting at 38.5 min [954 amu, $C_{76}(CH_2)_3$], 41.5 min [942 amu, $C_{76}Me_2$], and 52.2 min [940 amu, $C_{76}(CH_2)_2$]. An ^{1}H NMR spectrum of the 41.5 min fraction showed the presence of the peak pairs A/G and D/E together with the single peak C.

It is reasonable to assume that methylation will be directed towards either the bonds of highest π-electron density (see Introduction), or to give a product calculated to have high thermodynamic stability. Heats of formation were calculated for isomers corresponding to the more stable dihydro compounds in the Clare and Kepert listing,[10] on the basis that methyl derivatives corresponding to unstable dihydro compounds would be even less stable and can be discounted. The rounded off values given in Table S2 †, are relative to the most stable isomer calculated by each method.

The combined methods favour addition across the 1,6, 2,3 and 14,15 bonds. However, only one of these (1,6-bond) straddles a C_2 axis and will give a single NMR peak. We can therefore assign peak C to methylation across the 1,6-bond. The A/G peak pair that show an nOe can then be assigned to either 2,3- or 14,15-addition; note that ^{13}C NMR spectra would not distinguish the isomers.

This leaves three groups unaccounted for and which have remote methyl groups, most probably involving a 1,4- (*para*) addition motif. To try to identify these we consider further the relevant data in Table S2 †. For simplification, we discount isomers that have a calculated heat of formation greater than the minimum by 6 kcal mol^{-1}, these being the values at which appreciable increments in energy occur (see bold in Table S2 †). There is reasonable agreement for the remainder by both methods, giving the stability order of 2,14 > 11,30 > 2,5 > 17,35 > 3,6 (AM1) and 11,30 > 2,14 > 2,5 > 17,35 > 16,36 > 3,6 (DFT). Given that the formation of the 1,6 isomer is proven, we are inclined to regard the DFT values as the more reliable, and it is noted that only three of these isomers are predicted by the π-density calculations. On the basis of these values, the four identified unsymmetrical dimethyl isomers are most likely to be the following: 11,30; 2,14; 2,5; 17,35.

The nature of the oxides

(i) $C_{76}Me_2O$. One sample of 9.7 min eluent was recycled using a silica column, eluted with toluene at a flow rate of 1 ml min^{-1} This gave a peak at 16.8 min showing in the mass spectrum a peak at 958 amu ($C_{76}Me_2O$), and a single ^{1}H NMR peak at δ 2.96 proving that peak B in the main spectrum is due to the oxide. This structure is significant because it is only possible to have a single peak if (a) the two methyl groups lie across a C_2 symmetry axis, and (b) if the oxygen lies either between them (*i.e* inserts into the 1,6 bond) or inserts into the 71,76-bond, on the opposite side of the cage. This latter is improbable given especially that it is well established that oxygen inserts into FC–CF bonds;[33] in both cases weakening of the bond due to eclipsing interactions of the adjacent addends can be assumed to be responsible.

This compound must therefore be an ether rather than an epoxide, and is the first oxahomofullerene derived from other than [60]-[33,34] and [70]fullerene.[35] Insertion of oxygen into the 1,6-bond gives 1,6-oxahomo-1,6-dimethyl[76]fullerene (Fig. 4).

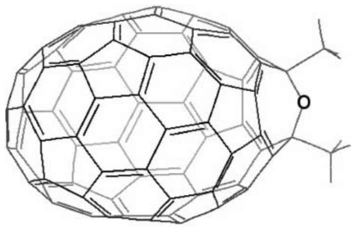

Fig. 4 1,6-oxahomo-1,6-dimethyl[76]fullerene.

(ii) $C_{76}Me_4O_2$. Th EI mass spectrum of this compound, which eluted at 8.0 min (run 4) gives a parent ion at 1004 amu with the main fragment ion at 944 amu ($C_{76}O_2$). The ^{1}H NMR spectrum showed two equal-intensity singlets at δ 2.63 and 2.38 *i.e.* close to that found for $C_{76}Me_2O$ but more upfield, this being the usual trend when there are more methyl groups present on a fullerene.[22] Here again the oxygen must have inserted between two equivalent pairs of symmetry-inequivalent methyl groups, giving the first example of a bis oxahomo[76]fullerene. Given the predictions of the most likely dimethyl compounds (Table 2) and eliminating all the para derivatives (1,4- so no insertion possible) and an oxahomo bis 1,6-dimethyl derivative (*i.e.* 1,6,71,76 (insertion would give a C_{2v} derivative and only one NMR line) the most probable derivatives are either 14,15,23,24- or 2,3,7,8-$Me_4C_{76}O_2$. *Note*: Both these derivatives have C_2 symmetry but it is difficult to see this without reference to models.

The energies of both possible isomers were calculated using DFT. Isomer 2,3,7,8-$Me_4C_{76}O_2$ was found to be more stable by 13.8 kcal mol^{-1}. This agrees with the DFT prediction of the 2,3-dimethyl isomer being more stable than the 14,15-isomer.

B. Fractions eluting at 11.2 min. A representative mass spectrum (Fig. 5) shows the presence of $C_{76}(CH_2)_2$ (940 amu) and $C_{76}(CH_2)_4$ (968 amu). The ^{1}H NMR spectra could not be resolved however, due to peak multiplicity and low sample size. It seems probable that these products arise from bridging by

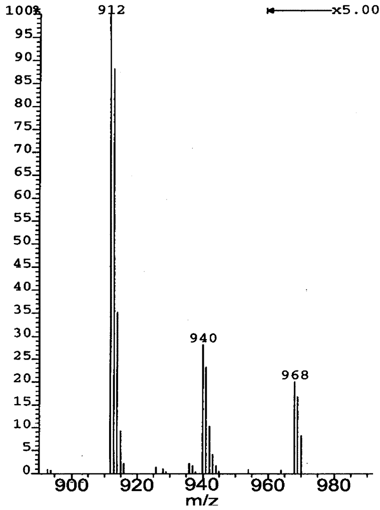

Fig. 5 EI mass spectrum (70 eV) of the 11.2 min HPLC eluent (see text).

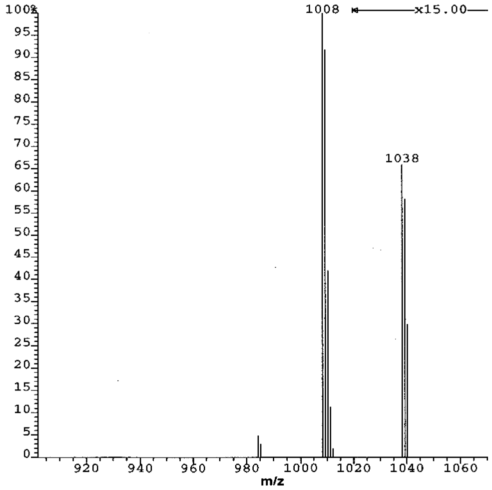

Fig. 6 EI mass spectrum (70 eV) for $C_{84}Me_2$.

multiple $(CH_2)_2$ groups rather than insertion into C–C bonds of CH_2 groups, otherwise ms peaks of 926, 954 amu *etc.* could be expected. The $–CH_2CH_2–$ groups could possibly originate from the THF used in the preparation.

(b) [84]Fullerene

Two runs were carried out, the main fractions being collected at 9.2 10.9, 12.3 and 13.6 min, each of which showed the presence of $C_{84}Me_2$ at 1038 amu (Fig. 6). The 9.2 min gave a single peak in the ^1H NMR at δ 2.88 indicating a C_s or C_2 product, the 10.9 min fraction gave equal intensity singlets at δ 1.986 and 1.971(5) indicative of a C_1 symmetry product. Quantities of the other fractions were too small for satisfactory characterisation. The results in comparison with those for [76]fullerene indicated a lower overall reactivity. A sample of 14.7 min retention time showed the presence of $C_{84}Me_2H_2$ at 1040 amu.

Acknowledgements

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