Preparation and characterisation of $C_{70}Ph_9OH$; the first fullerene with a single hydroxy group attached to the cage

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The fullerenol $C_{70}Ph_9OH$ is obtained as a minor product from the reaction of $C_{70}Cl_{10}$ with benzene/$FeCl_3$ and is chiral due to the attachment of a hydroxy group and a phenyl group across the 7,8-bond; this adjacency inhibits free rotation of the 8-phenyl group.

Recently we described the characterisation of $C_{70}Cl_{10}$,[1] its conversion into $C_{70}Ph_{10}$ and $C_{70}Ph_8$,[2] and the spontaneous oxidation of the latter to a cage-opened bis-lactone.[3] In $C_{70}Ph_{10}$ the two adjacent phenyl groups are prevented from rotating at room temperature.[2] We now report the formation and characterisation of $C_{70}Ph_9OH$, the first monohydroxyfullerene. Hydroxyfullerenes (fullerenols) hold the prospect of being important synthons in fullerene chemistry, but thus far only partly characterised polyhydroxyfullerenes have been made.[4]

To prepare $C_{70}Cl_{10}$ a freshly prepared solution of ICl (*ca.* 3 g) in dry benzene (20 cm^3) was added to [70]fullerene (87 mg) dissolved in dry benzene (250 cm^3), and the mixture heated until reaction was complete (*ca.* 20 min). (NB. The ICl must not be dispensed with metal spatulas since Lewis acid traces are produced causing Friedel–Crafts reactions.) Reaction can be monitored by TLC (silica gel, CCl_4): [70]fullerene produces a red-brown spot at the solvent front, whilst yellow $C_{70}Cl_{10}$ has an R_f value of 0.87. The cooled reaction mixture was washed with a saturated sodium thiosulphate solution (2 × 25 cm^3) and water (2 × 10 cm^3), and solvent was removed (vacuum) from the dried ($MgSO_4$) organic layer. Traces of aromatic impurities were removed by adding pentane to the residue, whence $C_{70}Cl_{10}$ precipitated; filtration and further pentane washing gave the pure material.

To prepare $C_{70}Ph_9OH$ a catalytic amount of $FeCl_3$ was added to a solution of $C_{70}Cl_{10}$ in benzene, and the mixture heated under reflux for *ca.* 20 min to give complete conversion of the chloride into three derivatives (TLC, silica gel, CCl_4, R_f values 0.58, 0.48, 0.05). Work-up as above, and column chromatography (silica gel, CCl_4), gave $C_{70}Ph_8$ (orange–red), then $C_{70}Ph_{10}$ (yellow).[2] Further elution with $CCl_4:CH_2Cl_2$ (99.5 : 0.5) and work-up gave $C_{70}Ph_9OH$ (13 mg, 8%) as a bright yellow solid.

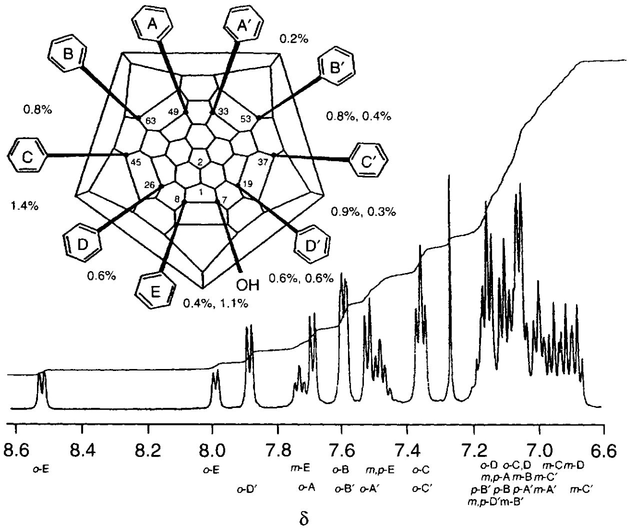

Fig. 1 ^1H NMR spectrum (−30 °C) for $C_{70}Ph_9OH$; Schlegel diagram inset shows NOE couplings between adjacent *ortho* hydrogens.

The structure of $C_{70}Ph_9OH$ is shown in the Schlegel diagram (inset to Fig. 1), and was deduced as follows: The EI mass spectrum (Fig. 2, 70 eV) shows m/z = 1551 amu. The (m + 1)/m peak height ratio (1.39) is in excellent agreement with that (1.40) calculated for $C_{70}Ph_9OH$. The fragmentation pattern shows loss of 17 amu (OH) followed by 77 amu (Ph) and the converse order; hydroxy loss appears to be the more facile. Regular losses of phenyl groups then occur with the alternating intensity pattern typical of phenylated fullerenes [due to the stabilities of the radical species $C_{70}Ph_n\cdot$ (n odd)]; traces of fullerenol down to $C_{70}Ph_4OH\cdot$ are detectable.

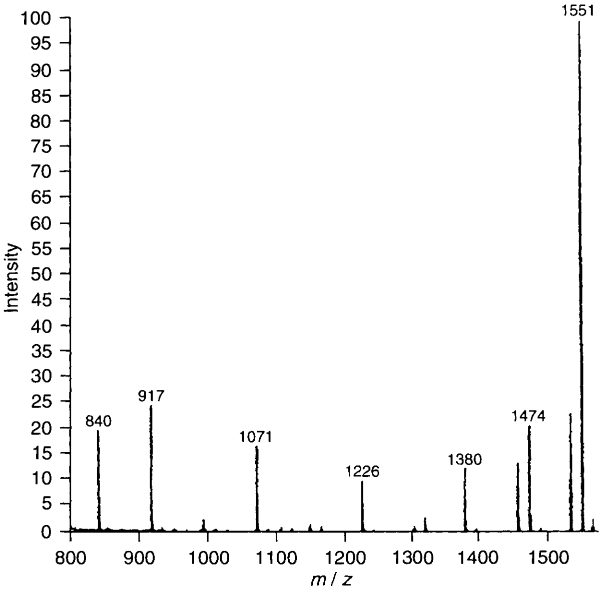

Fig. 2 EI mass spectrum for $C_{70}Ph_9OH$

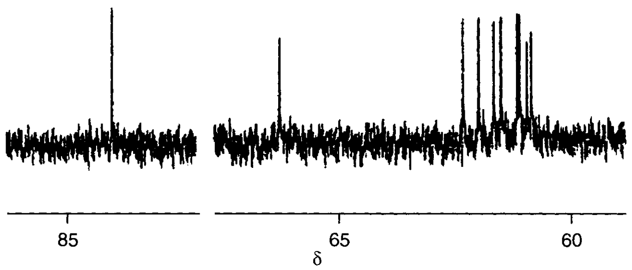

Fig. 3 ^{13}C NMR spectrum (sp^3 region) for $C_{70}Ph_9OH$

Table 1 Chemical shifts for *ortho* hydrogens in $C_{70}Ph_{10}$ and $C_{70}Ph_9OH$

Phenyl group	E	B	B′	A	A′	C	C′	D	D′
$C_{70}Ph_{10}$	7.55–8.0	7.61	7.61	7.58	7.58	7.41	7.41	7.13	7.13
$C_{70}Ph_9OH$	8.0–8.52	7.59	7.59	7.69	7.52	7.36	7.36	7.17	7.89

The mass spectrum is especially notable because hitherto, no EI mass spectrum of a fullerenol has been recorded, presumably due to ready elimination of water from adjacent hydroxy groups. This parallels the failure to obtain EI mass spectra for halogenated fullerenes (ready loss of hal_2) except when a single halogen is present, as in $C_{60}Ph_5Cl$.[5] Presumably the lack of a suitable partner for elimination of the OH group results in the higher stabilty of $C_{70}Ph_9OH$.

Cage carbons were distinguished from ipso-, *ortho*-, *meta*- and *para*-carbons by proton decoupling of the ^{13}C NMR spectrum. For [70]fullerene with ten addends and C_1 symmetry, sixty peaks of equal height should appear in the sp^2 region. Fifty-seven (three of double intensity as indicated) were found at δ 158.22, 156.33, 155.92, 155.81, 155.66, 155.37 (2C), 155.35, 155.32, 155.09, 155.88, 154.71, 154.45, 153.99, 153.83, 153.52, 153.10, 152.93, 152.60, 152.37, 152.17, 151.94, 151.63, 151.30, 151.21, 150.96, 150.10, 149.73, 149.57, 149.54, 149.27 (2C), 149.24, 148.80 (2C), 148.73, 148.14, 148.08, 147.94, 147.12, 147.11, 147.02, 146.91, 144.83, 144.50, 144.40, 144.08, 143.09, 142.51, 141.79, 139.42, 138.53, 137.95, 136.82, 136.26, 135.97, 135.07, 133.44, 132.56 and 132.06.

The nine ipso-carbons at δ 140.25, (139.53, 139.52, 139.35, 139.17), [138.75, 138.63 (2C), 138.48], comprise three clusters as indicated, and the most downfield peak can be attributed to the phenyl group next to OH. (For $C_{70}Ph_{10}$ the ipso peaks appeared at δ 142.78, 139.11, 139.09, 138.78 and 138.75.)[2] The remaining sp^2-hybridised carbons appear in three clusters, (*o*, *m*, *p*, respectively) at δ (128.22, 128.14, 128.05, 127.99, 127.97, 127.95, 127.91), (127.75, 127.63, 127.55, 127.49, 127.35), (126.84, 126.77, 126.72, 126.65, 126.50), with some coincidences.

The ten sp^3-hybridised cage carbons (Fig. 3) are at δ 84.07 (C–OH), 66.26 [8-Ph (E)], 62.31, 61.96, 61.64, 61.48, 61.14, 61.09, 60.94 and 60.84. Eight of them are grouped in pairs, consistent with the structure, and the peak locations are close to those identified for $C_{70}Ph_{10}$,[2] which gave δ 67.64 (C-7, 8); 61.97 (C-53, 63); 61.48 (C-33, 49); 61.03 (C-37, 45); 60.80 (C-19, 26).

^1H NMR spectra were obtained at −30 and +25 °C, and by means of 2-D COSY, 2-D Hartmann–Hahn), NOE, saturation and selective population transfer techniques the spectrum was fully analysed and the identities of the phenyl groups determined (Fig. 1); ring A was identified by a process of elimination. Both spectra show a sharp singlet at δ 3.16 due to the OH group, and ten groups of *ortho*-hydrogens. This is because phenyl group E is unable to rotate, hence the *ortho* hydrogens have different locations producing two sets of coupled doublets (Fig. 1). At higher temperature, these signals begin to merge as rotation becomes less impeded.

In Table 1 the chemical shifts for the *ortho* hydrogens for phenyl groups (A–E) in $C_{70}Ph_{10}$[2] and $C_{70}Ph_9OH$ are collated. Both data sets show a 0.5 ppm difference between the shifts for the *ortho* hydrogens of the non-rotating phenyl groups, and the shifts for phenyl groups B, C, and D are also similar for each molecule. The downfield shift orders of the two sides of the cage in $C_{70}Ph_9OH$ differ, being: $A > B > C > D$, and $D' > B' > A' > C'$, the signals of the *ortho* hydrogens of ring D′ being more downfield due to the adjacency of the OH group (which further confirms the structure). The $-I$ effect of the OH group also causes the signals for the *meta* and *para* hydrogens in ring D′ to coincide (*meta* hydrogens usually appear more upfield).

The mechanism of chlorine replacement by aryl groups in fullerenes is complex. For example formation of $C_{70}Ph_{10}$ from $C_{70}Cl_{10}$ occurs *via* $C_{70}Ph_8$ as intermediate, and not *via* $C_{70}Ph_8Cl_2$ as might be expected.[2] It is possible that the immediate precursor of the fullerenol is a monochloro compound $C_{70}Ph_9Cl$ that undergoes nucleophilic substitution by traces of water in the solvent; TLC analysis shows that the fullerenol is present before aqueous work-up. So far we have not isolated an analogous product from the reaction of water with $C_{60}Ph_5Cl$.[5]

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