Formation and Characterisation of $C_{70}Cl_{10}$

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[70]Fullerene reacts with ICl in benzene to give $C_{70}Cl_{10}$, shown by ^{13}C NMR spectroscopy to have C_s symmetry with chlorines located around the cage waist.

Whereas many of the addition patterns in [60]fullerene are now well established,[1] little is known about the regiochemistry of additions to [70]fullerene, especially when the addends are many and large.

For [60]fullerene, the patterns which apply to cycloadditions, reduction and addition of bulky addends such as bromine and chlorine differ.[2] Thus dipoles, dienes and transition metals add across a 1,2-bond, and in turn across octahedral equivalents,[1,3] whilst hydrogenation can occur across numerous adjacent high-order bonds.[4,5] Bromination follows two major patterns: in $C_{60}Br_6$ two bromines are adjacent,[6] whereas in $C_{60}Br_8$ the bromines display a 1,3- or 1,4-relationship;[6] the latter pattern is found also in $C_{60}Br_{24}$.[7] Chlorination with ICl produces $C_{60}Cl_6$ (isostructural with $C_{60}Br_6$).[8]

Iridium adds to [70]fullerene across the 1,2-bond[9] (for revised and contiguous numbering see Fig. 1), which is also the most reactive towards hydrogenation. Further reduction takes place across the 5,6-bond, but mainly at bonds equivalent to the 1,2-bond, giving *e.g.* the 1,2,3,4- and 1,2,5,6-tetrahydro derivatives.[4,5] Addition of pentamethylcyclopentadiene occurs primarily across the 1,2-bond.[10] Up to ten benzynes can be added, but their locations are not known.[11] Nitrile oxides cycloadd to the 1,2- and 5,6-bonds to give three isomeric isoxazolines.[12] Finally, photochemically-activated cycloaddition of disilirane is said to take place across the 20,21-bond (e,e-carbons)[13] of the equatorial belt.[14] However, calculations[15] predict preferable addition across C(7)–C(23) (d,d′-carbons) of the [70]fullerene waist. The product from this (C_2 symmetry) would account for the observed ^1H NMR data, especially the multiplicity of aromatic proton and methyl signals (*cf.* ref. 14).

We now report the reaction of iodine monochloride with a benzene solution of [70]fullerene, which produces an entirely new addition pattern. Preparative details will be given in a full paper. The solid decomposes slowly in air, attributed to instability arising from the adjacent and eclipsed chlorines; $C_{60}Br_6$ (with adjacent bromines) is likewise unstable. Some spectroscopic details for $C_{70}Cl_{10}$ are: IR (KBr, Fig. 2) ν/cm^{-1} 1456, 1430, 1206, 1159, 1105, 1076, 1060, 1040, 1034, 897, 832, 806, 801, 790, 767, 759, 746, 721, 714, 678, 663, 621, 603, 586, 561, 527, 508, 468, 423; UV (cyclohexane, Fig. 3) λ_{max}/nm 222.9, 323.5, 436.4, 484.1.

The 32 lines in the sp^2 region of the ^{13}C NMR spectrum (Table 1; 4 are of half intensity) are mostly *ca.* 3 ppm downfield compared with those in [70]fullerene.[13] There are 5 lines in the sp^3 region (all of the same intensity): the molecule has C_s symmetry, and must have ten addends. Addition of chlorine pairs along the longitudinal axis in the pattern found in $C_{60}Br_{24}$,[16] would give the correct pattern in the sp^2 region (there are only two ways of doing this without introducing additional symmetry, Fig. 1). However, either two or three of the on-axis carbons (depending upon the structures considered) would be flanked by carbons bearing chlorine, so the signals should be well downfield. Also, there is no reason for the reaction to stop once ten chlorines have been added: fourteen should be added.[16] Clearly, some other structure must be sought.

One line in the sp^3 region is much more downfield (δ 71.52) than the others, indicating two adjacent chlorines. In $C_{60}Cl_6$ the resonances for the carbons bearing adjacent chlorines (δ 69.4 and 66.5) are also downfield from the others.[10] The adjacency is further supported by restricted phenyl rotation in $C_{70}Ph_{10}$.[17] These data rule out either of the possibilities in Fig. 1.

Given that $C_{70}Cl_{10}$ contains only one plane of symmetry, addition *must* occur around the waist of the molecule. Addition across each of the bonds equivalent to the 20,21-bond (24,25-,

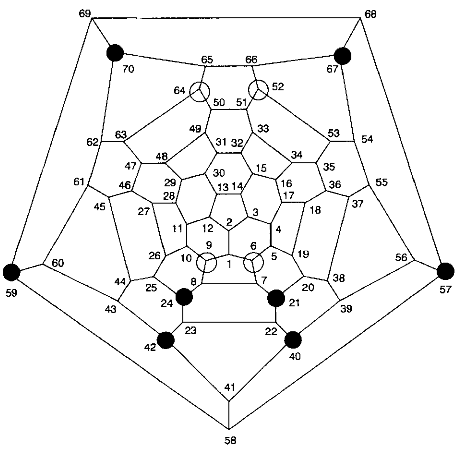

Fig. 1 Revised (contiguous) numbering for [70]fullerene. Two dispositions of chlorines are shown which would give the correct number of NMR lines but which are ruled out by the positions of the resonances. (Open circles show alternative locations for the fifth chlorine pair.)

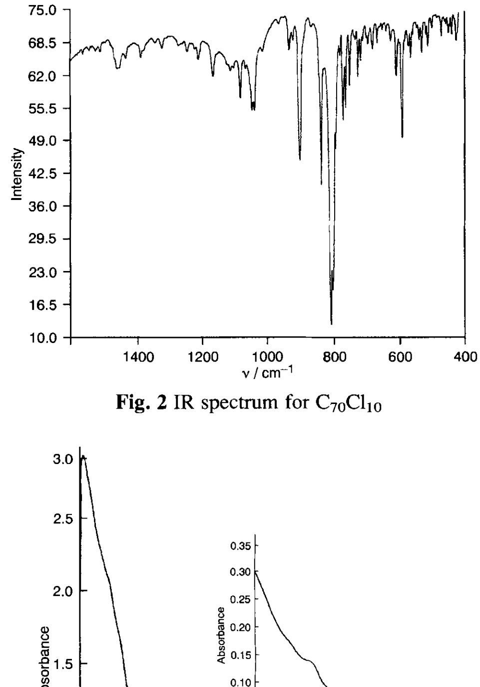

Fig. 2 IR spectrum for $C_{70}Cl_{10}$

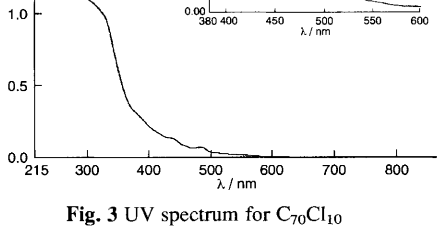

Fig. 3 UV spectrum for $C_{70}Cl_{10}$

35,56-, 46,47- and 50,51-bonds) would give too many symmetry planes, and five pairs of adjacent chlorines which would introduce great strain. One structure, (Fig. 4) however, has very attractive features:

(i) The halogens are all *para* to each other and are thus well separated except for the adjacent pair. This an important aspect discussed further below.

(ii) The structure conforms exactly to the observed NMR spectrum.

(iii) The molecule is unique for a halogenated fullerene in having no double bonds in pentagons (an important feature governing fullerene stability).[18] This appears to be the driving force for the pattern observed. [By contrast, alternative additions along the longitudinal axis (Fig. 1) would introduce double bonds into several pentagons.]

(iv) The proposed structure has no less than four pairs of additions [C(19)–C(37), C(26)–C(45), C(33)–C(53), C(49)–C(63)] each in the low-energy disposition predicted by Cahill and coworkers.[15] This suggests that disilirane may also add to [70]fullerene across C(7)–C(23) [rather than C(20)–C(21)] as noted above.

Table 1 ^{13}C NMR shifts for $C_{70}Cl_{10}$ ($CDCl_3$ lock signal) with relative intensities and provisional assignments

δ	Intensity	Assignment	δ	Intensity	Assignment
153.43	2.08	C(2)	146.96	5.65	
153.34	5.12		146.18	5.67	
152.45	2.33	C(58)	146.03	5.88	
151.84	5.56		145.99	5.61	
151.62	5.19		145.72	5.56	
151.4222	9.78		143.41	6.21	
151.4205			141.60	6.59	
151.31	5.32		139.05	3.81	C(41)
151.27	5.38		136.62	6.84	
150.87	5.24		136.41	7.08	
150.48	5.19		135.62	6.92	
150.46	5.44		134.67	7.36	
148.987	4.97		133.50	7.05	
148.982	3.19	C(1)	71.52	6.40	C(7)/C(8)
148.75	5.39		58.98	5.79	
148.11	5.64		58.58	5.89	
147.70	5.75		58.39	6.97	
147.66	7.19		58.37	6.67	
147.65	6.28				

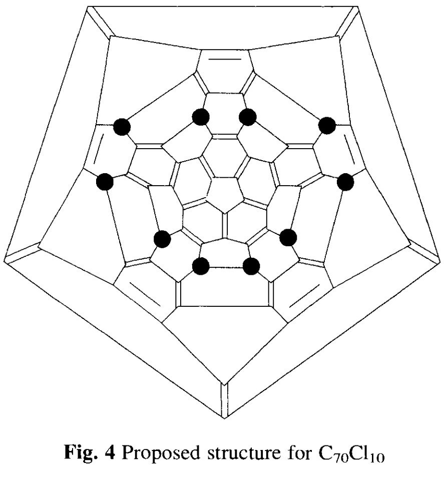

Fig. 4 Proposed structure for $C_{70}Cl_{10}$

(v) In [70]fullerene, the carbons corresponding to those on the symmetry axis resonate at δ 150.07 and 146.82, the former being due to those in the cap pentagon. In the chloro derivative, signals for the carbons on the symmetry axis appear at δ 153.43, 152.45, 148.99 and 139.05. It is reasonable to conjecture that the first two of these are due to the carbons in the axial pentagonal rings, *i.e.* C(2) and C(58), and that the resonance at δ 148.99 is due to C(1) which is near to two chlorine atoms, leaving the resonance at δ 139.05 attributable to C(41). Although this is upfield from the corresponding value in the parent fullerene, the same is true of many of the resonances in $C_{60}Cl_6$.

One other very similar structure [having adjacent chlorines on C(22) and C(23) rather than C(7) and C(8)] could generate the same NMR spectrum and also has no double bonds in pentagons; these two possibilities cannot be distinguished at present. Other arrangements are inconsistent with NOE data obtained on the phenyl derivatives and require unfavourable dispositions of double bonds.

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