Will Fullerene Compounds $C_{78}X_6$ be Readily Formed?

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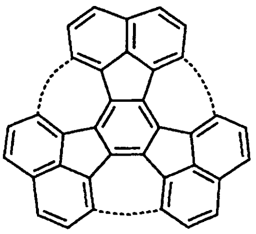
All stable fullerenes contain the C_{36} moiety based on decacyclene, suggesting that addition reactions in which this moiety is retained should be favoured; in particular, $C_{78}X_6$ compounds may be readily formed.

A common feature of stable fullerenes that have either been isolated and characterized,[1,2] or have had their structures inferred[3–5] is that they each contain the C_{36} fragment derived from decacyclene (**1**).



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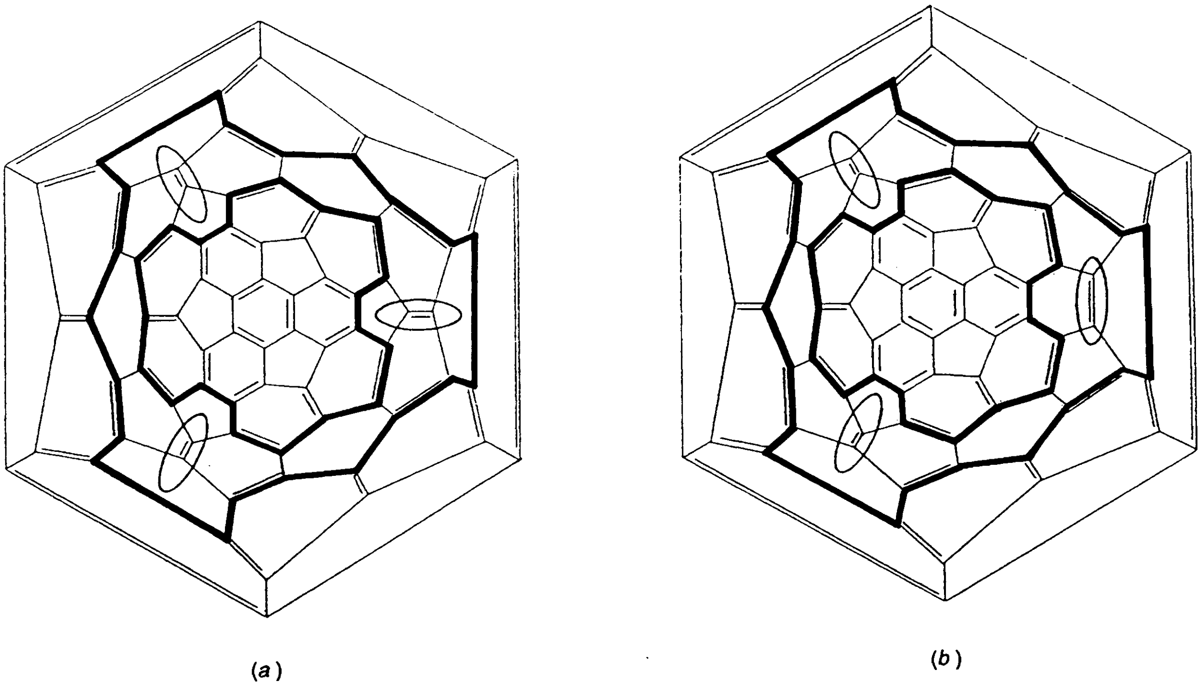
This observation suggests that fullerenes may be synthesized by dehydrogenative ring coupling of decacyclene (readily available) and another aromatic fragment. However, at this time most, if not all, of the associated aromatic fragments are unknown; two decacyclene molecules cannot couple to give the (isolated pentagon) D_{6d} isomer of C_{72}.

The commonality of the decacyclene moiety suggests that it is particularly stable (it contains ten hexagonal rings all of which are benzenoid). It is proposed that reactions of fullerene cages in which the C_{36} fragment is conserved with full retention of aromaticity within the fragment, are likely to give stable products. It turns out that of the two pairs of D_{3h} and C_{2v} isomers of C_{78}, those (one of each) that are predicted by simple Hückel theory to be the most stable appear able to give simple derivatives with minimum loss of aromaticity in the fullerene cage, and full retention of the delocalized integrity of the two C_{36} moieties. Analyses for stable fullerenes of known or inferred structures are as follows.

C_{76}.—The D_2 isomer of C_{76}[2] consists of two C_{36} fragments coupled by four isolated carbons each of which comprises one carbon of a pentagonal ring. It is not possible therefore to form a $C_{76}X_4$ derivative by addition across a bond of high order without substantial bond reorganization within both C_{76} fragments, and corresponding loss of aromaticity. We conclude therefore that compounds $C_{76}X_4$ will be rather unstable.

C_{78}.—In the more stable pair of the D_{3h} and C_{2v} isomers of C_{78}, two decacyclene moieties [bold outline, Figs. 1(*a*), (*b*)] are connected by three pairs of carbon atoms (encircled), themselves joined across a bond predicted[5] to be of high order. Addition across these bonds will thus not disturb the aromaticity of either of the C_{36} fragments. Addition to these molecules at the sites identified seems very probable, and this belief is encouraged by the decrease in reasonance energy (per atom) of 0.0449β and 0.0441β, respectively, for formation of the addition derivatives of the D_{3h} and C_{2v} isomers. This is significantly less than for addition to C_{60} (see below). A comparable addition cannot take place on the D_3 isomer of C_{78}.



(*a*) (*b*)

Fig. 1 D_{3h} and C_{2v} isomers of C_{78}, showing predicted addition sites (encircled), with retention of two decacyclene moieties (bold outline). The isomers are those of each D_{3h} and C_{2v} pair, predicted[3,5] to have the higher stability.

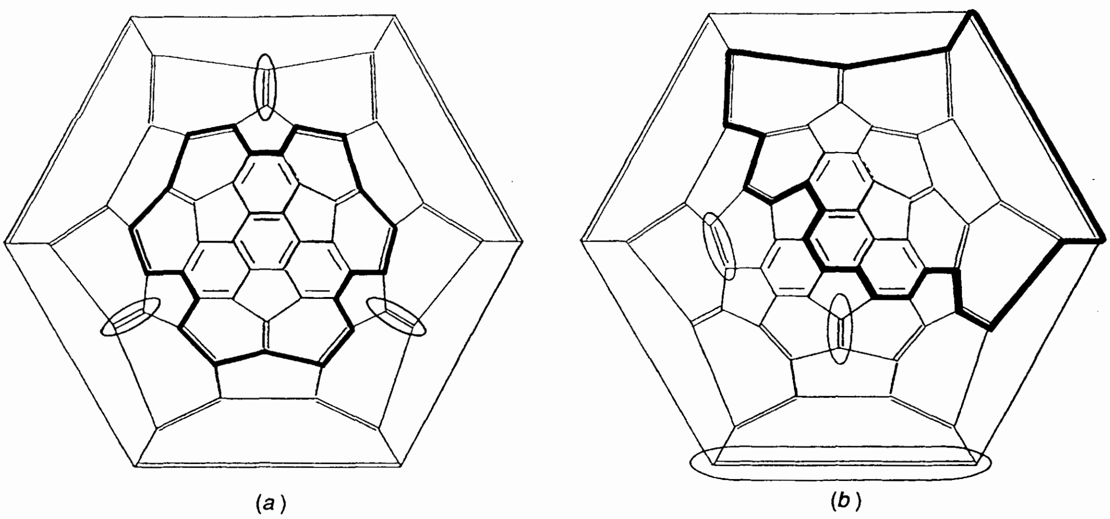


Fig. 2 Alternative modes of addition across three high-order bonds (encircled) of C_{60} with retention of a decacyclene moiety. Each structure has three-fold symmetry.

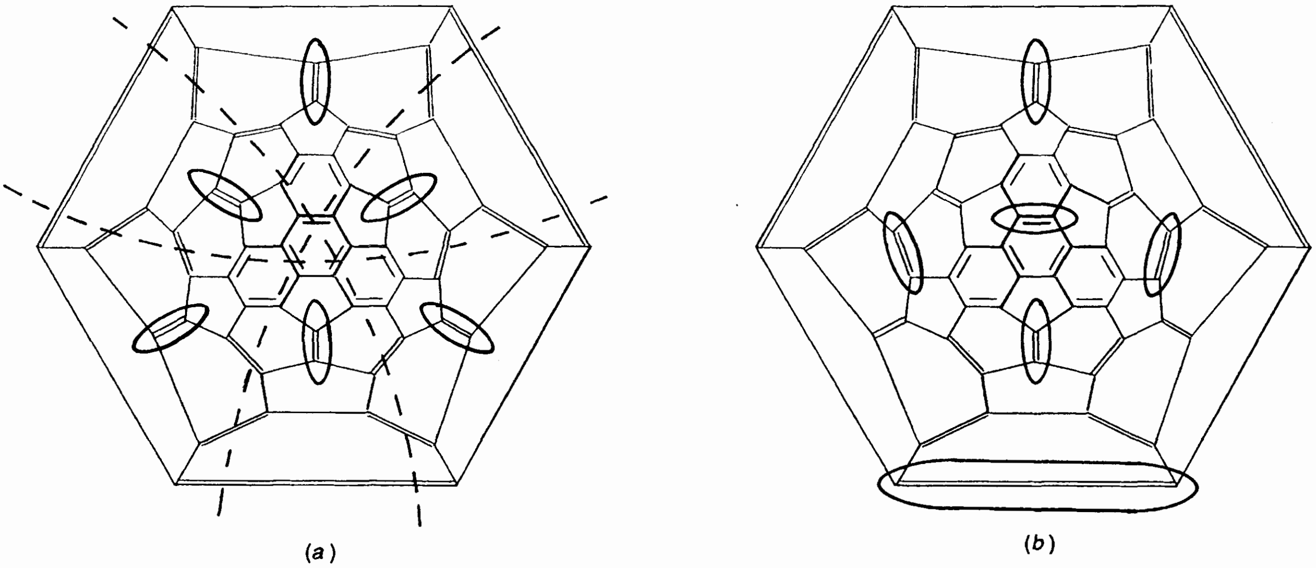


Fig. 3 Alternative modes of addition across six high-order bonds (encircled) of C_{60}. Structure 3(*a*) has three equatorial bands of conjugation. Structure 3(*b*) is the result of octahedral addition.

C_{84}.—The T_d and D_2 isomers of C_{84} are predicted to be the most stable.[4,5] Only the latter can be formed from two decacyclene moieties, and connected by six pairs of carbon atoms situated across bonds predicted to be of high order.[5] Addition without loss of aromaticity of either fragment to give $C_{84}X_{12}$ derivatives is thus possible. However, this will be accompanied by loss of aromaticity in eight out of the twenty-eight benzenoid rings in the original structure, so may occur under relatively forcing conditions.

C_{90}.—The D_{5h} isomer is predicted to be particularly stable.[5] In this, two decacyclene moieties are joined by a fragment containing eighteen carbons situated across nine pairs of bonds predicted to be of high order.[5] Addition to give $C_{30}X_{18}$ derivatives without disruption of conjugation in the decacyclene moieties is thus feasible in principle, but here aromaticity is lost in ten out of the thirty benzenoid hexagonal rings in the original fullerene, so reaction should be more difficult than in the case of C_{84}.

C_{60} *and* C_{70}.—These molecules contain only one decacyclene moiety so different considerations apply here. There is evidence that stable derivatives of C_{60} can be formed by the addition of six atoms or groups, *e.g.* in fluorination[6] and methylation.[7] For fluorination, the involvement of just one hexagonal ring was tentatively proposed,[6] but this now seems less likely than alternatives, each of which retains the decacyclene fragment. These are shown in Figs. 2(*a*), (*b*), and involve loss of resonance energy per atom of 0.0564β and 0.0549β, respectively, on formation. The latter structure is thus predicted to be the more favourable one and this is supported by consideration of the corresponding structures [Figs. 3(*a*), (*b*)] arising from symmetrical addition of a further six groups. The structure in Fig. 3(*a*) retains eight benzenoid rings and has three equatorial bands of conjugation, indicated by the broken lines. The structure in Fig. 3(*b*) (octahedral addition) also retains eight benzenoid rings which here are isolated and therefore energetically more favourable. Moreover octahedral addition has very recently been identified in one reaction,[8] and further addition to the octahedral structure can lead to tetrahedral $C_{60}X_{36}$ which is more likely to be the structure of $C_{60}H_{36}$ reported to have been formed on hydrogenation, rather than the isolated double bond structure that was proposed.[9]

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