PERKIN 2 COMMUNICATION

Structural characterisation of $C_{60}H_{18}$; a C_{3v} symmetry crown

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$C_{60}H_{18}$ has been shown by ^1H NMR spectroscopy to be 1,2,3,4,8,9,10,16,17,18,22,23,24,36,37,38,39,40-octadecahydro[60]fullerene, a crown-shaped molecule with C_{3v} symmetry, and a sub-structure of T $C_{60}H_{36}$; both hydride structures are derived from multiple addition of 6 H in a constant pattern governed by the semi-aromaticity of [60]fullerene.

Although the first derivatives of [60]fullerene to be described were $C_{60}H_{36}$ and $C_{60}H_{18}$ [1] their structures have proved elusive, due to rapid light-catalysed oxidative degradation which occurs, especially in solution.[2] For $C_{60}H_{36}$, ^1H NMR spectra indicated that either a mixture of isomers or other hydrogenated components (resulting from degradation) were present.[1] The discovery that fluorination parallels hydrogenation, with $C_{60}F_{36}$ and $C_{60}F_{18}$ being high stability derivatives,[3] suggested an alternative means of structural determination. The subsequent preparation of pure $C_{60}F_{36}$ and characterisation by ^{19}F NMR showed that the T isomer (predicted to be the most stable)[4–6] was the most abundant among the four isomers present.[7]

Hydrogenation of solid [60]fullerene at high temperature and high pressure permits greater control over the extent of reaction, whilst the absence of solvent reduces subsequent manipulation and the risk of attendant oxidation (*cf.* ref. 2). Products that accompany increasing reduction of [60]fullerene in this way are coloured brown, brick-red ($C_{60}H_{18}$), deep orange and pale lemon-white ($C_{60}H_{36}$). A sample of $C_{60}H_{18}$ thus produced, was provided by M.E.R., Tucson, Arizona. The EI mass spectrum (Fig. 1) showed it to consist mainly of $C_{60}H_{18}$, together with traces of mono-epoxide and $C_{60}H_{36}$. This result was confirmed by HPLC (Fig. 2), which indicated that very minor amounts of $C_{60}H_x$ (x = 18–36) were present; under the conditions used, $C_{60}H_{18}$ has the same retention time as [60]fullerene. A sample left in air for 12 months contained a considerable quantity of epoxides.

The IR spectral bands (Fig. 3) appear at 2920, 2847, 1610, 1471, 1272, 1243, 1220, 1201, 1179, 601, 574, 544, 535, 502, 484, 476, 463 and 404 cm^{-1}. The UV–VIS spectrum gave bands at $\lambda(CH_2Cl_2)$ 232, 234 (sh), 236 (sh), 238 (sh), 261, 305, 323 (sh), 328 (sh), 330 (sh), 332 (sh), 338 (sh), 341, 343 (sh) and 391 (sh); (toluene) 414, 428, 446, 461, 476 (all shoulders) nm. The oxidative degradation of hydrogenated fullerenes is UV-

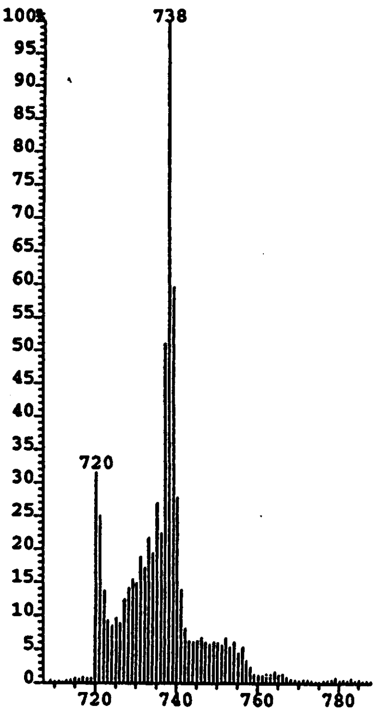


Fig. 1 EI mass spectrum of $C_{60}H_{18}$

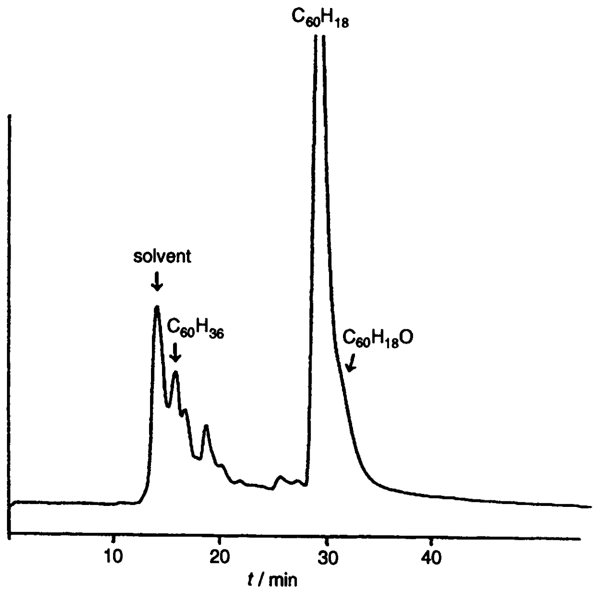


Fig. 2 HPLC trace (Cosmosil column, toluene eluent, 0.25 ml min^{-1}) for $C_{60}H_{18}$

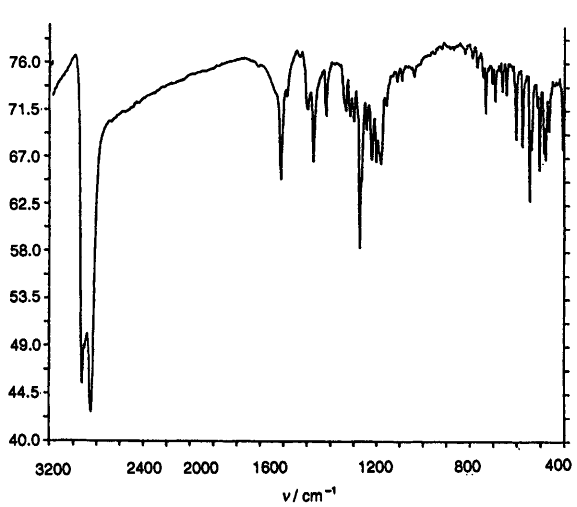


Fig. 3 IR spectrum (KBr) of $C_{60}H_{18}$

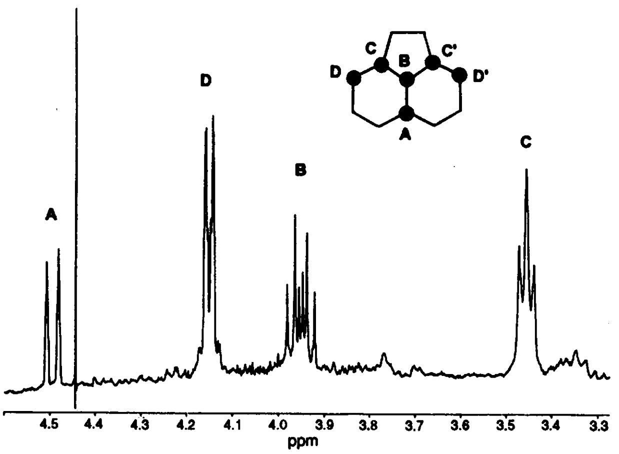


Fig. 4 ^{1}H NMR spectrum (500 MHz, RT) of $C_{60}H_{18}$ with structural motif (inset)

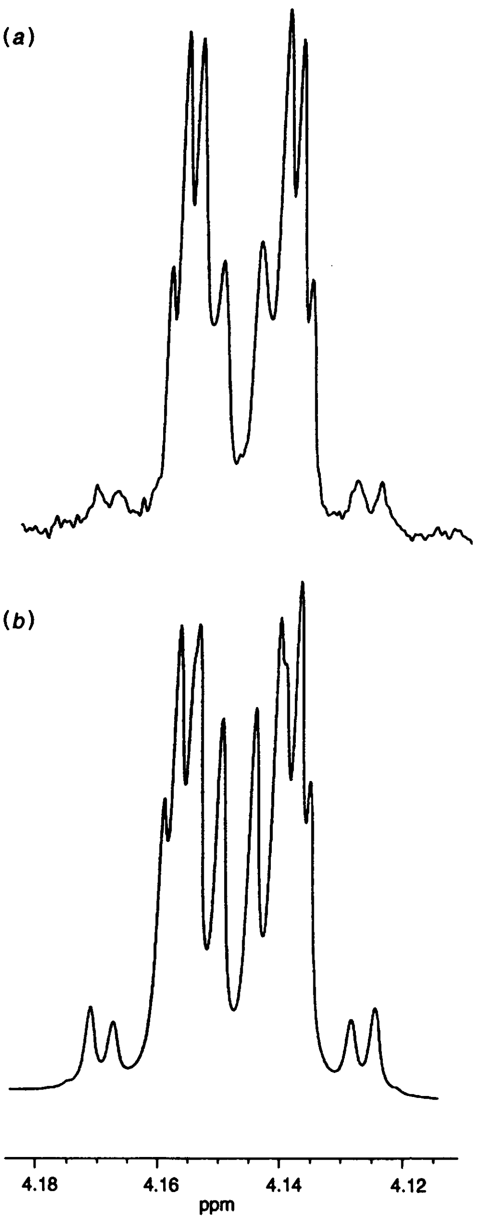


Fig. 5 Expanded spectrum at δ 4.15 with (*a*) selective decoupling at δ 4.49 and (*b*) simulated spectrum

catalysed,[2] and it was noticeable that the dichloromethane solution of $C_{60}H_{18}$ quickly became cloudy due to oxidation, after the spectrum had been recorded.

The 18 protons of $C_{60}H_{18}$ afford the spin system AA'A"BB'B"CC'C"C'''C''''C'''''DD'D"D'''D''''D'''''. It is not practical to analyse this spin system as a whole, but fortunately the problem is simplified, first by the wide separation of the chemical shifts and secondly by the symmetry that reduces the system to three groups each of six protons. The six protons give rise to a ^{1}H NMR spectrum (Fig. 4, CS_2, $CDCl_3$ lock) comprising four bands in a 1:2:1:2 ratio (at δ 4.49, d, *J* 12.8 Hz; 4.15, m, *J* 9.9 Hz; 3.95, d of t, *J* 8.3 and 12.8 Hz; 3.45, m, *J* 8.3 and 9.9 Hz). This is consistent only with the motif shown on the spectrum, in which the hydrogens A, B, C and D, are identified. The assignment is based on the multiplet patterns and the size of the couplings. [The singlet at δ 4.44, the intensity of which varied with the sample, is due to an unidentified impurity; a background hump in the spectrum between δ 2.7 and 4.5, is assigned to minor hydrogenated species, notably $C_{60}H_{36}$ (*cf.* ref. 2) as indicated by HPLC.]

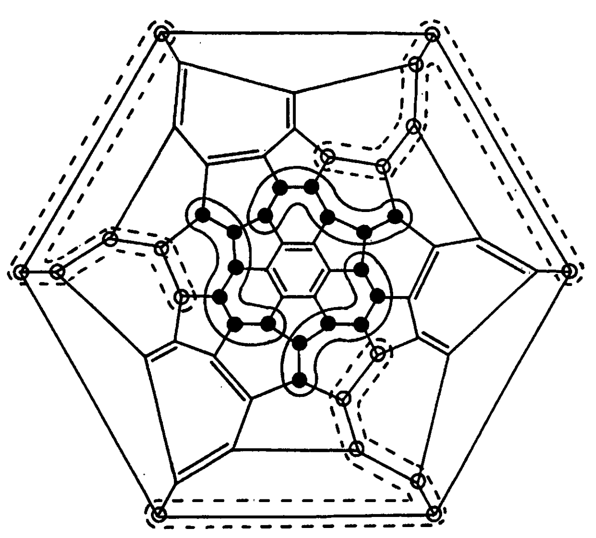
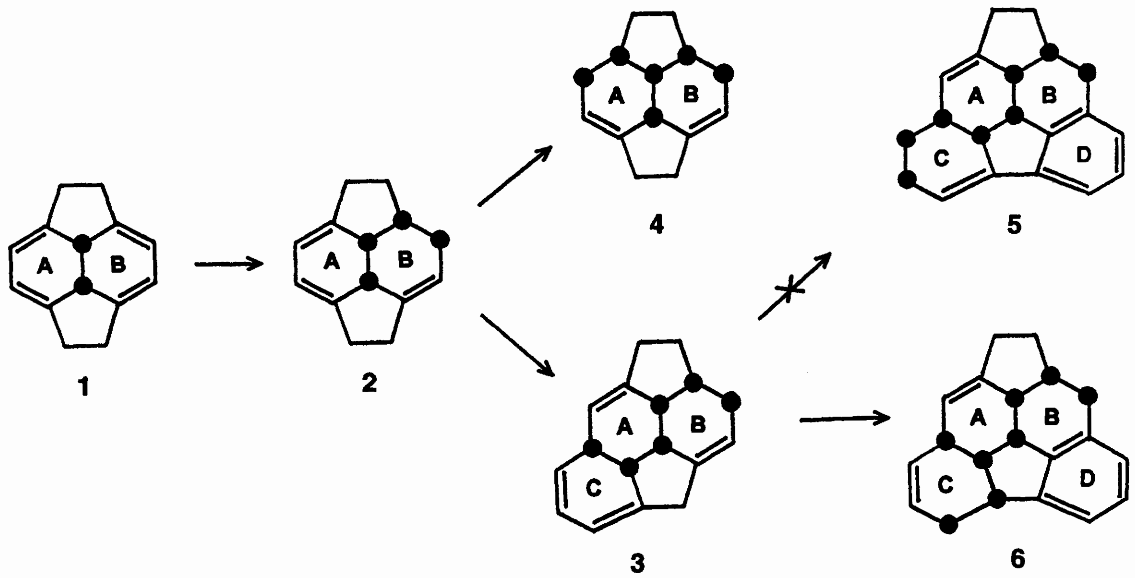


Fig. 6 Schlegel diagram of: $C_{60}H_{18}$ (filled circles) and $C_{60}H_{36}$ (filled plus open circles); encirclement indicates the constant 6 H addition pattern that can produce both structures

Closer inspection of multiplet A by resolution enhancement revealed that each branch of the doublet was a pseudo-quintet, due to long-range coupling of 2.2 Hz to the D protons, as established by a selective decoupling experiment. The pseudo-quintet structure arises through five-bond coupling to two D protons, each having large (>2.2 Hz) couplings to another chemically equivalent D proton, thus giving rise to a virtual coupling to the A proton. This observation proves that the six proton motifs must lie directly adjacent to each other around the cage.

This conclusion is further supported by an analysis of the D multiplet, which was first simplified by selective decoupling of the A multiplet to give the spectrum shown in Fig. 5. Given the wide shift difference between the C and B multiplets, multiplet D can now be treated as the AA' part of an AA'BB' spin system. The result of this analysis is shown in Fig. 5 and gives the values $\delta_A = 4.15$, $\delta_B = 3.45$, $J_{AB} = 9.9$ Hz, $J_{AB'} = 0$ Hz, $J_{AA'} = 8.4$ Hz, $J_{BB'} = 0$ Hz. Again the observation of the 8.4 Hz coupling for $J_{AA'}$ (which corresponds to couplings between D-type atoms of adjacent motifs), proves the motifs to be adjacent to each other on the cage.

Only one structure for $C_{60}H_{18}$ is thus possible, and is produced solely by addition across bonds of high π-bond order. This is the C_{3v}-symmetry crown structure (Fig. 6, filled circles) predicted by calculations to be particularly stable.[8] Notably, C_{3v} $C_{60}H_{18}$ is a sub-structure of *T* $C_{60}H_{36}$ (Fig. 6, open and filled circles). Moreover, both structures can be formed by repetition of a single 6 H addition pattern as shown in Fig. 6 (outlined groups). This pattern can be shown to arise logically from consideration of the aromaticity of [60]fullerene, a subject of considerable discussion (*e.g.* ref. 9). Whilst fullerenes behave



Scheme 1 Proposed addition pathway leading ultimately to $C_{60}H_{18}$ (and $C_{60}H_{36}$)

largely as alkenes,[5] our work on hydrogenation[10] shows that significant delocalisation of electrons occurs. Thus whereas further hydrogenation of 1,2-dihydro[60]fullerene (sub-structure **1**, Scheme 1) takes place across each of the eight distinct interpentagonal double bonds, addition occurs mainly (28%) across the 3,4-position (50% in the case of hydrogenation *via* diborane[11]). This gives the most eclipse-hindered isomer (**2**, Scheme 1) and must be due to increased localisation of the electrons in the adjacent hexagons as a result of the first addition. Clearly, this situation can only arise if significant delocalisation is present at the outset. The same explanation accounts for oxygen being located across the 1,2- and 3,4-positions in $C_{60}O_2$.[12] Very recent *ab initio* calculations also predict that the 1,2,3,4-isomer should be the most stable one.[13]

Further addition could then take place across the double bond remaining in one hexagon (ring B), but this will produce some eclipsing strain (predicted to be unfavourable);[8,13] in general it appears (see below) that eclipsing strain can be tolerated only if there is an accompanying increase in aromaticity. Thus the preferential addition in ring A gives rise to either of the sub-structures **3** and **4** (Scheme 1), both of which are predicted [13] to be particularly stable; three-fold repetition of either ultimately produces $C_{60}H_{18}$. Motif **3** is the least hindered and the most stable, and further reduction will take place preferentially in ring C to give either **5** or **6**. Continuation of the former pattern results ultimately in circumnavigation of the cage in a zig-zag manner to give $C_{60}H_{20}$ which contains no aromatic rings, and which models have shown to be very highly strained. By contrast, the alternative **6** ultimately leads to $C_{60}H_{18}$ in which the hexagonal ring D becomes aromatic through the increased delocalisation that becomes possible once adjacent pentagons have reduced angle strain arising from addition to them.

As can be seen from Fig. 6, six-fold repetition of the addition pattern **3** (Scheme 1) leads to *T* symmetry $C_{60}H_{36}$ (in which the destabilisation arising from eclipsing strain in the four fully reduced hexagons is offset by the four highly delocalised aromatic rings).

Whilst the pathway derived from 1,2,3,4-tetrahydro[60]fullerene appears to be the dominant one, it is interesting to note that six of the other seven possible tetrahydro isomers also fit into the C_{3v} $C_{60}H_{18}$ structure. Hence pathways derived from them and which likewise do not require rearrangement, are feasible. Only the 1,2,55,60-isomer (which constituted a mere 4% of the product in hydrogenation by diimide) [10] is incapable of leading directly to $C_{60}H_{18}$.

Only one other isomer involving the $C_{60}H_{18}$ motif appears to be possible for $C_{60}H_{36}$, *i.e.* that involving two motifs centred on opposite poles. This would produce a D_{3d} structure with an equatorial ring of isolated double bonds and a similar ^{1}H NMR spectrum to that of $C_{60}H_{18}$, but evidence for this structure has so far not been obtained.

Finally, we comment on the singlet at δ 4.44. If this is due to a symmetrical hydrogenated [60]fullerene, it must contain more than four hydrogens, since the resonance appears more upfield than those due to $C_{60}H_4$ isomers.[2] Structures consistent with the symmetry requirements are either $C_{60}H_6$ with hydrogens *in* one hexagonal ring or $C_{60}H_6$ with hydrogens *exocyclic* to a hexagonal ring. (Fullerenes with low hydrogen contents are unstable towards our mass spectrometry conditions and so would not appear in the spectrum.) The former structure contains no aromatic rings, and the eclipsed hydrogens cause instability.[8,13] The latter contains a ring rendered aromatic by the addition in the adjacent pentagons, and has 1,4-addition across hexagons. This latter feature also occurs in the formation of $C_{60}Cl_6$ (though the overall structure is quite different) and in $C_{70}Cl_{10}$.[14] Such a structure for $C_{60}H_6$, could, if followed by six-fold addition across the appropriate interpentagonal bonds, lead also to $C_{60}H_{18}$. However, this pathway would seem to be improbable in view of the dominant formation of precursor 1,2,3,4-tetrahydro[60]fullerene as noted above.

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