The Structure of $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$, formed *via* Electrophilic Aromatic Substitution

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Reaction of $C_{60}Cl_6$ with benzene/$FeCl_3$ yields $C_{60}Ph_5Cl$ which is readily reduced to $C_{60}Ph_5H$, the main product of reacting C_{60} with Br_2/$FeCl_3$/benzene; both compounds have been characterised by NMR spectroscopy.

The sp^2-hybridised carbon framework and the associated cage strain makes [60]fullerene a potent electrophile.[1] [60]Fullerene appears to be more electrophilic than [70]fullerene, as indicated by the ^1H resonances in the NMR spectra of hydrogenated [60]fullerenes lying considerably downfield from those for hydrogenated [70]fullerenes[2,3] and by the equilibrium constants for reaction of [60]- and [70]-fullerenes with *N*,*N*-dimethylaniline.[4]

We showed previously that $C_{60}Ph_{12}$ was amongst the products obtained in electrophilic substitution of benzene by [60]fullerene in the presence of Br_2/$FeCl_3$.[5] Friedel–Crafts reaction of polychlorinated [60]fullerenes with benzene gave products containing up to 22 phenyl groups.[6] We have now isolated some 10 products (some as yet uncharacterised) from the former reaction, find that the main product is $C_{60}Ph_5H$, and that this is also formed by reacting $C_{60}Cl_6$ (which we described recently)[7] with benzene/$FeCl_3$ followed by reduction.

$C_{60}Ph_5Cl$ was prepared by heating $C_{60}Cl_6$[7] with benzene–$FeCl_3$ for 20 min, cooling, washing the benzene layer with water, separating and drying ($MgSO_4$). The residue obtained after benzene removal was set aside to crystallise from carbon tetrachloride, and gave translucent orange crystals (68%). These crystals contain CCl_4 trapped in the lattice, for on heating to *ca.* 80 °C they become opaque, the loss of CCl_4 was also monitored by IR spectroscopy. The mass spectrum (Fig. 1, EI, heated DCI probe), the first obtained for a chlorinated fullerene, confirmed the molecular formula as $C_{60}Ph_5Cl$. The IR spectrum showed strong phenyl C–C bands and 3084, 3057, 3025, 1598, 1493, 1463, 1447, and 695 cm^{-1}, weak C–Cl bands at 790 and 771 cm^{-1} (these disappeared on reduction) and cage C–C bands at 735, 585, 566, 560 and 543 cm^{-1}.

The ^{13}C NMR spectrum of $C_{60}Ph_5Cl$ (Table 1), is very similar to that of $C_{60}Cl_6$,[7] *viz.* 26 peaks of intensity 2 and two peaks of intensity 1 in the sp^2 region, and four peaks of intensity ratio 1:1:2:2 in the sp^3 region. All signals are shifted downfield, relative to those for $C_{60}Cl_6$ suggesting that the phenyl is more electron withdrawing than chlorine. [The phenyl groups cannot conjugate with the π-electrons of the cage (orthogonal p-orbitals), and hence the electron-releasing +M effect is absent.] The resonances at δ 147.78 and 146.87 for the (remote) C-55 and C-60, are only slightly downfield from the corresponding resonances in $C_{60}Cl_6$ (δ 147.64 and 146.38, respectively),[7] suggesting that the chemical shifts are a function of distance from the addends. We provisionally assign the most down-field resonances at δ 156.31 and 153.26 to C-3/C-12 and C-13/C-14, respectively.

The proposed structure requires twelve peaks in the aromatic sp^2 region of intensity ratios 1:1:2:2:2:

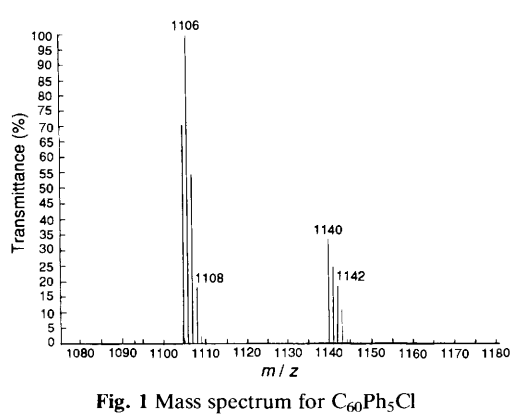

Fig. 1 Mass spectrum for $C_{60}Ph_5Cl$

Table 1 ^{13}C NMR shifts for $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$ (500 MHz, $CDCl_3$ lock signal) with relative intensities[a] and provisional assignments see footnotes [b–v]

$C_{60}Ph_5Cl$		$C_{60}Ph_5H$	
δ($CHCl_3$)	Intensity	δ(CS_2)	Intensity
156.31[b]	8.39	155.58[b]	6.59
153.26[c]	7.95	151.80[c]	8.35
150.73	7.71	151.64	6.62
149.92	8.12	150.80	6.84
148.41	8.65	148.35	6.72
148.35	9.40	148.31	7.19
148.30	10.75	148.24	6.94
148.29	9.79	147.96	7.04
148.11	8.31	147.83	7.22
147.91	8.16	147.68[d]	2.98
147.78[d]	4.01	147.67	6.29
147.48	8.01	147.32	6.66
147.02	8.52	147.17	6.79
146.89	8.63	146.74	7.12
146.87[d]	5.00	146.65	6.54
146.32	7.52	146.46[d]	3.39
144.95	8.93	145.67	6.88
144.88	8.07	145.34	6.90
144.22	8.15	145.16	6.95
144.04	8.80	144.87	6.64
143.95	8.66	144.85[e]	4.90
143.86	7.76	144.07	6.46
143.59	8.37	144.00	7.37
143.39	9.11	143.93	7.42
143.31	8.59	143.91	7.51
143.17	8.50	143.84	6.50
143.02[e]	5.72	143.77	7.33
142.96	8.70	143.22	7.03
142.56	7.96	143.87	6.85
138.19[f]	9.16	138.94[f]	9.01
136.68[g]	10.0	138.80[g]	8.22
129.73[h]	15.2	128.55[i]	17.93
128.43[i]	43.1	128.48[h]	7.47
128.38[j]	45.5	128.23[j]	19.86
128.22[k]	39.4	127.77[k]	19.62
128.15[l]	43.3	127.57[l]	18.28
127.51[m]	18.1	127.39[n]	6.01
127.45[o,p]	31.1	127.27[q]	7.65
126.89[r]	7.29	127.12[m]	6.11
75.91[s]	9.43	126.84[r]	3.03
62.98[t]	12.7	62.73[u]	3.06
60.39[u]	22.1	60.42[v]	2.97
57.72[v]	19.2	58.42[t]	2.24
		58.31[s]	2.36

[a] Relative to the values in the same column only. [b] C-3, C-12. [c] C-13, C-14. [d] C-55/C-60. [e] *ipso*-C, ring A. [f] *ipso*-C, rings BC. [g] *ipso*-C, rings DE. [h] *ortho*-C, ring A. [i] *ortho*-C, rings BC. [j] *ortho*-C, rings DE. [k] *meta*-C, rings BC. [l] *meta*-C, rings DE. [m] *meta*-C, ring A. [n] *para*-C, rings BC. [o] Two almost coincident double intensity peaks. [p] *para*-C, rings BC, DE. [q] *para*-C, rings DE. [r] *para*-C, ring A. [s] C-2 (sp^3). [t] C-1 (sp^3). [u] C-4, C-11 (sp^3). [v] C-15, C-30 (sp^3).

2:2:2:4:4:4:4, as observed (Table 1), and these have been assigned on the basis of inductive effects and peak intensities; the *ipso* peaks were identified by comparison of proton-coupled and -decoupled spectra. The ^{1}H NMR spectrum of $C_{60}Ph_5Cl$ (500 MHz, $CDCl_3$) shows δ 7.95 (4 H, m, *ortho*-H, rings BC), 7.64 (d, 4 H, *J* 7.95 Hz, *ortho*-H, rings DE), 7.35 (m, 6 H), 7.32 (d, 2 H, *J* 7.25 Hz), 7.29 (d, 4 H, *J* 7.35 Hz), 7.23 (d, 2 h, *J* 7.85 Hz), 7.15 (d, 1 h, *J* 7.35 Hz) and 7.11 (d, 2 H, *J* 8.0 Hz).

From the spectra, we assigned the structure shown in Fig. 2 (X = Cl) *i.e.* 2-chloro-1,4,11,15,30-pentaphenyl-1,2,4,11,15,30-hexahydro[60]fullerene.[8] The alternative structure with the 2-chloro and 1-phenyl groups interchanged (which is also consistent with the NMR data) is ruled out since steric hindrance must be the cause of the failure to replace all of the chlorines in $C_{60}Cl_6$ by phenyls. It is also ruled out by the structure of the hydro derivative (below). $C_{60}Ph_5H$ was prepared in two ways: In the first, $C_{60}Ph_5Cl$ was dissolved in benzene and an excess of triphenylphosphine was added to give, after 24 h, fine red needles which were recrystallised from benzene. Chlorine is readily removed under these conditions,[9] and the intermediate (aromatic) cyclopentadienyl anion, further stabilised by the −I inductive effect of the phenyl groups, acquires a proton from the (wet) solvent. The mass spectrum shows the parent ion at 1106, and also reveals the presence of small amounts of O and CH_2 derivatives (1122 and 1136), though these are unresolved in the NMR spectrum. The most likely addition sites lie across the highly localised 3,14- and 12,13-bonds, which would destroy the symmetry so that no NMR signals would be recorded during a realistic accumulation time. The main difference between the IR spectra of $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$ is the absence of the C–Cl bands in the latter.

When [60]fullerene was also heated with benzene/Br_2/$FeCl_3$ for 24 h[5] the product was dissolved in hexane and then purified

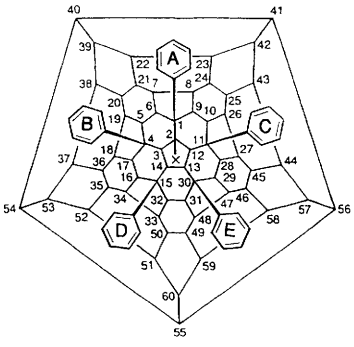

Fig. 2 Schlegel diagram of the structures of $C_{60}Ph_5X$, (X = Cl, H)

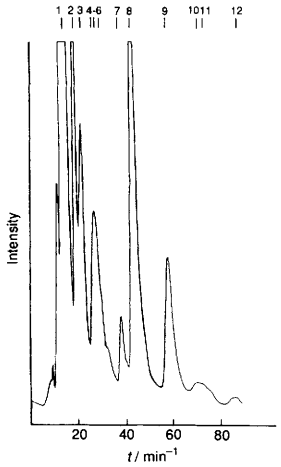

Fig. 3 HPLC trace of the product of reaction of [60]fullerene with benzene;bromine;$FeCl_3$ (peak no. 1 is [60]fullerene)

by HPLC using a 41.4 mm × 25 cm preparative Rainin Dynamax 60 Å column (8 μm cyano column) operated at 40 ml min^{-1} with hexane elution. The main fraction (peak No. 8, Fig. 3) which eluted after 43.5 min, gave bright red crystals following removal of solvent; the relative intensities of the other components is batch-variable.

The ^{13}C NMR spectra were run for both samples in CS_2 ($CDCl_3$ lock) and the resonances were found to be within 0.02 ppm of each other, with similar peak intensities; one sample was also run in $CDCl_3$, in which there were small and position-dependent downfield shifts of between 0.19 and 0.63 ppm. The spectrum (Table 1) shows the same pattern found for $C_{60}Cl_6$ and $C_{60}Ph_5Cl$. The resonances for the two carbons on the symmetry axis at δ 147.68 and 146.46 are again in similar positions to those in the precursor molecules. The majority of the resonances for the hydrogenated compound are upfield compared to those for the chloro precursor, suggesting that reduction in strain is partly responsible for the difference. The twelve resonances for the phenyl ring carbons have the required intensity ratios, and were assigned as for $C_{60}Ph_5Cl$ above.

The ^{1}H NMR spectrum (500 MHz CS_2) exhibited a complex series of multiplets and doublets between δ 7.75 and 7.00, and a sharp singlet at δ 5.2. NOE analysis (to be described in the full paper) of the interactions between the cage hydrogen and those at the *ortho* positions of the phenyl rings, unambiguously confirmed our proposed structure for $C_{60}Ph_5H$ as 1,2,4,11,15,30-hexahydro-1,4,11,15,30-pentaphenyl[60]fullerene (Fig. 2, X = H).†

Formation of $C_{60}Ph_5Cl$ from $C_{60}Cl_6$ at room temp. takes many weeks, and involves formation of two unidentified intermediate products (TLC).

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Footnote

† Likewise (*cf*; ref. 8), this can be abbreviated to 2-hydro-1,4,11,15,30-pentaphenyl[60]fullerene.

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8 This name may be shortened in general usage to 2-chloro-1,4,11,15,30-pentaphenyl[60]fullerene, since no ambiguity results from this; the numbering system is that recommended in R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1993, 813.
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