Methylation of [70]fullerene

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Methylation of [70]fullerene by different methods yields products indicative of two reduction manifolds. One involves addition principally at the polar region, the other involves addition around the equator, this diverse behaviour paralleling that found previously in hydrogenation; different steric requirements of the reagents are probably responsible. Methylation by reduction with Al–Ni alloy–NaOH–dioxane–THF followed by reaction with MeI gives $C_{70}Me_n$ (n = 2, 4, 6, 8, 10) (equatorial addition). These products are isostructural with the corresponding $C_{70}Ph_n$ species despite being formed *via* a different reaction type (the eight-fold addend being also the most abundant in each reaction), indicating that a fundamental property governs [70]fullerene addition. Methylation by reaction with lithium followed by quenching with methyl iodide gives $C_{70}Me_n$ containing up to twenty-six methyl groups, $C_{70}Me_6$ being the most abundant species. The isolated $C_{70}Me_2$ consists mainly of a 3.4 : 1 ratio of the 1,2- and 5,6-isomers (polar addition), together with smaller amounts of five other unsymmetrical isomers. One of these latter (together with a further isomer) is produced from nucleophilic substitution of $C_{70}Cl_{10}$ by MeLi which also gives $C_{70}Me_n$ (n = 4, 6, 8) as mixtures of uncharacterised isomers in low yields. Like their phenylated counterparts, both $C_{70}Me_8$ and $C_{70}Me_{10}$ are fluorescent; $C_{70}Me_8$ forms a tetra-oxide on standing in air and light as does $C_{70}Ph_8$.

Introduction

Methylation was one of the first fullerene reactions to be investigated, with lithiation of [60]fullerene followed by quenching by methyl iodide giving addition of up to 24 methyl groups, $C_{60}Me_6$ and $C_{60}Me_8$ being major products.[1] Although the small size of the methyl group and the reasonable stability of the methylfullerenes towards EI mass spectrometry made the reaction suitable for elucidating mechanistic features of fullerene additions, the polymethylation was a disincentive to further work.

The availability of high pressure liquid chromatography (HPLC) columns dedicated to fullerene separation has now enabled progress to be made. In preliminary work we confirmed the ready occurrence of polymethylation, characterised $C_{60}Me_6$, $C_{60}Me_8$, 1,2- and 1,4-$C_{60}Me_2$, determined that six isomers of $C_{60}Me_4$ are produced, and showed also that some of the methylated species are very susceptible to atmospheric oxidation.[2] More recently we showed that reaction of $C_{60}Cl_6$ with MeLi gave $C_{60}Me_5O_2OH$ (a bis epoxyfullerenol),[3] together with an isomeric cage-opened ketone,[4] $C_{60}Me_5Cl$, $C_{60}Me_6$, $C_{60}Me_5OOH$, $C_{60}Me_4PhO_2OH$ (from impurity in the $C_{60}Cl_6$) and $C_{60}Me_{12}$.[5]

We now describe details of methylation of [70]fullerene either by reduction of the fullerene to give anions (two methods) followed by reaction with methyl iodide, or by nucleophilic substitution of the chlorofullerene with methyllithium.

Experimental

HPLC separations used a 250 × 10 mm Cosmosil Buckyprep column operated at a flow rate of 4 ml min^{-1} with elution either by toluene or toluene–heptane, as stated. ^1H NMR spectra were run at 500 MHz, ^{13}C NMR at 125 MHz, and EI mass spectra at 70 eV. Product and spectroscopic details are summarised in Table 1.

I. Reduction by lithium metal

In a typical experiment, [70]fullerene (20 mg), lithium metal (*ca.* 20 mg, excess) and dry THF (5 cm^3) were sonicated with ultrasound for 4 h at room temperature in a 25 cm^3 three-necked flask under N_2. Methyl iodide (excess) was then added, causing an instant colour change from green–brown to brown–black. HCl (2 M) was added to the mixture which was extracted with toluene, washed with water, dried ($MgSO_4$) and pre-purified by passing through a column of silica gel (70–230 mesh, toluene elution). Further separation by HPLC (toluene elution) yielded the derivatives $C_{70}F_n$ with retention times (min) for n = 2 (9.9); 4 (6.2); 6 (4.6); 8 (4.2); 8/10 (3.8). These each gave excellent mass spectra (*e.g.* for $C_{70}Me_2$ and $C_{70}Me_4$, Figs. 1 and 2). The yields of each were < 1 mg except for $C_{70}Me_2$ (*ca.* 2 mg), so that only for this latter compound was there sufficient for ^1H NMR analysis.

II. Reduction by Al–Ni alloy and aqueous NaOH–DMSO–THF followed by quenching with MeI

It was our intention to form dianions and hence obtain $C_{70}Me_2$, our method being based on the formation of anions from fullerenes by Al–Ni–NaOH, which gives either the mono-, di- or trianion in the solvents THF, DMSO–THF, or DMSO, respectively.[6] However, we obtained a much wider range of derivatives.

[70]Fullerene (25 mg), Al–Ni alloy (250 mg, excess), solid NaOH (1.5 g), dry DMSO (20 cm^3), and dry THF (20 cm^3) were placed in a 100 cm^3 Schlenk flask. Degassed water (5 cm^3) was added, and the mixture stirred under argon at room temperature for 4 h. The initially-formed black suspension suddenly turned olive green after 20 min. The solution, maintained under argon, was transferred into a 50 cm^3 Schlenk flask, and an excess of MeI was added, causing an instantaneous colour change to brown–black; stirring was continued overnight. The toluene-extracted mixture was washed with water, dried ($MgSO_4$) and HPLC separated to give $C_{70}Me_n$ derivatives with retention times (min) for n = 2 (9.2); 4 (8.2); 6 (6.8); 8 (5.3); 10 (4.5). These differ from those described under condition **I** because different isomers are involved. The main component was $C_{70}Me_8$, the mass spectrum for which is shown in Fig. 3. A dihydro product $C_{70}Me_2H_2$ (with retention time 12.1 min) was also obtained.

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Table 1 Methylated [70]fullerene derivatives

Method	Products	No.	NMR data
I	1,2-$C_{70}Me_2$	1	Peak pair centred at δ 2.31
	5,6-$C_{70}Me_2$	2	Single peak at δ 2.356
	$C_{70}Me_2$	3	Peak pair A centred at δ 2.76
	$C_{70}Me_2$	4	Peak pair B centred at δ 2.48
	$C_{70}Me_2$	5	Peak pair C centred at δ 2.32
	$C_{70}Me_2$	6	Peak pair D centred at δ 2.18
	$C_{70}Me_2$	7	Peak pair E centred at δ 2.07
	$C_{70}Me_4$		Very low yield
	$C_{70}Me_6$		Very low yield
	$C_{70}Me_{8/10}$		Very low yield
II	7,8-, 7,19-, or 7,23-$C_{70}Me_2$	8	Single peak at δ 2.07
	7,19,23,37-$C_{70}Me_4$	9	Two peaks at δ 2.24 and 2.21
	7,19,23,37,44,53-$C_{70}Me_6$	10	Three peaks at δ 2.454, 2.38, 2.28
	7,19,23,27,33,37,44,53-$C_{70}Me_8$	11	Four peaks at δ 2.535, 2.533, 2.407, 2.34
	7,19,23,27,33,37,45,49,53,63-$C_{70}Me_{10}$	12	Five peaks at δ 2.515, 2.511, 2.454, 2.443, 2.425
	$C_{70}Me_2H_2$[a]	14	Peaks at δ 3.84 (H) and 2.10 (Me)
III	$C_{70}Me_2$	7	Peak pair E centred at δ 2.07
	2,5(?)-$C_{70}Me_2$	13	Peak pair G centred at δ 2.37
	$C_{70}Me_4$		Very low yield
	$C_{70}Me_6$		Very low yield
	$C_{70}Me_8$		Very low yield

[a] See text.

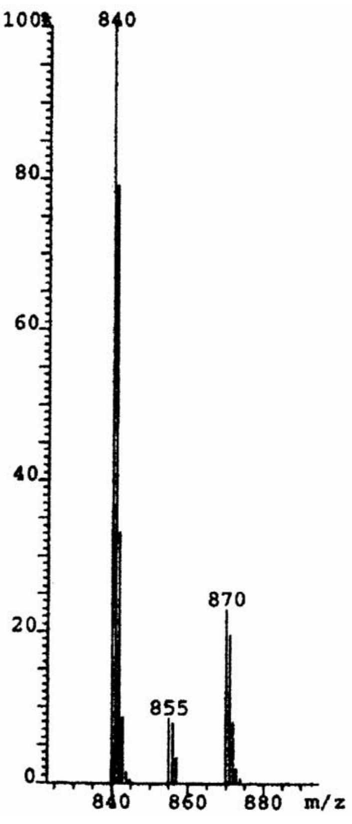

Fig. 1 EI mass spectrum (70 eV) for $C_{70}Me_2$ obtained from reaction of [70]fullerene with Li–MeI.

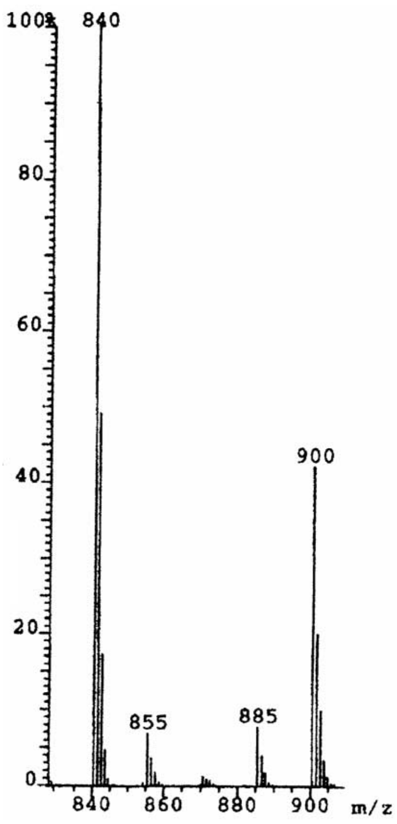

Fig. 2 EI mass spectrum (70 eV) for $C_{70}Me_4$ obtained from reaction of [70]fullerene with Li–MeI.

III. Nucleophilic substitution of $C_{70}Cl_{10}$

$C_{70}Cl_{10}$ was prepared as described previously.[7] An excess of MeLi solution (4 cm^3 of 1 M in 11 : 9 THF : cumene) was stirred with $C_{70}Cl_{10}$ (30 mg) at room temperature, under N_2. The yellow solution turned brown–black immediately, and stirring was continued overnight. The mixture was extracted with toluene, washed with water, dried ($MgSO_4$), and separated by HPLC to give $C_{70}Me_n$ ($n = 2, 4, 6, 8$) in low yields.

Results and discussion

The main features that emerge from this work are:

1. The methylated products differ according to the method used, indicating different addition pathways. A predominant feature is methylation around the equator, paralleling chlorination and arylation.

2. As in the case of methylation of [60]fullerene by Li–MeI, the addend level exceeds that which is predicted theoretically.

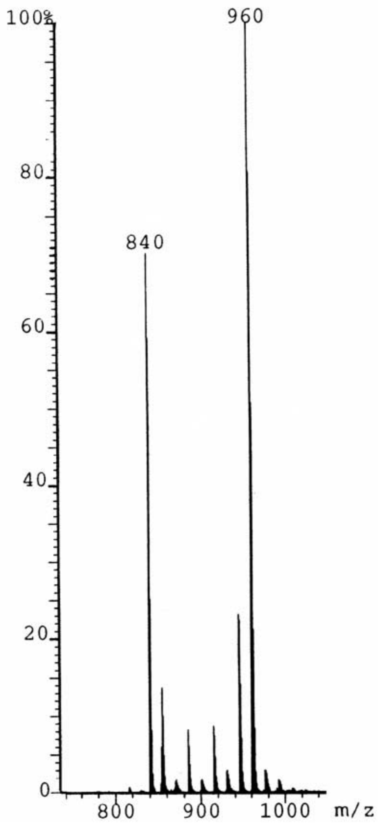

Fig. 3 EI mass spectrum (70 eV) for $C_{70}Me_8$ obtained from reaction of [70]fullerene with Al–Ni–aq. NaOH–MeI.

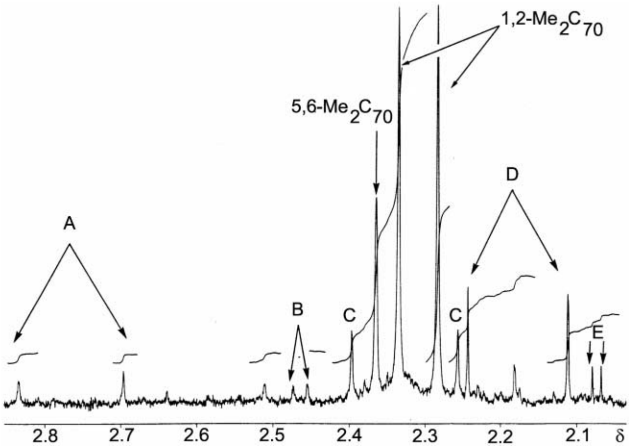

Fig. 4 ^1H NMR spectrum of $C_{70}Me_2$ obtained from the reaction of [70]fullerene with Li–MeI.

Methylation by lithium reduction followed by reaction with MeI (I)

The ^1H NMR spectrum of $C_{70}Me_2$ (Fig. 4) obtained under this condition showed three main peaks comprising an equal-intensity NOE-coupled peak pair centred at δ 2.31 (1,2-Me_2C_{70}, **1**) and a single peak at δ 2.356 (5,6-Me_2C_{70}, **2**), the intensity ratio being 3.4 : 1. The structures are shown in Fig. 5. Most reactions of [70]fullerene give combinations of 1,2- and 5,6-additions, the 1,2-/5,6-ratios varying from 1.12 to 27.5;[8] (some 'infinite' ratios reported in early work are due probably to incomplete product characterisation).

The NMR spectrum shows five other pairs of peaks (labelled A–E, centred at δ 2.76, 2.48, 2.32, 2.18 and 2.07, compounds **3**–**7**) due to minor components that could not be separated. None can involve addition across the symmetry plane; one pair may be the 7,21 isomer, since addition across this bond occurs in other reactions.[9] Some of these derivatives could involve

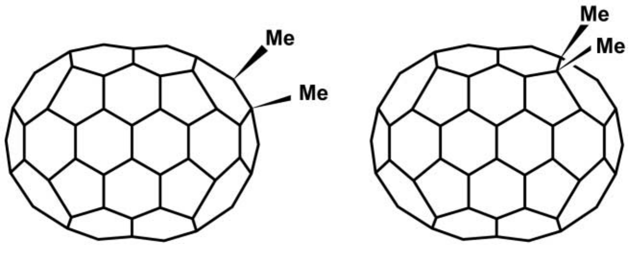

Fig. 5 Structures of 1,2- and 5,6-Me_2C_{70} (**1**,**2**).

para-addition (as occurs with [60]fullerene[10]), but only the 1,4- and 2,5-isomers are feasible asymmetric possibilities. Other isomers would necessarily involve wider separation of the methyl groups, *e.g.* in 4,10-Me_2C_{70}, (see Fig. 6 for numbering).

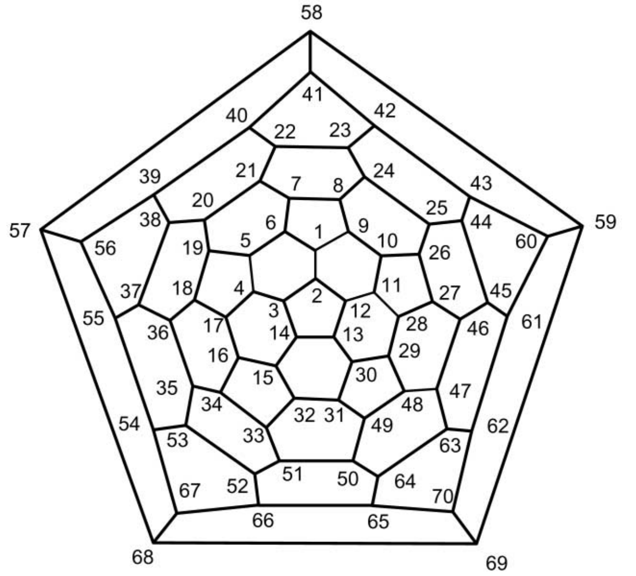

Fig. 6 Numbering for [70]fullerene.

Alternatively, oxides formed on standing may be present; $C_{60}Me_2$ readily forms mono-oxides (either epoxy- or oxahomo-fullerenes) in this way.[5]

The quantities of $C_{70}Me_4$, $C_{70}Me_6$, $C_{70}Me_8$ and $C_{70}Me_{10}$ obtained as described in the Experimental were sufficient for mass spectrometry only.

Reduction by Al–Ni alloy–aq. NaOH–DMSO–THF followed by quenching with MeI (II)

The $C_{70}Me_2$ obtained in this reaction (compound **8**) gave a mass spectrum identical to that shown in Fig. 1. A single peak in the ^1H NMR at δ 2.07 allows for four possibilities: (a) 1,2-addition across the 5,6-bond (discounted since this compound is already identified as giving a single peak at δ 2.356); (b) 1,2-addition across the 7,8-bond to give a C_s symmetry product (*cf.* the reaction with benzyne);[11] (c) *para* addition across either the 7,23- or 7,19 bond giving C_2 or C_s symmetry products, respectively (Fig. 7).

Each of (b) or (c) is on the pathway to formation of $C_{70}Me_n$ ($n = 4, 6, 8, 10$, see below) under this reaction condition. Option (b) involves addition across a 6,5-bond, the reaction with benzyne, driven by the need there to have 1,2-addition, being the only known example; we may reasonably discount it in the present reaction case. For the formation of $C_{70}Ph_2$ from $C_{70}Cl_{10}$ it was assumed that 7,19-addition was involved,[12] but we are now disinclined to this view since 7,23-addition is energetically more favourable. Neither of these two options is distinguishable by ^{13}C NMR, but the upfield peak position in the ^1H NMR is consistent with location of the methyl groups near the less electronegative equator, and thus the 7,23 isomer.

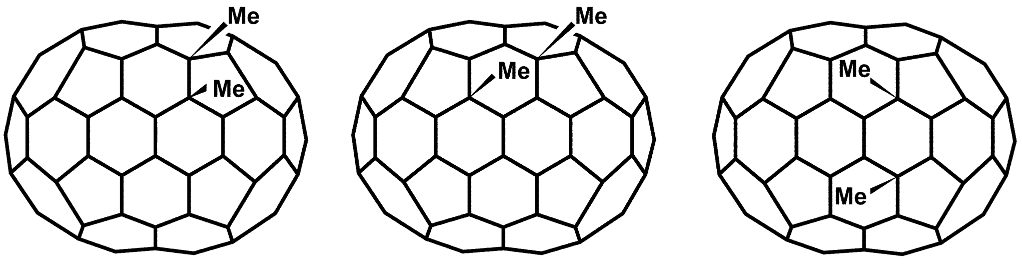

Fig. 7 The possible 7,8-, 7,23- and 7,19-isomers for $C_{70}Me_2$ (**8**).

$C_{70}Me_4$ (9). The ^1H NMR spectrum comprises two equal intensity singlets at δ 2.24 and 2.21 consistent with a product of either C_s or C_2 symmetry. The compound must be isostructural with C_s $C_{70}Ph_4$[12,13] and thus is 7,19,23,37-tetramethyl-7,19,23,37-tetrahydro[70]fullerene (Fig. 8), which is derivable from either of the two favoured options for (**8**).

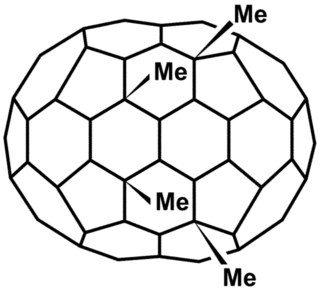

Fig. 8 Structure of 7,19,23,37-$C_{70}Me_4$ (**9**).

$C_{70}Me_6$ (10). Three lines of equal intensity at δ 2.454, 2.38 and 2.28 in the ^1H NMR spectrum are consistent with 7,19,23,37,44,53-hexamethyl-7,19,23,37,44,53-hexahydro[70]fullerene (Fig. 9), isostructural with C_s $C_{70}Ph_6$.[13]

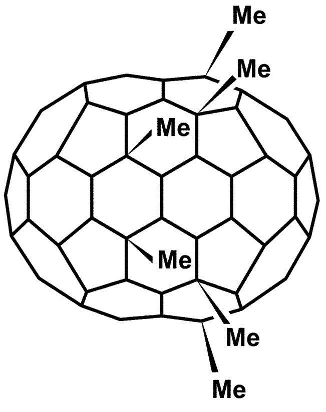

Fig. 9 Structure of 7,19,23,37,44,53-$C_{70}Me_6$ (**10**).

$C_{70}Me_8$ (11). Just as $C_{70}Ph_8$ is the main product from phenylation of $C_{70}Cl_{10}$,[13,14] so $C_{70}Me_8$ (fluorescent) is the main product from reaction of C_{70} with Ni–Al–MeI, and this is discussed below; Fig. 3 shows the mass spectrum. The ^1H NMR spectrum comprises four equal intensity lines at δ 2.535, 2.533, 2.407 and 2.34, the latter pair being NOE coupled. The C_s symmetry was confirmed by ^{13}C NMR, which gave four peaks for the cage sp^3 carbons at δ 53.77, 53.60, 53.37 and 53.11, and four for the methyl carbons at δ 31.25, 30.11, 29.78, and 29.21. The compound is 7,19,23,27,33,37,44,53-octamethyl-7,19,23,27,33,37,44,53-octahydro[70]fullerene (isostructural with $C_{70}Ph_8$[13,14]) and the structure (Fig. 10) has been confirmed by X-ray crystallography.[15] There is a regular upfield shift of 7.40 ± 0.2 ppm for the cage sp^3 carbon resonances for the methyl compared to the phenyl compound.

$C_{70}Me_{10}$ (12). This compound, formed in less amount than $C_{70}Me_8$, is fluorescent (yellow) like the isostructural $C_{70}Ph_{10}$[13,14] and the EI mass spectrum showed the parent ion at 990 amu with peaks of alternating intensities (*cf.* Fig. 3) due to stepwise loss of methyl groups. Five equal intensity lines at δ 2.515, 2.511, 2.454, 2.443 and 2.425 in the ^1H NMR spectrum confirm the C_s symmetry. The compound is 7,19,23,27,33,37,45,49,53,63-decahydro-7,19,23,27,33,37,45,49,53,63-decamethyl[70]fullerene, and the structure is shown in Fig. 10.

Nucleophilic substitution of $C_{70}Cl_{10}$ (III)

The $C_{70}Me_2$ obtained from nucleophilic substitution of $C_{70}Cl_{10}$ by MeLi consists of two isomers (^1H NMR spectrum, Fig. 11) The minor isomer (labelled EE) is the same as compound **7** shown in Fig. 4 and the upfield location of the methyl groups indicates them to be attached to a region of the cage of low electronegativity *i.e.* near the equator. This, and the asymmetry indicate **7** to be the 7,21 isomer. The other isomer (compound **13**) gives two peaks (GG) at δ 2.57 and 1.97. This very wide 0.6 ppm separation indicates attachment to regions of substantial electronegativity difference, and given the asymmetry, only a 2,5-isomer is feasible.

These isomers involve attachment of methyl at sites not occupied by chlorine in the $C_{70}Cl_{10}$ precursor, possibly *via* an S_N2' mechanism (recently identified in alkylation of fluorofullerenes).[16]

The $C_{70}Me_4$, $C_{70}Me_6$ and $C_{70}Me_8$ obtained by this route were sufficient for mass spectrometry only.

$C_{70}Me_2H_2$ (13). This was obtained by alkylation method **II**. Hydrogenation increases the HPLC retention time to 12.1 min compared to either $C_{70}Me_2$ (9.2 min) or $C_{70}Me_4$ (8.2 min), as found also with hydrogenated derivatives of phenylated fullerenes.[17] The peaks at 871 and 870 amu in the mass spectrum (Fig. 12) are typical of hydrogen loss from the hydrofullerenes. The upfield singlets at δ 3.84 (H) and 2.10 (3 H, Me) in the ^1H NMR spectrum indicate either C_s or C_2 symmetry with location of the addends near the equator. This limits the alternatives to either (i) 7,23-(C_2)- or 7,8-(C_s)-dimethyl-7,8,22,23-tetrahydro[70]fullerene or (ii) 7,19-(C_s)- or 5,6-(C_s)-dimethyl-5,6,7,19-tetrahydro[70]fullerene (see Fig. 6 for addend locations). There was insufficient material for ^{13}C NMR spectroscopy, but this would not in any event distinguish these alternatives.

Parallels between phenylation and methylation

(i) Both reactions give $C_{70}X_n$ (X = Ph, Me; $n = 2, 4, 6, 8, 10$) with $n = 8$ dominant, these levels resulting from addition around the equator. This pattern is obtained because it reduces the unfavourable electron distribution around the equator, but requires two addends to be adjacent.[18] This is energetically satisfactory when the addends are chlorine, hence $C_{70}Cl_{10}$ is readily obtained.[7] However, for larger addends such as methyl and phenyl, the products become less stable due to their higher steric requirements, so that the eight rather than the ten addend level becomes dominant in each case.

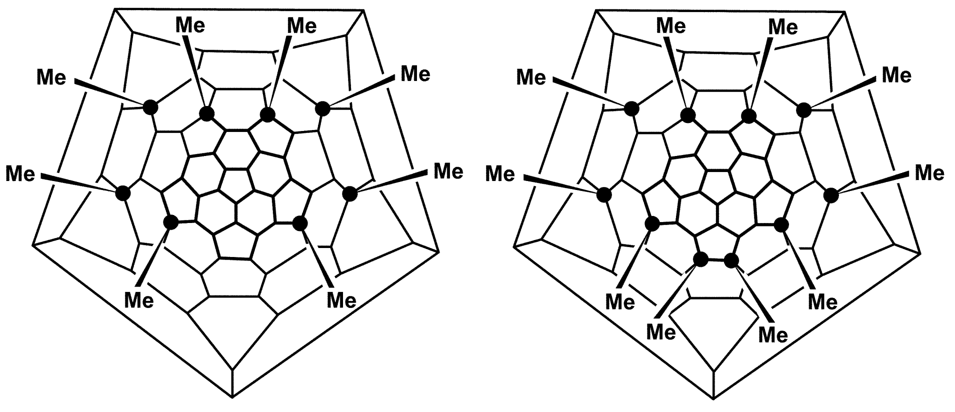

Fig. 10 Structures of $C_{70}Me_8$ (**11**) and $C_{70}Me_{10}$ (**12**).

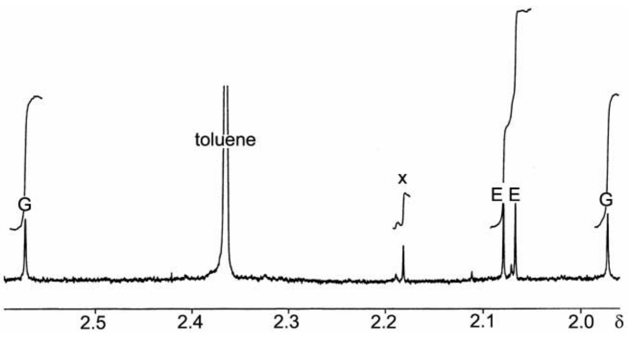

Fig. 11 ^1H NMR spectrum of $C_{70}Me_2$ obtained from the reaction of $C_{70}Cl_{10}$ with Li–MeI.

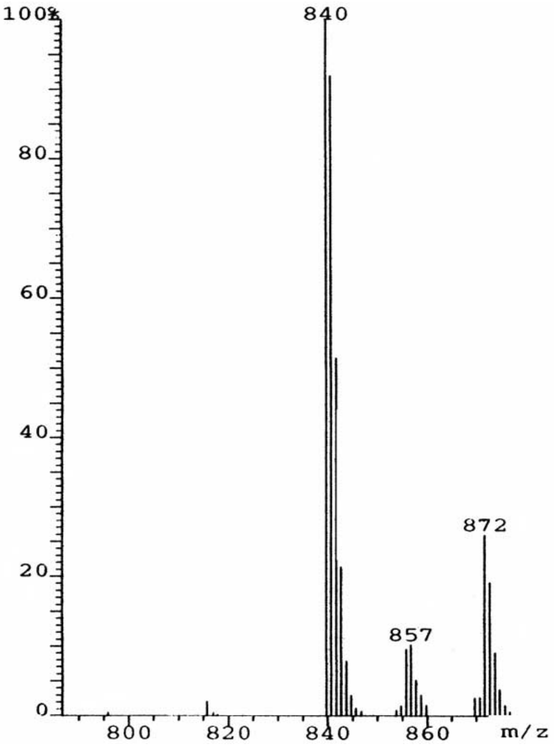

Fig. 12 EI mass spectrum (70 eV) for $C_{70}Me_2H_2$.

(ii) A further similarity between the phenyl and methyl compounds is the fluorescence (green–yellow) of $C_{70}Me_8$ *cf.* $C_{70}Ph_8$.[14] This reinforces the conclusion[13] that the fluorescence is largely independent of the nature of the addends but depends instead upon the disposition of the conjugated bonds in the addended cage. On standing in light and air for four weeks, $C_{70}Me_8$ also converts to a tetra-oxide (1024 amu), just as $C_{70}Ph_8$ oxidises to $C_{70}Me_8O_4$, an open-cage bis-lactone.[19] The tetra-oxide has a green fluorescence.

Parent ion/fragment ion ratios. The mass spectra of $C_{70}Me_n$ show parent ion : C_{70} intensity ratios for the values of *n*: 0.20 (2); 0.25 (4); 0.30 (6); 1.41 (8); 1.82 (10), demonstrating a general feature of addended fullerenes *viz.* greater stability towards mass spectrometry, the greater the addition level. The EI mass spectra of the fluorofullerene oxides $C_{60}F_nO$ ($n = 4, 6, 8$) provide recent examples of this property.[20]

Positions of methyl resonances *vs.* number of addends. The average values (δ) for the chemical shifts of the methyl hydrogens for $C_{70}Me_n$ are 2.07, 2.23, 2.37, 2.45, 2.47 for *n* values of 2, 4, 6, 8, 10, respectively. There is thus a downfield shift with increasing number of addends, which contrasts with the behaviour of methylated [60]fullerenes. This may be related to the fact that unlike [70]fullerene, [60]fullerene becomes more aromatic upon addition. A comparable result was observed in the ^{3}He NMR spectra of $i^3HeC_{70}H_n$.[21]

Level of methylation and reagent dependence. As with methylation of [60]fullerene the very high addition level is unexplained. For [60]fullerene, calculations indicate that it can accommodate only 12 electrons in $Li_{12}C_{60}$,[22] whereas reaction of [60]fullerene with Li–MeI gives much higher methylation levels.

The methylation pattern for [70]fullerene is reagent dependent. Hydrogenation of [60]fullerene with di-imide gives a 1,2,3,4-hydrogenation pattern,[23] whereas with aq. Zn–Cu, hydrogens are added as pairs spaced around the equator,[24] indicating greater steric hindrance under this latter condition. For [70]fullerene, di-imide reduction gives a 1,2,3,4-hydrogenation pattern,[23] whereas reduction with aq. Zn–Cu[25] gives the same equatorial pattern (involving 1,4-addition) that we observe in methylation with Ni–Al, and in chlorination.[7] By contrast, methylation by Li–MeI gives a 1,2-addition pattern, leading to 1,2- and 5,6-$C_{70}Me_2$.

Acknowledgements

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