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Formation of $C_{70}Ph_{10}$ and $C_{70}Ph_8$ from the Electrophile $C_{70}Cl_{10}$

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Abstract: In the presence of ferric chloride, benzene readily undergoes electrophilic substitution by $C_{70}Cl_{10}$ to give both yellow $C_{70}Ph_{10}$ and orange-red $C_{70}Ph_8$, each of which is luminescent. Their structures have been characterised by ^1H and ^{13}C NMR spectroscopy [including nOe and two-dimensional (COSY) analysis], and by UV, IR, and mass spectrometry. $C_{70}Ph_{10}$ is not formed directly from $C_{70}Cl_{10}$, but rather by further phenylation of the intermediate $C_{70}Ph_8$. The adjacent phenyl groups of $C_{70}Ph_{10}$ are sterically prevented from rotating at room temperature.

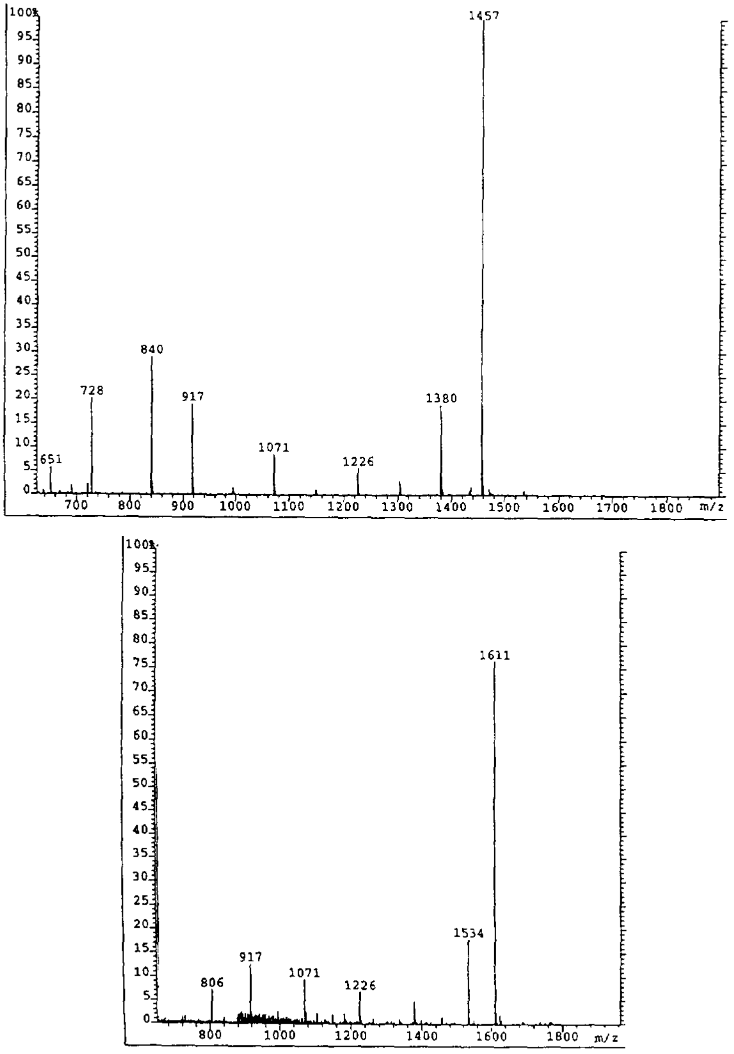
Recently we described the formation and characterisation of $C_{70}Cl_{10}$, the first [70]fullerene derivative in which multiple addends are arranged around the waist of the molecule.[1] The driving force for the observed addition pattern (which is thus far unique for a fullerene derivative possessing bulky addends) appears to be the lack of a double bond in any pentagonal ring in the product, this having been identified as an important factor governing the stability of fullerenes.[2] Previously we also prepared $C_{60}Cl_6$,[3] and showed that reaction of it with benzene in the presence of ferric chloride produced $C_{60}Ph_5Cl$ as a result of electrophilic substitution by the halogenofullerene into benzene;[4] $C_{60}Ph_6$ and a range of other aromatic derivatives can be prepared under suitable conditions.[5] We have also described recently, the preparation of an open-cage fullerene derivative, $C_{70}Ph_8O_4$.[6] We now report the preparation and characterization of both $C_{70}Ph_8$ and $C_{70}Ph_{10}$.

EXPERIMENTAL

7,8,19,26,33,37,45,49,53,63 -Decachloro[70]fullerene[7]- This was prepared as described previously.[1]

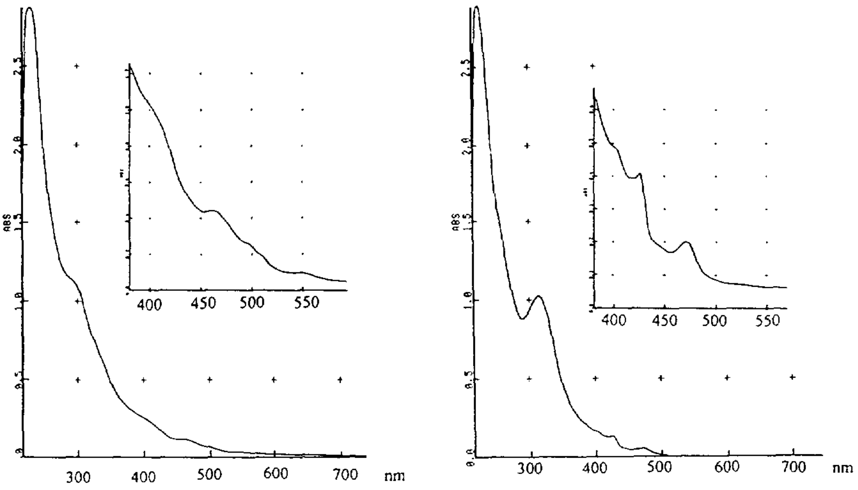
7,19,23,27,33,37,44,53-Octaphenyl[70]fullerene. Decachloro[70]fullerene (20 mg, prepared as above) was dissolved in dry benzene (50 cm^3), insoluble material (arising from a small amount of decomposition of the chloro compound which occurs on prolonged standing) was removed by filtration, and a catalytic amount of ferric chloride was added. The mixture was heated under reflux for 15 min. After being allowed to cool to room temperature, the mixture was washed with water (2 x 10 cm^3) and the separated organic layer dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a pale orange solid which was purified by column chromatography (SiO_2/CCl_4), the first orange-yellow fraction ($R_f = 0.81$) being collected. Removal of the solvent and recrystallisation of the pale orange solid from dichloromethane gave orange-red crystals of $C_{60}Ph_8$ (17 mg, 66%). The retention time under HPLC conditions (4.5 mm x 25 cm Cosmosil column, elution with toluene at 1ml/min) was 25.9 min, that for [70]fullerene under the same conditions being 110 min.

The mass spectrum (EI conditions, Fig. 1a) shows the parent ion at 1457 amu; the alternation in peak intensities of the fragmentation ions arising from the loss of the phenyl groups is typical of numerous spectra that we have obtained for phenylated fullerenes.

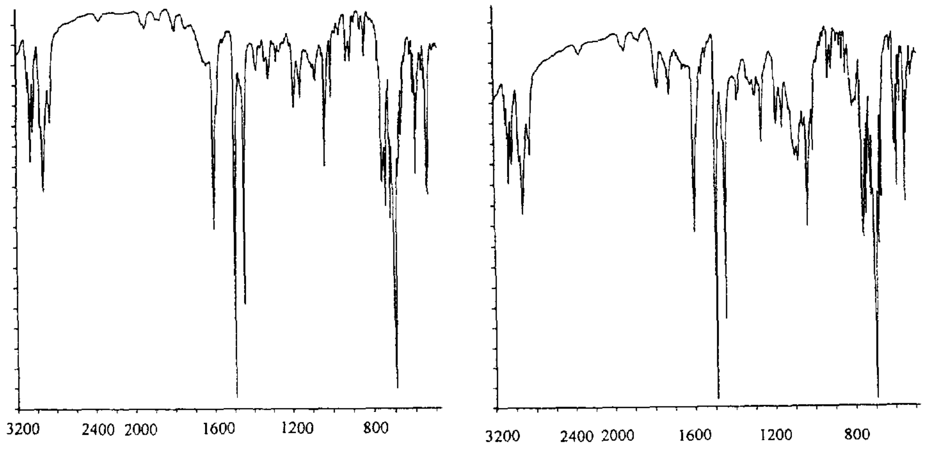


Figures 1a EI mass spectrum for $C_{70}Ph_8$ (above)
1b EI mass spectrum for $C_{70}Ph_{10}$ (below)

The UV/VIS spectrum (cyclohexane, λ_{max}/nm 227.7, 296.5, 408.5, 460, 496, 509 and 550) is shown in Fig. 2a. The IR spectrum (KBr disc, ν/cm^{-1} 3084, 3057, 3029, 2954, 2923, 2852, 1780, 1721, 1653, 1598, 1583, 1492, 1446, 1384, 1314, 1293, 1261, 1186, 1157, 1 094, 1078, 1051, 1032, 926, 908, 839, 805, 778, 767, 754, 739, 731, 715, 708, 694, 677, 664, 595, 590, 583, 570, 544, 536 and 512) is shown in Fig. 3a.

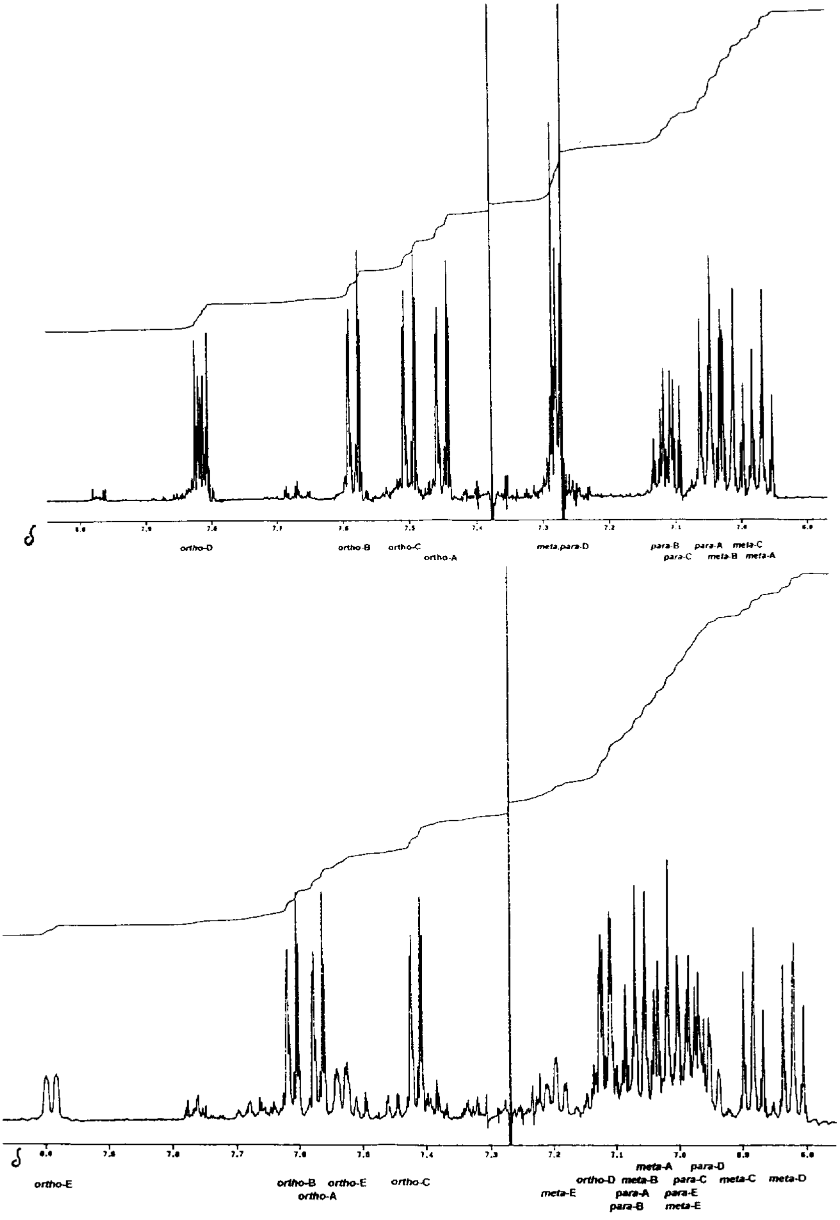


Figures 2a,b UV/VIS spectra for $C_{70}Ph_8$ and $C_{70}Ph_{10}$.



Figures 3a,b IR spectra (KBr) for $C_{70}Ph_8$, and $C_{70}Ph_{10}$.

The ^1H NMR spectrum (Fig. 4a, $CDCl_3/CS_2$, 75:25) shows four different environments for the phenyl groups and thus the C_s symmetry of the product. The relationship between the phenyl groups was established by nOe measurements, the enhancements in either direction being shown on the Schlegel diagram (Fig. 5a), which also shows the locations of the phenyl groups deduced as described under the discussion. No other nOe enhancements were observed. The spectrum shows that the downfield shifts for the proton resonances in each ring [established by 2D (COSY) experiments] are in general: *ortho* > *para* > *meta*. The assignments are given in Table 1.



Figures 4a ^{1}H NMR spectrum for $C_{70}Ph_8$ (above)
4b ^{1}H NMR spectrum for $C_{70}Ph_{10}$ (below)

Table 1 ^1H NMR shifts for $C_{70}Ph_8$ and $C_{70}Ph_{10}$

$C_{70}Ph_8$			$C_{70}Ph_{10}$		
δ	Intensity	Assignment	δ	Intensity	Assignment
7.816-7.794	4 H	*ortho*-H, ring D	8.000-7.983	2 H	*ortho*-H, ring E[a]
7.575-7.556	4 H	*ortho*-H, ring B	7.544-7.525	2 H	*ortho*-H, ring E[b]
7.488-7.464	4 H	*ortho*-H, ring C	7.626-7.600	4 H	*ortho*-H, ring B
7.437-7.418	4 H	*ortho*-H, ring A	7.580-7.561	4 H	*ortho*-H, ring A
7.289-7.260	6 H	*meta,para*-H, ring D	7.430-7.405	4 H	*ortho*-H, ring C
7.131-7.095}		*para*-H, ring B	7.214-7.180	2 H	*meta*-H, ring E[a]
7.110-7.088}		*para*-H, ring C	7.129-7.109}		*ortho*-H, ring D
7.050-7.030}		*para*-H, ring A	7.145-7.090}	6 H	*para*-H, ring B
7.062-7.018}		*meta*-H, ring B	7.100-7.045)		*para*-H, ring A
7.019-6.970}		*meta*-H, ring C,	7.086-7.055)		*meta*-H, ring B
6.985-6.930}	18 H	*meta*-H, ring A	7.035-7.004)		*meta*-H, ring A
			7.025-6.970)		*para*-H, ring E
			7.022-6.990)		*meta*-H, ring E[b]
			7.015-6.960)		*para*-H, ring C
			7.000-6.945)	18 H	*para*-H, ring D
			6.899-6.868	4 H	*meta*-H, ring C
			6.837-6.805	4 H	*meta*-H, ring D

[a] Pointing towards the cage cap.
[b] Pointing away from the cage cap.

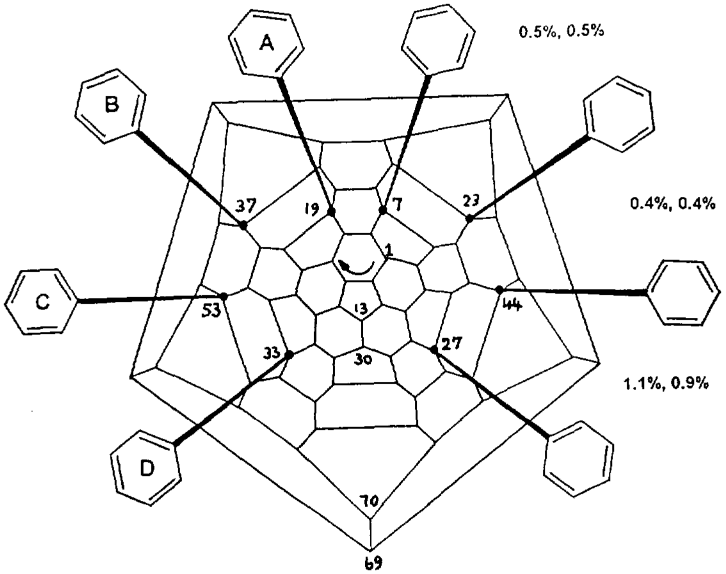


Figure 5a Schlegel diagram for $C_{70}Ph_8$, showing the nOe enhancements in each direction, and the aryl ring identifiers corresponding to those on the ^1H NMR spectrum.

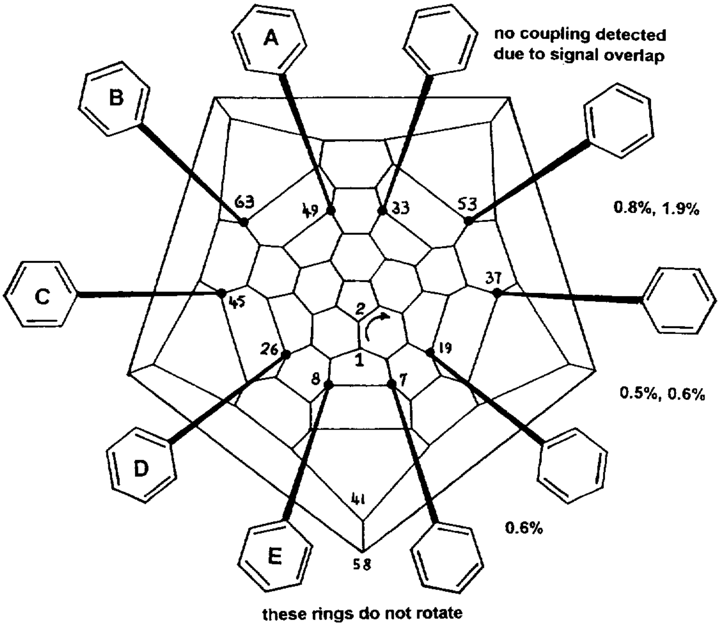


Figure 5b Schlegel diagram for $C_{70}Ph_{10}$, showing the nOe enhancements, and the aryl ring identifiers corresponding to those on the ^1H NMR spectrum; note that rings E have restricted rotation due to steric interactions (see Text).

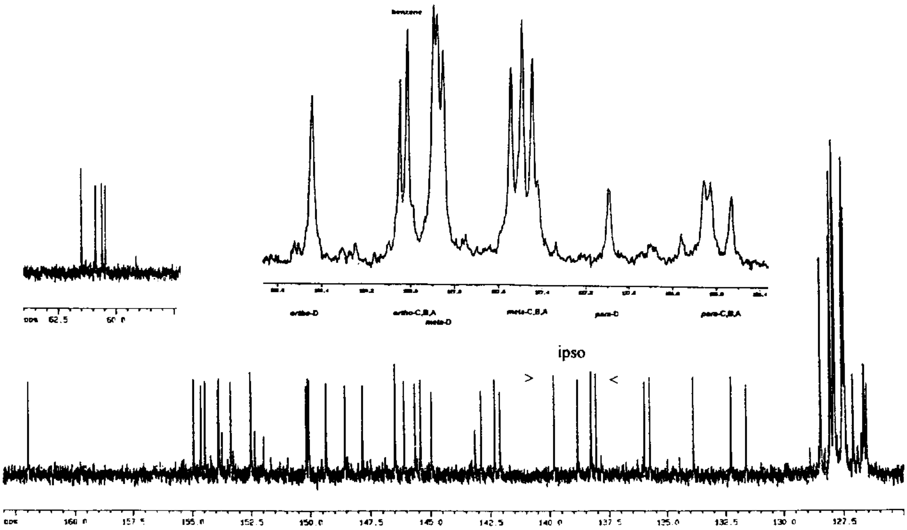


Figure 6a ^{13}C NMR spectrum for $C_{70}Ph_8$. Inset shows sp^3 region, and expansion of the aromatic sp^2 region with assignments; benzene trace is due to lattice-trapped solvent.

Table 2 ^{13}C NMR shifts for $C_{70}Ph_8$ and $C_{70}Ph_{10}$ (500 MHz, $CDCl_3$)

$C_{70}Ph_8$			$C_{70}Ph_{10}$		
δ	Intensity	Assignment[a]	δ	Intensity	Assignment[a]
161.95	0.10		156.28	1.98	
154.92	0.10		155.71	1.98	
154.62	0.09		155.30	2.08	
154.44	0.10		155.26	2.26	
153.89	0.09		155.04	2.20	
153.85	0.10		154.40	1.98	
153.71	0.04	C69/C70	153.85	0.69	C41/C58
153.35	0.10		153.79	2.05	
152.52	0.11		153.43	1.10	C41/C58
152.50	0.10		153.28	1.96	
152.33	0.04	C69/C70	152.57	1.98	
151.97	0.04	C13	152.35	1.81	
150.17	0.09		151.23	1.88	
150.09	0.10		150.99	1.91	
150.04	0.10		149.44	2.17	
149.33	0.10		149.32	2.08	
148.54	0.09		149.26	2.13	
147.80	0.09		149.19	2.00	
146.47	0.10		148.49	1.00	C1/C2.
146.46	0.10		148.20	2.25	
146.09	0.10		148.15	2.03	
145.63	0.10		147.82	2.08	
145.40	0.10		147.10	2.08	
144.95	0.09		146.94	2.06	
143.13	0.05	C30	144.04	2.06	
142.87	0.09		142.78	2.07	*ipso*, ring E
142.32	0.10		142.47	2.24	
142.10	0.09		140.94	1.04	C1/C2
139.81	0.11	*ipso*, ring D	139.11	2.35	*ipso*, ring B
138.82	0.10	*ipso*, ring B	139.09	2.49	*ipso*, ring A
138.25	0.11	*ipso*, ring C	138.78	2.47	*ipso*, ring C
138.05	0.11	*ipso*, ring A	138.75	2.28	*ipso*, ring D
135.98	0.10		137.43	2.11	
135.76	0.10		136.64	2.25	
133.86	0.10		136.11	2.36	
132.25	0.10		135.39	2.21	
131.61	0.09		132.33	2.13	
61.49	0.13	C27,33	131.11	1.79	*ortho*[b], ring E[c]
60.87	0.11	C23,37	130.97	1.81	*ortho*[b], ring E[d]
60.60	0.11	C44,53	67.64	2.39	C7,8
60.44	0.11	C7,19	61.97	2.36	C53,63
			61.48	2.51	C33,49
			61.03	2.40	C37,45
			60.80	2.44	C19,26

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[a] Provisional; see corresponding Figures 5 for numbering. [b] The other aryl carbon signals could not be distinguished from that due to traces of benzene. [c] Assumed to be the pair pointing towards the cage cap. [d] Assumed to be the pair pointing towards the cage equator.

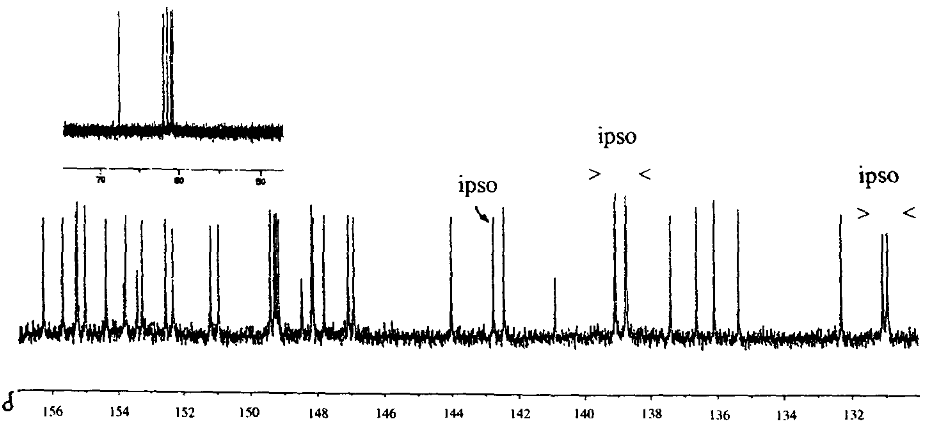


Figure 6b ^{13}C NMR spectrum for $C_{70}Ph_{10}$; inset shows sp^3 region.

The ^{13}C NMR spectrum for $C_{70}Ph_8$ (Fig. 6a, $CDCl_3$) shows the correct nuumber of peaks and intensities for the proposed structure, and the chemical shifts and provisional peak assignments are given in Table 2.

7,8,19,26,33,37,45,49,53,63-Decaphenyl[70]fullerene[7]- This compound can be made without needing [70]fullerene to be completely free of [60]fullerene, since the byproducts are easily removed during purification. A *ca.* 90:10 mixture of [70]- and [60] fullerenes (85 mg) was dissolved in dry benzene and reacted with ICl in benzene as described above. When formation of the chlorinated species was complete, the reaction was cooled slightly and a catalytic quantity of ferric chloride was added, causing an exothermic reaction (the solution began to reflux). When this had subsided, the reaction mixture was heated under reflux for 4 h. The cooled solution was then washed with saturated sodium thiosulphate (2 x 25 cm^3, and water. The orange organic layer was separated, dried ($MgSO_4$) and concentrated to give a dark oily residue from which a solid was precipitated by the addition of pentane (20 cm^3). Filtration yielded a dry yellow solid which was washed with pentane (2 x 10 cm^3). The resultant dry solid was dissolved in carbon tetrachloride (20 cm^3), and the volume reduced under vacuum to *ca.* 2 cm^3. The dark red solution was left to stand overnight, during which crystals of $C_{60}Ph_5Cl$ formed; these were removed by filtration, and washed with carbon tetrachloride (the crystalline $C_{60}Ph_5Cl$ does not readily redissolve). The volume of the filtrate was reduced to a minimum and chromatographed on silica gel (CCl_4 as eluent). A long thin column (35 cm x 1 cm) was used together with a very slow rate of CCl_4 elution (about 1 drop/5 s). Residual orange $C_{60}Ph_5Cl$ eluted first followed by distinct bright yellow $C_{70}Ph_{10}$. Solvent removal from this fraction gave a pale yellow luminscent solid, having an R_f value of 0.71.

The retention time under the HPLC conditions used for $C_{70}Ph_8$ was 16.8 min, *i.e.*, the more highly functionalised compound (same function) elutes first, a common feature of the Cosmosil column. By contrast, $C_{70}Ph_8O_4$ [6] has a retention time of 33.9 min. under these conditions.

The mass spectrum (EI conditions, Fig. 1b) shows the parent ion for $C_{70}Ph_{10}$ at 1611 amu, and again the greater stabilities of fragmentation ions containing an odd number of phenyl groups, is apparent. Figures 2b and 3b, respectively, show the spectra for UV/VIS (cyclohexane, λ_{max} 224, 313,, 401, 426, 471), and IR (KBr) ν/cm $^{-1}$ 3084, 3057, 3030, 2923, 2853, 1599, 1583, 1493, 1446, 1314, 1187, 1079, 1032, 1003, 928, 908, 838, 778, 754, 729, 721, 716, 694, 679, 670, 663, 658, 643, 606, 598, 593, 586, 550, 538, and 533.

Details of the ^1H and ^{13}C NMR spectra are given in Tables 1 and 2, respectively. The ^1H NMR spectrum is shown in Fig. 4b together with assignments deduced by 2D (COSY) experiments; the aryl ring identifiers correspond to those shown in the Schlegel diagram (Fig. 5b). This diagram also shows the magnitude of the nOe enhancements between adjacent aryl groups; no enhancements could be measured between aryl groups A and B, because of peak overlap. The ^{13}C NMR spectrum is shown in Fig. 6b.

DISCUSSION

The phenylated fullerenes promise to be the forerunners of a very wide range of aryl derivatives having interesting spectroscopic and other properties. In particular the spontaneous oxidation of $C_{70}Ph_8$ to the tetra-oxide having an eleven-membered hole in the cage, and which can eliminate CO_2 to close the hole giving $C_{68}Ph_8$ a new type of fullerene,[6] clearly has great encapsulation potential as well as theoretical ramifications. We have made [70]fullerene derivatives possessing either 2, 4, 6, 8, or 10 phenyl groups, and have fully characterized the latter two (which are both luminescent). Because of their importance we provide here full experimental and spectroscopic details, together with very detailed analysis of the chemical shifts since we anticipate that this will provide the basis for structural analyses of a wide range of compounds of this type. Other components that have been identified so far (by mass spectrometry only) are $C_{70}Ph_9O$ and $C_{70}Ph_{14}$ (the existence of which has been predicted theoretically),[8] and we hope to report details later as they become available.

Phenylation mechanism.- The reaction evidently is an electrophilic substitution of the chlorofullerene into benzene, with ferric chloride acting as a normal Friedel-Crafts catalyst. However, the reaction times show that the reaction is not straightforward, since $C_{70}Ph_8$ is formed (with concurrent loss of two chlorine atoms) considerably more readily than $C_{70}Ph_{10}$, and indeed is an intermediate along the reaction pathway to it. Thus the last two phenyl groups in $C_{70}Ph_{10}$ add across a C=C bond which is in a pentagon, removal of this unfavourable feature[2] evidently being the driving force for the reaction. Further confirmation of this reaction pathway was provided by reacting $C_{70}Ph_8$ with toluene/$FeCl_3$ which produced $C_{70}Ph_8(tolyl)_2$, m/z = 1640. The addition of the final two aryl groups to the cage appears then to involve Friedel-Crafts alkylation *via* alkenes,[9] though further experiments will be needed to elucidate the precise mechanistic details.

Structural characterization.- Both the ^1H and ^{13}C NMR spectra confirm the C_s symmetry of each product. The chemical shifts for the *ortho* hydrogens in the ^1H NMR spectrum for $C_{70}Ph_8$ show the same pattern as do the *ipso-*, *ortho-*, *meta-*, *and para* carbons in the ^{13}C NMR spectrum, *i.e.* one pair of phenyl groups experiences a significantly more electronegative environment than the other three. Based on other arguments (below) we conclude that this is the pair *D* (see Fig. 5a), which is reasonable because they are in the region of a pentagon containing a double bond, and the consequent strain produces a downfield chemical shift.[10] This factor, together with the nOe couplings enables us to assign the resonances to the remaining phenyl groups as in Fig. 5a. It should be noted that the ^1H NMR spectrum shows that all of the phenyl groups are able to rotate freely at room temperature.

In contrast to the above, the ^1H NMR spectrum for $C_{70}Ph_{10}$ shows that the *ortho*- and *meta* hydrogens for one pair of phenyl groups are non-equivalent, and thus these groups are unable to rotate freely at room temperature. The shifts for the *para* hydrogens and *ipso* carbons do not of course depend on conformation and so only one set of resonances is found for each of these in the corresponding spectra. Since no restriction on rotation occurred in $C_{70}Ph_8$, we may with confidence assign the non-rotating phenyls to the adjacent pair. Furthermore, the -I effect of the adjacent phenyl groups should cause the chemical shifts for this pair to be more downfield than those for the others, and this is evident in the shifts for the *ortho*- and *meta* hydrogens, and the *ipso* carbons. We make the assumption that the pair of *ortho* hydrogens giving rise to the more downfield signal is that which points towards the pentagonal polar cap of [70]fullerene, since this is the more electron-deficient region of the molecule. We employed similar arguments to assign the methyl resonances in the unsymmetrical adduct formed between pentamethylcyclopentadiene and [70]fullerene,[11] and notably, the difference in shifts for methyls (pointing towards the cage, as in the case of the *ortho* hydrogens here) in the two different environments was *ca.* 0.45 ppm, as here.

Having identified the non-rotating phenyl groups, we have been able to unambiguously assign the other phenyl groups by means of nOe analysis as shown on the Schlegel diagram, Fig. 5b. By contrast, the assignment of the corresponding phenyl groups in $C_{70}Ph_8$ is more speculative, but is shown to be correct in the following way: We compare the *ortho* resonances for rings A-D in both phenylated compounds, and we know the correct sequence for $C_{70}Ph_{10}$, and there are two (only) sequences for $C_{70}Ph_8$. Now it is reasonable to assume that on going from the former compound to the latter, that there will be a regular change in δ for the sequence of $D \rightarrow A$. For the sequence as assigned this is correct, the changes being as follows: *A*, - 0.15; *B*, - 0.05; *C*, 0.06; *D*, 0.70, and this is shown schematically in Fig. 7. If however, the sequence in $C_{70}Ph_8$ is reversed, no regular correlation is obtained.

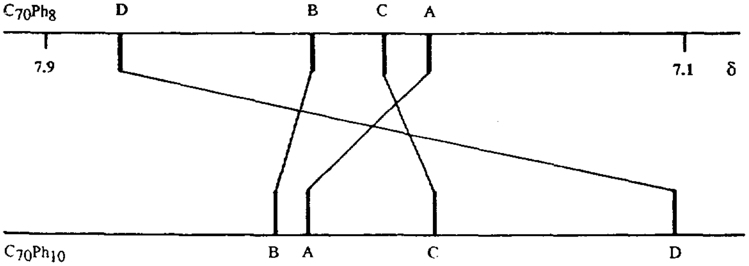
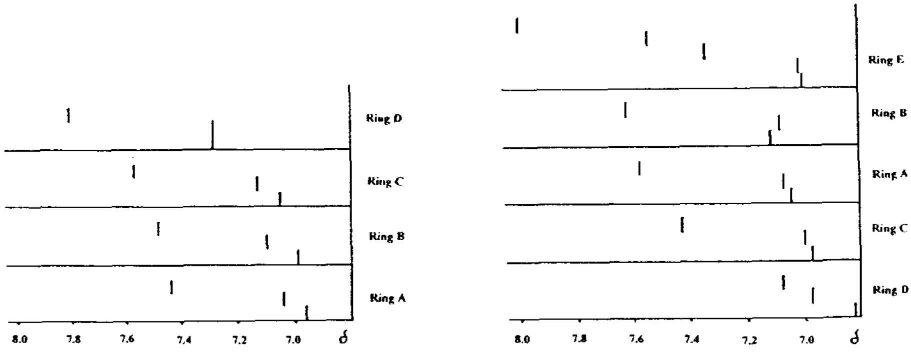


Figure 7 Schematic showing the relationships between the chemical shifts for the *ortho* hydrogens of rings *A* - *D* in $C_{70}Ph_8$ and $C_{70}Ph_{10}$.

We provisionally assign the resonances for the sp^3 carbons (Table 2) on the assumption that the sequence parallels that for the *ipso*-carbons which in turn parallels that for the *ortho*-hydrogens (which can be unambiguously identified for $C_{70}Ph_{10}$). The shifts for these carbons in $C_{70}Ph_{10}$ and $C_{70}Ph_8$ may be compared with those for $C_{70}Cl_{10}$[1] as follows: 67.64, 61.97, 61.48, 61.03, 60.80; (-), 61.49, 60.87, 60.60, 60.44; 71.52, 58.98, 58.58, 58.39, 58.37. The most downfield resonance for the Ph_{10} and Cl_{10} compounds apart, the remaining values are comparable, with the phenyl values being *ca.* 2.5 ppm more downfield; assignment of the two downfield resonance to the adjacent carbons that have addends is clearly correct. The spread of the other values in the Ph_{10} and Ph_8 compounds are almost identical (1.17 and 1.05 ppm, respectively).

Comparison of the resonances for the on-axis carbons is also informative and enables us to update our provisional assignments of these resonances in $C_{70}Cl_{10}$.[1] The shifts for $C_{70}Ph_{10}$, $C_{70}Ph_8$, and $C_{70}Cl_{10}$ are, respectively: 153.85, 153.43, 148.49, 140.94; 153.71, 152.33, 151.97, 143.03; 153.43, 152.45, 148.98, 139.05. The most downfield pair of resonances for each compound are reasonably similar, and may be inferred to relate to those carbons most remote from alterations to the cage structure *i.e.*, C69 and C70/ C41 and C58. (Note that these are the same carbon pairs, the numbering being altered due to the requirement of using lowest locants.) Furthermore, of the most upfield pair, those for $C_{70}Ph_8$ are very substantially more downfield than the others, and it is reasonable to assume, given the structural difference between the Ph_8 compound on the one hand, and the Ph_{10} and Cl_{10} compounds on the other, that they relate to the resonances for the on-axis carbons that are nearest to the strained pentagonal ring. Thus we provisionally assign the resonances at 151.97 and 143.03 to C30 and C13, respectively; if these are confirmed subsequently, our provisional assigments for $C_{70}Cl_{10}$ will need amending.

Substituent Effects.- A vast range of the effects of substituents on benzene (both kinetic and spectroscopic) have been amassed over many decades. It may be anticipated that these data will become greatly supplemented by the effects of fullerene substituents, given the enormous range of possibilities arising from the size of the cages. Here we present the first analysis of any kind, and Figures 8a,b, show the mid-points of the ^1H NMR resonances (*o*, *m*, *p*, descending) for the phenyl rings in $C_{70}Ph_8$ and $C_{70}Ph_{10}$, respectively. Although there are some slight anomalies between the *meta*- and *para* positions, in general it can be seen that the spread of the resonance positions for each ring increase the more downfield the resonance region. This seems reasonable, and suggests that such correlations will be of general use in establishing the structures of other aryl derivatives of fullerenes.



Figures 8a, b Schematic showing the mid-point of the resonances in the ^1H NMR spectrum due (in descending order) to the *ortho-*, *meta-* and *para* hydrogens of the phenyl rings in $C_{70}Ph_8$ and $C_{70}Ph_{10}$, respectively; there are two sets of *o*- and *m*-lines for ring E of the latter.

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