$C_{70}H_{36}$ is Probably an Aromatic Compound

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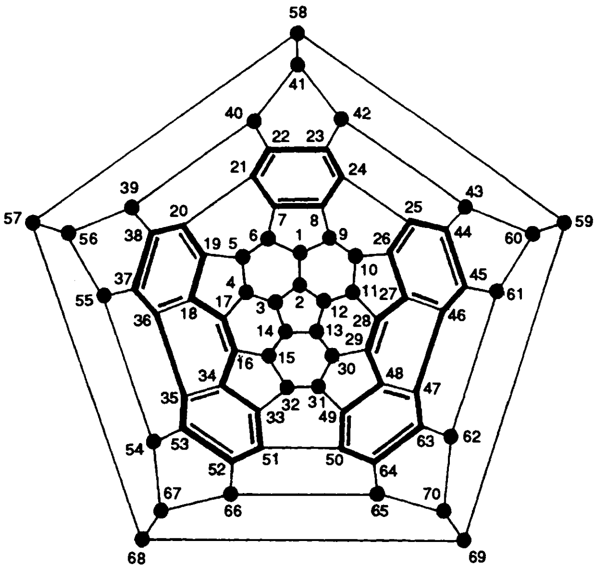
Three isomers of $C_{70}H_{36}$ can in principle exist that have around the equator of the molecule either two phenanthrenoid rings and one benzenoid ring (two isomers), or one phenanthrenoid ring and two naphthalenoid rings. Their ensuing aromatic stability accounts for the observed inhibition of further reduction. Formation of $C_{70}H_{70}$ from $C_{70}H_{36}$ should be harder than formation of $C_{60}H_{60}$ from $C_{60}H_{36}$ because a greater loss of resonance is involved.

There have been many recent reports concerning the formation of $C_{70}H_{36}$,[1-4] and structures for this species, based on calculations for selected isomers, have been proposed.[2,3] The selection was based on the assumption that one double bond would be located in each of the twelve pentagonal rings of [70]fullerene, a similar arrangement (now known not to give the most stable isomer) having been proposed earlier[5] for $C_{60}H_{36}$. However, these structures for $C_{70}H_{36}$ are unable to account for the cessation of reduction once 36 hydrogen atoms have been added. We now propose three alternative structures which not only have features that account for this phenomenon, but also predict the observed formation of $C_{70}H_{38}$ and $C_{70}H_{40}$ under forcing conditions.[4]

1. Both we,[6] and Fowler *et al.*[7] have emphasized that formation of many fullerene derivatives is governed by the increase in aromaticity that results; addition at the octahedral sites is a prime example. We proposed that the structure of $C_{60}H_{36}$ is tetrahedral (T symmetry) because this contains four benzenoid rings, and the consequent aromatic stability then accounts for the inhibition of further reduction.[6] (*N.B.* Electron delocalisation in the hexagonal rings of [60]fullerene is poor because the resultant bond shortening in the three adjacent pentagonal rings will increase strain.[8] However, once these latter become partly reduced the strain effects are reduced, and greater delocalisation can then occur.) Subsequent calculations have all confirmed that this conjugated structure should be the most stable one.[3,9-11] It is also significant that the four hydrogen atoms of any of the eight $C_{60}H_4$ isomers which can, and are known[12] to exist, can be fitted into the T isomer for $C_{60}H_{36}$. Hence further reduction of these isomers, which constitute the second stage of hydrogenation (the first being formation of 1,2-dihydro[60]fullerene), can lead to the T isomer of $C_{60}H_{36}$ without any rearrangement. $C_{60}H_{36}$ can in principle also be obtained by reduction of octahedral $C_{60}H_{12}$ which is almost certainly along the hydrogenation pathway since octahedral addition is a common feature of the chemistry of [60]fullerene;[6,13] two of the $C_{60}H_4$ isomers are structural precursors of $C_{60}H_{12}$. $C_{60}H_{36}$ is also colourless[14] which is consistent with the proposed structure.

2. Because $C_{60}H_{36}$ can be produced under Birch reduction conditions, it was proposed that it must contain all isolated double bonds, with one in each pentagonal ring.[5] However, the Birch reduction mechanism cannot lead to the proposed structure, the formation of a wholly non-conjugated product is contrary to normal chemical behaviour, $C_{60}H_{36}$ is formed under other reducing conditions,[1,2,14,15] and [60]fullerene structures with double bonds in pentagons are generally unfavourable.[8] Moreover, there is no reason for the reduction to stop once thirty-six hydrogens have been added.

3. Since $C_{70}H_{36}$ is evidently also stable, there must likewise be a reason why reduction tends not to proceed further. Steric crowding is an improbable cause because if (say) 36 hydrogens were the maximum that could be accommodated around [60]fullerene, the maximum for [70]fullerene would be greater. An electronic explanation must be sought, and we suggest that $C_{70}H_{36}$ can have neither isolated double bonds nor, in consequence, double bonds in pentagons unless they are conjugated (which increases the C–C bond length and so reduces strain). Three structures (**I**–**III**) which uniquely satisfy all these requirements are shown in the Schlegel diagrams in Figs. 1–3. (The numbering shown for [70]fullerene supersedes that given provisionally in ref. 16 and has the advantage of being both fully contiguous, and having the most reactive bond numbered 1,2- as in [60]fullerene.) In the Schlegel diagrams, the aromatic moieties are outlined for clarity.



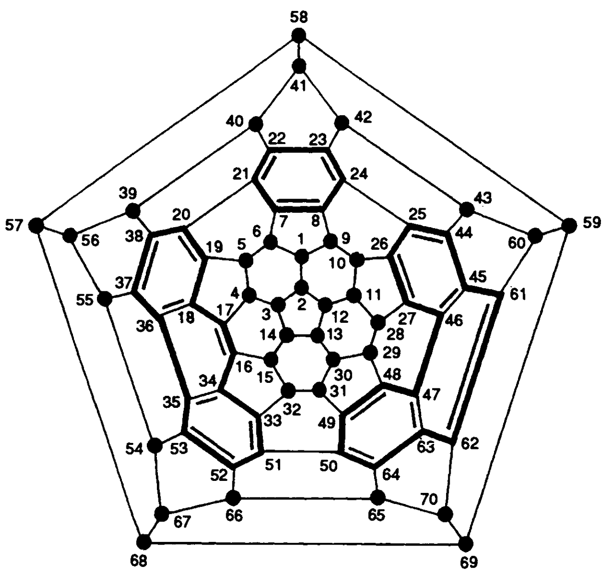
I

Fig. 1 Schlegel diagram for isomer **I** of $C_{70}H_{36}$; filled circles represent sites occupied by hydrogen atoms

Significant features of the proposed structures are as follows.

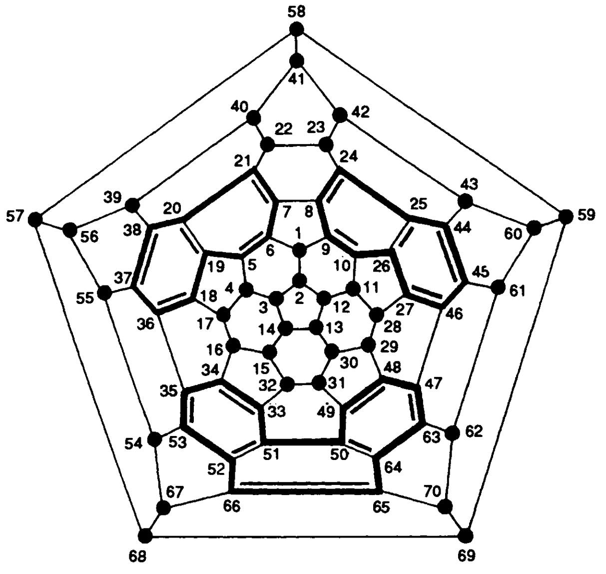
(*i*) Structures **I** and **III** have C_s symmetry. Structure **II** has C_2 symmetry and is the most evenly hydrogenated, having eighteen hydrogens at each end of the molecule.

(*ii*) The resonance energies (HMO calculated, $\beta = 75.3$ kJ mol^{-1}) of the aromatic moieties of structures **I**, **II** and **III** are 1059, 1058 and 1067 kJ mol^{-1}, respectively. These values are considerably greater than the value (900 kJ mol^{-1}) calculated for the structures proposed in the literature (which has a band of five *para*-linked benzenoid rings), and lend strong support to our view that **I**–**III** are much more probable structures. The



II

Fig. 2 Schlegel diagram for isomer **II** of $C_{70}H_{36}$; notation as for Fig. 1



III

Fig. 3 Schlegel diagram for isomer **III** of $C_{70}H_{36}$; notation as for Fig. 1

calculated resonance energies suggest that $C_{70}H_{36}$ consists of a mixture of isomers, with isomer **II** dominant in view of its greater symmetry.

(*iii*) Just as addition across the 9,10-bond of phenanthrene involves a relatively small loss of resonance energy, so addition across the same bond of the phenanthrene moieties in **I**, **II** and **III** results in a relatively small loss of resonance energy, (80 kJ mol^{-1} for each of the C16–C17/C28–C29 bonds in **I** and for the C16–C17/C61–C62 bonds in **II**, and 94 kJ mol^{-1} for the C65–C66 bond in **III**). The model therefore predicts that some formation of $C_{70}H_{38}$, and to a lesser extent $C_{70}H_{40}$ may be detectable, and indeed this is the case.[4]

(*iv*) Non-hydrogenation of bonds C5–C6, C9–C10 and C31–C32 in **I**, C5–C6, C9–C10 and either C31–C32 or C65–C66 in **II**, and C16–C17, C22–C23 and C28–C29 in **III** may give reasonably stable structures (though the number of double bonds in pentagons is increased). $C_{70}H_{34/32/30}$ may therefore be reasonably stable, and it is notable that hydrogenation of [70]fullerene with hydrogen gas under pressure indicated some formation of $C_{70}H_{30}$.[17]

(*v*) Our proposed structures can in principle be attained by reduction of the isomers of $C_{70}H_4$ known to exist.[12]

What Species Should be Formed by Vigorous Reduction?—Vigorous reduction should overcome the energy barrier created by the proposed aromaticity of $C_{60}H_{36}$ and $C_{70}H_{36}$. For the former, once one benzenoid ring undergoes partial addition, then the greater localisation of the two remaining double bonds in that hexagon will facilitate further reduction there. Reduction is likely to occur in sixfold increments leading to $C_{60}H_{42/48/54/60}$, and evidence for $C_{60}H_{42}$ and $C_{60}H_{48}$ has indeed been obtained.[14] For $C_{70}H_{36}$, the next reduction levels should be $C_{70}H_{38}$ and $C_{70}H_{40}$ as described above. For structures **I** and **II** reduction should occur thereafter in sixfold increments as each benzenoid ring is reduced, giving $C_{70}H_{46/52/58/64/70}$ as the reduction levels. For **III**, subsequent addition to each naphthalenoid ring and then each benzenoid ring would give $C_{70}H_{42/46/52/58/64/70}$ as the next levels. Since a greater loss of resonance is required to form $C_{70}H_{70}$ from $C_{70}H_{36}$ (*ca.* 1060 kJ mol^{-1}) than to form $C_{60}H_{60}$ from the proposed structure for $C_{60}H_{36}$ (602 kJ mol^{-1}), we may conjecture that formation of $C_{70}H_{70}$ will be the more difficult.

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