

Theoretical characterisation of $C_{70}Cl_{10}$: the rôle of 1,4-addition across hexagonal rings

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Four isomeric structures of decachloro[70]fullerene are compatible with the ^{13}C NMR spectrum and qualitative stability rules; explicit calculation at the semi-empirical level shows the most stable isomer to be that which maximises the number of 1,4-chlorine additions whilst excluding double bonds from pentagons.

Recently, Birkett *et al.*¹ reported the chlorination of [70]-fullerene with a solution of iodine monochloride in benzene. The reaction was carried out under reflux for 20 min and gave decachloro[70]fullerene in quantitative yield; the solid product decomposes slowly in air suggesting the presence of chlorine on at least two adjacent carbon atoms. Further evidence for the structure was obtained from the ^{13}C NMR spectrum which has 32 lines in the sp^2 region (4 of half intensity) and 5 in the sp^3 region; the molecule therefore has C_s symmetry (no other group is compatible) with 33 pairs and 4 unique carbon atoms and 10 addends occurring as 5 symmetry-equivalent pairs. The adjacency of a pair of chlorine addends is confirmed by a single, markedly downfield signal at $\delta = 71.52$. Two structures were suggested (ref. 1, Fig. 4) which are consistent with the ^{13}C NMR evidence and which have two desirable properties, *viz.* that they could arise by consecutive 1,4-addition across hexagons² (more stable than 1,2-addition for addends with larger steric requirements than hydrogen) and that double bonds are excluded from pentagons.³ On the experimental evidence alone, these structures are indistinguishable. It is therefore of interest to investigate whether other structures are also consistent with the evidence, and further, to determine the most stable structure for $C_{70}Cl_{10}$ by calculation of relative energies.

To identify plausible structures for $C_{70}Cl_{10}$, the treatment of ref. 1 is formalised as follows. We seek those addition patterns that (a) are compatible with the ^{13}C NMR spectrum in having C_s symmetry and all sp^3 sites in mirror pairs, (b) have no double bonds in pentagons, and (c) also have a minimal n_{adj} (the number of adjacent pairs of chlorine atoms) compatible with (b). It is known¹ that for two structures (a) and (b) can be satisfied with $n_{adj} = 1$, so that the minimal number of adjacencies is either 1 or 0, but are there other candidates obeying the three criteria? Exactly two more exist, as demonstrated by the following argument.

$C_{70}Cl_{10}$ has 30 double and 75 single CC bonds, with Cl positions implicitly defined by junctions of three single bonds. The bonding pattern is conveniently illustrated as a Schlegel diagram (Fig. 1). The preserved mirror plane is taken to be one of the five vertical planes of the original C_{70} cage [choice of the horizontal plane leads rapidly to inconsistency with either (a) or (b)]. Requirement (b) fixes 60 single bonds along the pentagon edges, and avoidance of $n_{adj} = 2$ in (c) fixes 16 bonds *exo* to the pentagons as 8 mirror pairs of doubles (the unmarked edges in Fig. 1). Avoidance of unique sp^3 sites fixes the two bonds (α) in the plane as double, leaving at this stage 27 edges (three unique and 12 mirror pairs) to be assigned to 12 double and 15 single bonds. Parity requires that either one or all of the unique bonds

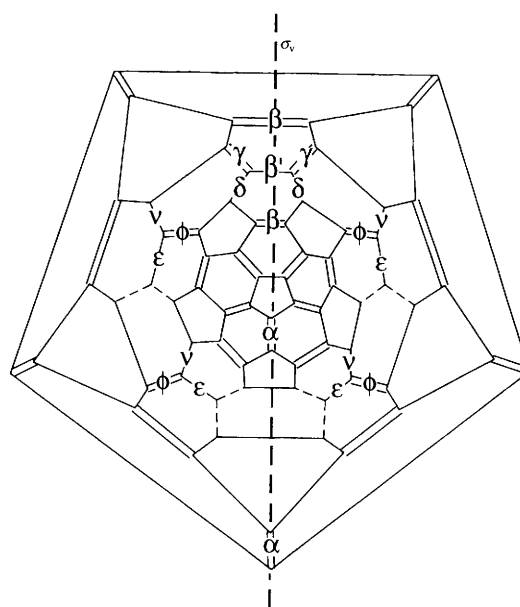


Fig. 1 Schlegel diagram of $C_{70}Cl_{10}$ cages. The full single and double bonds are fixed by criteria (b) and (c) and then the orders of the marked bonds α to v are deduced as described in the text. The 8 dotted bonds include 4 doubles, which can be chosen in only 4 distinct ways to comply with C_s symmetry.

(β) should be single, but the only choice that avoids $n_{adj} > 1$ is to make the central bond of the set (β') single and the others double. This choice fixes a pair each of double (γ) and single (δ) bonds, leaving 10 pairs of edges (ϵ and neighbours) to be assigned to 4 pairs of doubles and 6 of singles. The central (ϵ) edge of each motif must be single if all doubles are to be accommodated; its neighbour ϕ must be double to avoid $n_{adj} \geq 2$ and hence v must be single. Distribution of one double and one single bond over the two remaining neighbours of ϵ leads to four distinct isomers of $C_{70}Cl_{10}$ that obey (a), (b) and (c) and have only one pair of adjacent sp^3 carbon atoms. Two of these were given in ref. 1, two are new. All four are illustrated in Fig. 2 where the C_{70} spheroid is displayed as if cut open along half of the mirror seam. All four are compatible with the experimental evidence.

To distinguish between the four candidates A–D, the standard enthalpies of formation were calculated for fully optimised structures using the semi-empirical MNDO method (MOPAC, Version 6.00⁴). For comparison, structures and energies were also calculated for two isomers of $C_{70}Cl_{10}$

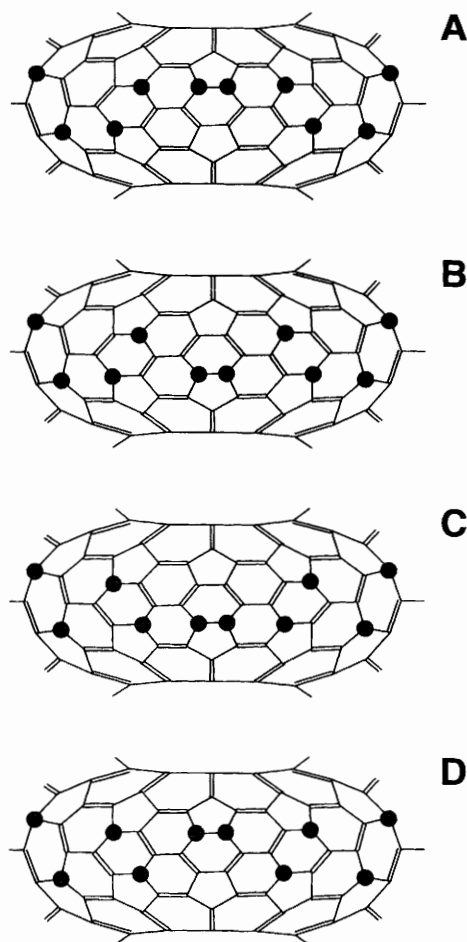


Fig. 2 The structures of the four possible isomers A–D that fulfil the experimental and theoretical criteria. In C_{70} itself the MNDO bond lengths are all 1.40 ± 0.01 Å, showing less variation than shown in the experimental (neutron diffraction⁸) structure. The computed variation is greater in $C_{70}Cl_{10}$. In isomer A C–C bond lengths (MNDO) are 1.63 Å (for the unique sp^3 – sp^3 bond), 1.54 ± 0.01 Å (for the 28 sp^3 – sp^2 bonds), 1.44–1.49 Å (for the formal single bonds in which neither carbon bears a chlorine). Hexagons with 1,4-addends have either two double bonds in the range 1.40–1.41 Å or one short double bond (1.38 Å). Double bonds from the polar pentagons are also in the range 1.39–1.41 Å. The sp^3 carbon atoms stand proud of the surface inducing non-planarity in the equatorial hexagons which is seen as deviations of 15–20° from the ideal torsional angles of 180°.

(E and F) also discussed in ref. 1, and for a hypothetical D_{5h} structure in which all ten equatorial carbons bear a chlorine. The results are listed in Table 1.

Isomer A is more stable than its nearest rival within the set of four by 73 kJ mol^{-1} , a convincing margin that is likely to survive improvement of the theoretical treatment. The high energies of E and F illustrate the penalty associated with forcing double bonds into pentagons; G shows the high cost of multiple chlorine adjacencies.

The order of stabilities $A > B \sim C > D$ can be rationalised by counting the (1,4) pairings of addends: A has 9 such pairs, B and C have 7 and D has only 5; these numbers also run parallel to the counts of formal benzene rings in the structures A–D

Table 1 Calculated enthalpies of formation of isomers of decachloro[70]fullerene. A–D (see Fig. 2) are the only candidates compatible with the experimental ^{13}C NMR spectrum that exclude double bonds from pentagons and minimise Cl adjacencies. E and F were discussed and discarded in ref. 1 because they have double bonds in pentagons. G has too high a symmetry (D_{5h}) but is included to show the high cost of Cl adjacency

Isomer	$E/\text{kJ mol}^{-1}$
A	2949
B	3022
C	3032
D	3105
E	3268
F	3209
G	3645

i.e. 12, 10, 10, 8, respectively. Calculations by Henderson *et al.*² indicate that the favoured isomers of $C_{60}H_2$ and $C_{70}H_2$ are those arising from 1,2-addition across a 6:6-ring fusion or a 1,4-addition across a hexagon. They suggest that for an addend with a greater steric requirement than hydrogen, 1,4-addition may be favoured and this is supported by calculations on halo[60]fullerenes.⁵ C_{70} differs from C_{60} in that multiple, sterically favourable, 1,4-addition to the equatorial hexagons can be achieved without forcing double bonds into pentagons; in C_{60} all hexagons have three pentagonal neighbours and the characterised halofullerenes $C_{60}Br_6$, $C_{60}Br_8$ ⁶ and $C_{60}Br_{24}$ ⁷ all have some forced double bonds in pentagons. Maximisation of the number of 1,4-additions subject to the exclusion of double bonds from pentagons may be a general pattern in C_{70} halogenation. Under the conditions of the experiment (refluxing benzene) halogen shifts are known to occur (*e.g.* 1,2-dibromobut-3-ene rearranges to 1,4-dibromobut-2-ene at 60 °C) and hence it is reasonable to anticipate that the isomer with the greatest thermodynamic stability will dominate the product. Our conclusion is that this is isomer A of decachloro[70]-fullerene.

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