The Pattern of Additions to Fullerenes [and Discussion]

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The pattern of additions to fullerenes

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Conjugation in C_{60} is not as extensive as was originally anticipated because, for various reasons, the pentagon rings avoid containing double bonds. As a consequence, there is extensive bond localization and the molecule, which is quite reactive, and displays superalkene rather than superaromatic properties. C_{70} behaves in a similar fashion; other fullerenes may follow suit. Additions predominate and C_{60} is particularly susceptible to nucleophilic attack. Added groups may also be readily replaced by nucleophiles, although the reaction mechanism is uncertain at present. The functionalized molecule tends to revert to the parent fullerene at moderate temperatures, and characterization of reaction products by mass spectrometry is thus particularly difficult. This fact, coupled with the complexity of the addition products, makes work with fullerenes exacting. A selection of reactions studied to date and the progress made towards identifying various patterns of addition are described.

1. Introduction

When spectroscopic evidence for the existence of C_{60} was first obtained, a view prevailed that it would be a very unreactive molecule. This conclusion was based on the assumption that with a possible 12500 resonance structures (Klein *et al.* 1986), C_{60} would be superaromatic. However, the earlier molecular orbital calculations (Bochvar & G'alpern 1973) correctly predicted that there would be substantial bond fixation in the molecule; more recently, the bond lengths have been determined by neutron diffraction studies to be 1.391 Å and 1.455 Å (David *et al.* 1991); other methods give similar values.

Thus C_{60} is a superalkene rather than a superaromatic and readily undergoes additions. Bond fixation arises because structures with double bonds in pentagonal rings are unfavourable in carbocyclic chemistry, due probably to the increase in strain that would result from bond-shortening; this phenomenon is particularly well demonstrated by the bond lengths in corannulene (figure 1 (Barth & Lawton 1971)). The structure of C_{60} is such that avoidance of high-order bonds in the pentagonal rings results in complete bond alternation in each 'benzenoid' hexagonal ring. If fullerene isomers are drawn such that the double bonds are exocyclic to the pentagonal rings, then those which have the highest proportion of benzenoid rings tend to be the most stable ones (Taylor 1991, 1992*a*; Fowler 1992), however, this factor may be of diminished importance for higher fullerenes. A consequence of the favoured bond alternation is that the pentagonal rings ideally lie *meta* to one another (I, figure 2) as they each do in C_{60}. By contrast, if they lie either *ortho* or *para* to one another (II, III, figure 2), then at least one pentagonal ring must contain a high-order bond. It is noteworthy therefore that each of the numerous published mass

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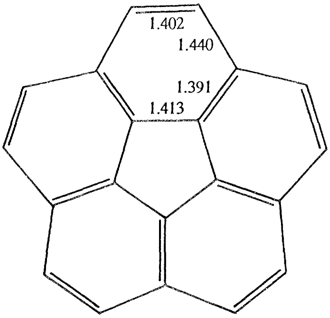
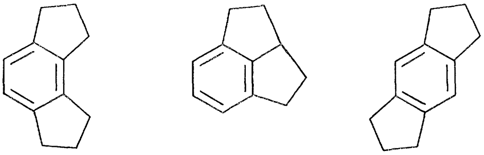
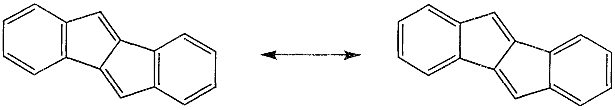


Figure 1. Bond lengths (in Å) in corannulene.



I II III

Figure 2. Dispositions of two pentagonal rings adjacent to a hexagonal one.



8π 16π

Figure 3. Antiaromaticity introduced by adjacency of pentagonal rings.

spectra of higher fullerenes show C_{80} to be particularly unstable; in the icosahedral isomer, all pentagonal rings lie in the *para* relation (Taylor 1992*a*). The unfavourability of the *ortho* arrangement also provides an explanation of the isolated pentagon rule (IPR), i.e. the most stable fullerenes are those with isolated pentagons (Schmalz *et al.* 1986, 1988), interpreted originally in terms of minimization of strain (Kroto 1987). The presence of adjacent pentagons is unfavourable because this leads to regions of antiaromaticity within the molecules (figure 3 (Schmalz *et al.* 1986, 1988; Taylor 1991).

The sp^2-hybridized carbon atoms of the fullerene cages are more electronegative than sp^3-hybridized carbon and have electron-withdrawing ($-$I) effects (Bent 1961). This creates a tendency for fullerenes to react with nucleophiles, an additional reason for this being that addition of a nucleophile converts one of the pentagonal rings of the pyracyclene units within the molecule (figure 4) into a 6π-aromatic system. The high electron affinity and consequent oxidizing behaviour of C_{60} likewise results from the addition of two electrons to give two aromatic pentagonal rings (figure 4) (Wudl 1992). The presence of six pyracyclene units in C_{60} accounts for the observed formation of polyanions (Bausch *et al.* 1991).

The electron-deficient nature of C_{60}, and its behaviour as an alkene rather than as an aromatic was clearly shown by reaction with η^5-$C_5Me_5Ru(MeCN)_3^+(CF_3SO_3^-)_3$, a reagent which invariably reacts with aromatic rings, losing all three cyanomethane

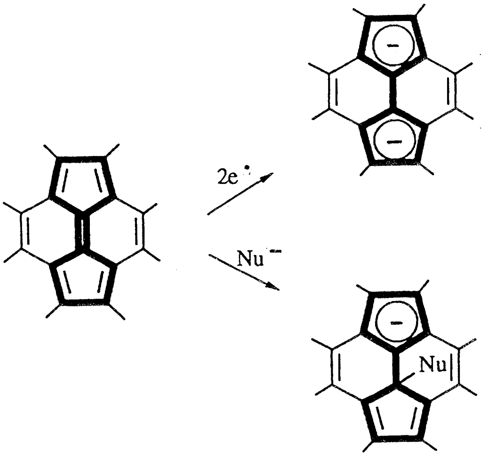


Figure 4. Addition of either two electrons, or a nucleophile to a pyracyclene unit of C_{60}.

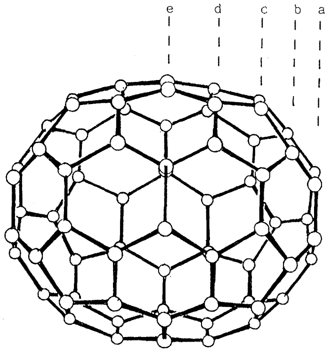


Figure 5. Bond notation for C_{70}: the c–c, a–b, and e–d bonds have the highest π-bond order.

groups in the process and giving η^6 coordination. Instead, only one group was displaced indicating that coordination to a single C_{60} bond had occurred in the manner of an electron-deficient alkene (Fagan *et al.* 1991*a*).

Addition could be expected to take place across the high-order (inter-pentagonal) bonds, which are all equivalent in C_{60}. In C_{70} the high order bonds, c–c, a–b, and e–d bonds (figure 5), have calculated (Hückel) π-bond orders of 0.602, 0.597 and 0.545 respectively (P. J. Knowles & R. Taylor, unpublished results); *ab initio* calculations give comparable results (Baker *et al.* 1991). There is, however, a second factor that needs to be taken into account, which is the eclipsing that results when two groups are adjacent, resulting in steric strain. Most organic molecules are able to twist to relieve this strain, and for those that cannot (e.g. alkenes) the *cis* groups are attached to sp^2-hybridized carbons and are thus further apart. In fullerenes, however, the rigidity of the cage severely restricts bond rotation necessary to reduce eclipsing interactions. As a result, attachment of bulky groups follows a different pattern to that involving either small groups or those with bridged groups (for which steric interactions do not apply). Both patterns of addition to C_{60} are now evident.

Attempts have been made to predict possible addition patterns. One approach considers the predominance of the decacyclene moiety in stable fullerenes, leading to the possibility that addition in which this moiety is retained would produce stable

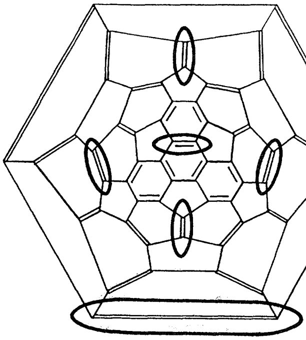


Figure 6. Octahedral addition sites (encircled) for C_{60}.

products (Taylor 1992*b*). Two addition patterns of $3X_2$ are then possible; further addition of $3X_2$ to each product in a symmetrical way leads to two further products, one of which is the octahedral derivative (figure 6); an example of the latter has now been identified (see §2*a*(iv)). This approach also indicates that some $C_{78}X_6$ compounds might be especially stable since two decacyclene moieties can be retained therein.

A second method involves calculating the stabilities of 1,2- and 1,4-addition products (figure 7). Under conditions of low steric requirement, 1,2-addition will be preferred, because location of double bonds in pentagonal rings is unfavourable. However bulky reagents will sterically interact when *cis* to each other, so 1,4-addition is then preferred. Hydrogen and fluorine are thus predicted to favour 1,2-addition, whereas chlorine, bromine and iodine will favour 1,4-addition (Dixon *et al.* 1992). Preliminary results confirm these predictions (§§2 and 3).

The strain introduced in the addition compounds causes them to readily eliminate and revert back to the parent fullerene. This makes mass spectroscopic identification of derivatives particularly difficult. A further difficulty encountered in the chemistry of fullerenes lies in the multitude of addition products that can, in principle, be obtained. For example, for C_{60} the number of products *discounting isomers* that can be produced on addition of a reagent X_2 will equal the number of 'double' bonds, i.e. 30. If isomers are included then many hundreds are possible. Development of C_{60} chemistry is therefore very much more difficult than that of benzene. It is also complicated by the low solubility of C_{60} in organic solvents, and by the fact that derivatives are themselves mostly more soluble, which facilitates polysubstitution; hydroxy and amino derivatives of C_{60} are water-soluble. The additions are described under the two main categories outlined above.

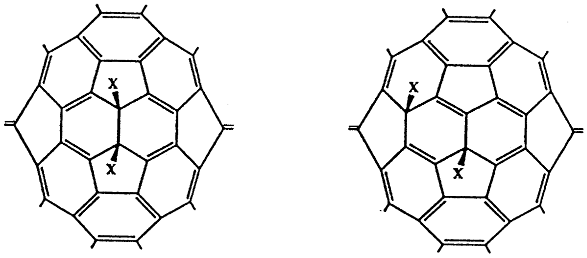
2. Addition of reagents with low steric requirements

Two types of addition are considered here: those involving a single moiety bonded to each of the two adjacent carbon atoms, and those involving two small atoms or groups.

(*a*) *Moieties bonded to adjacent cage carbons*

(i) *Oxygen*

Early work with C_{60} indicated that oxygen could be readily attached, and the observed photochemical degradation of C_{60} in benzene (Taylor *et al.* 1991) has been shown (Creegan *et al.* 1992) to produce $C_{60}O$. This compound has the epoxide (figure



1,2-addition 1,4-addition

Figure 7. Products of either 1,2- or 1,4-addition to C_{60}.

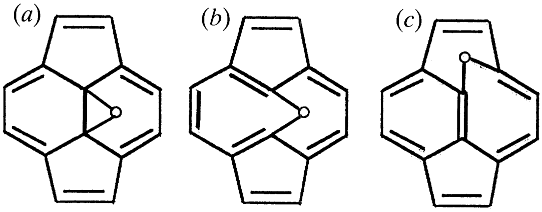


Figure 8. Conceivable structures from addition of oxygen to C_{60}.

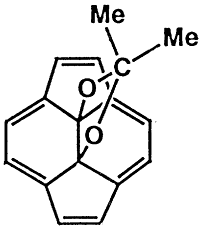


Figure 9. 1,3-Dioxolane derivative of C_{60}.

8*a*) rather than the oxidoannulene structure (figure 8*b*), the preference for avoiding inclusion of double bonds in the pentagonal rings evidently being important here (see §2*a*(v)). Recent calculations indicate that the most stable structure should in fact be the oxidoannulene (figure 8*c*) in which oxygen occupies a 5,6-ring junction (Raghavachari 1992). The advantage of this structure is that it retains the benzenoid character of one of the hexagonal rings, and models show it is considerably less strained. The comparable structure resulting from carbene addition has recently been identified (§2*a*(v)).

The epoxide is also formed from the reaction of C_{60} with dimethyldioxirane, and the 1,3-dioxolane (figure 9) is also obtained (Elemes *et al.* 1992). Photochemical irradiation of C_{60} in hexane had previously been shown to result in the addition of 2–5 oxygens, and also various methylene groups (the results depend upon the fullerene purity) (Wood *et al.* 1991). In this work, two oxygens were found to add to C_{70}.

(ii) *Osmium tetroxide*

Osmium tetroxide adds to C_{60} in the presence of pyridine to give an osmate ester (Hawkins *et al.* 1990). Replacement of pyridine by 4-*t*-butylpyridine yields material suitable for single crystal X-ray spectroscopy (Hawkins *et al.* 1991; Hawkins 1992*a*) which shows that addition has occurred across one of the high-order bonds (figure

Figure 10

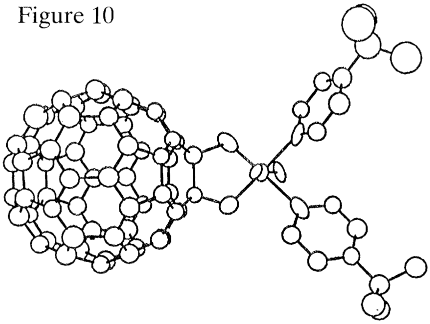


Figure 11

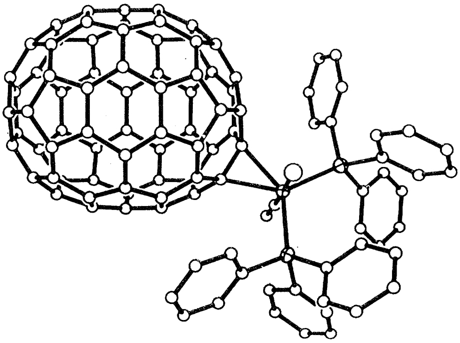


Figure 10. Adduct of C_{60} with osmium tetroxide.

Figure 11. Adduct of C_{70} with $Ir(CO)Cl(PPh_3)_2$.

10). Bis-osmylation of C_{60} is feasible but the positions of each of the second osmate groups has yet to be determined (Hawkins 1992*b*). If octahedral locations (figure 6) are involved, two disubstituted and three trisubstituted derivatives are possible. These intermediates can readily be converted into hydroxy compounds and hence, in principle, into polymers by reaction with chlorides of dicarboxylic acids.

(iii) *Iridium*

The 6,6-ring fusion site is also involved in reaction with $Ir(CO)Cl(PPh_3)_2$ to give $(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2 . 5C_6H_6$ (Balch *et al.* 1991*a*); the reagent here is known to give stable η^2 adducts with electron-deficient alkenes (Vaska 1968). The same reagent reacts with the a–b bond in C_{70} (figure 11). The c–c bond has the slightly higher bond order (see §1), but steric considerations may favour formation of the observed product (Balch *et al.* 1991*b*). An iridium complex in which one of the phenyl groups on phosphorus was replaced by *p*-benzyloxybenzyl gave a derivative in which the phenyl groups chelated the fullerene cage of the adjacent molecule giving rise to an infinite chain of ordered molecules (Balch *et al.* 1992). A further iridium complex of C_{60}, $(\eta^5\text{-indenyl})(CO)Ir(\eta^2\text{-}C_{60})$ has been prepared (Koefod *et al.* 1991).

(iv) *Platinum, palladium, iron, and nickel*

The addition of platinum provides information on multiple additions to C_{60}. Reaction with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ resulted in single-fold addition to give $(Ph_3P)_2Pt\eta^2\text{-}C_{60}$ (Fagan *et al.* 1991*a*), and similar derivatives have been made using nickel and palladium derivatives (Fagan *et al.* 1992). The corresponding triethylphosphine platinum compound, gave six groups coordinated to C_{60} in an octahedral manner (figure 12) (Fagan *et al.* 1991*b*). Addition of two platinum groups produces three isomers, one of which is the expected 1,9-*trans* isomer (figure 13). However, the others were deduced to be either the 1,4-, 1,6-, 1,7-, or 1,8-isomers, none of which is on the pathway to octahedral addition, suggesting that adduct migration must accompany reaction.

Reaction of C_{60} with the complex $Pd_2(\text{dibenylideneacetone})_3 . CHCl_3$ results in displacement of the ligand to give $C_{60}Pd_n$. The value of n is increased if larger stoicheiometric amounts of the complex are used, but was never less than 1.0 when excess C_{60} was used. On heating the complex $C_{60}Pd$ (considered to consist of a linear

Figure 12

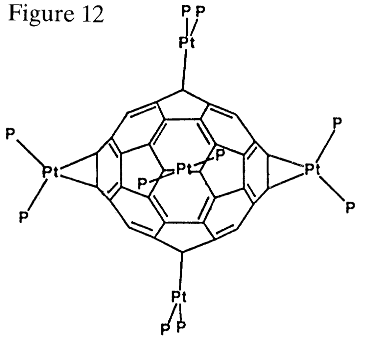


Figure 13

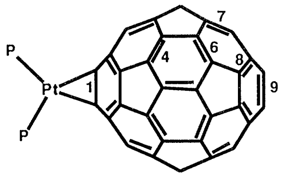


Figure 12. Octahedral co-ordination of platinum to C_{60}; the sixth platinum group is behind the cage.

Figure 13. Possible bond locations of the second group in diadducts of platinum with C_{60}.

Figure 14

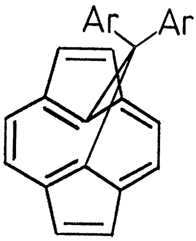


Figure 15

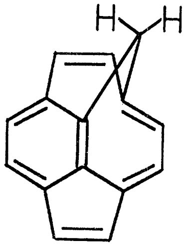


Figure 14. Bonding structure in diarylfulleroids.

Figure 15. Bonding structure in the parent fulleroid, $C_{61}H_2$.

chain of palladiums bonded to two C_{60} molecules), C_{60} is regenerated, and the value of n increases to *ca.* 3.0, indicating the formation of a three-dimensional polymer (Nagashima *et al.* 1992).

The formation of both $C_{60}Fe^+$ and $C_{70}Fe^+$ have been described (Roth *et al.* 1991; Jiao *et al.* 1992), as has the dumb-bell-shaped complex $C_{60}Ni^+C_{60}$ (Huang & Frieser 1991). In these compounds, coordination to the high π-density bonds is probable.

(v) *Diaryldiazomethane*

The reaction of aryldiazomethanes with C_{60} results (after loss of nitrogen from the initial bridged intermediate) in positioning of Ar_2C across one of the high order bonds to give 'fulleroids' (figure 14). *para*-Substituents in the aryl ring include Me, OMe, Br, Me_2N, and OCOPh, and up to six diarylcarbon groups can be attached, suggesting an octahedral array. Derivatives of fluorene can also be attached (Suzuki *et al.* 1991; Wudl 1992). A significant feature of this work is that if the aryl rings contain either hydroxy or amino groups then the possibility of producing fullerene polymers emerges. Some derivatives appear to exist in at least two isomeric forms; the predominant one is shown in figure 14, and differs from that obtained in the analogous oxygen addition (figure 8). There is evidently a fine balance between the various structural factors which favour either the open or closed bridge forms. (It has now been shown that the diarylfulleroids have the closed bridge structure analogous to that in figure 8*a* (F. Wudl, personal communication).) This is also demonstrated

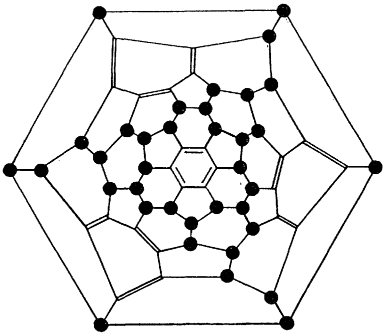


Figure 16. Possible tetrahedral structure for $C_{60}H_{36}$; filled circles denote hydrogen locations.

by the structure of the parent fulleroid (figure 15), for here a 1,5-shift appears to occur to give 6,5-bridging (Suzuki *et al.* 1992*b*). This structure has the advantage that it restores the benzenoid character of one of the hexagonal rings; the low steric requirement of hydrogen should also enhance the C–C–C angle at the expense of the H–C–H angle, thereby facilitating bridging of the greater carbon–carbon distance.

By using of *m*- and *p*-bridging groups, fulleroids with two C_{60} cages have also been prepared (Suzuki *et al.* 1992*a*).

(*b*) *Addition of separate atoms or groups*

(i) *Hydrogen*

A preliminary report of the Birch reduction (liquid ammonia) of C_{60} indicated addition of 36 hydrogens to the cage (Haufler *et al.* 1990). However, various later workers find that this reaction gives products containing amino groups (due to the ease of addition of nucleophiles to the cage). A structure proposed for $C_{60}H_{36}$, with all double bonds non-conjugated and in pentagonal rings, must be considered unlikely. A tetrahedral structure has also been proposed (Dunlap *et al.* 1991), but the most promising candidate would seem to be one with benzene rings (with little delocalization restriction) at the apices of a tetrahedron (figure 16). Mass spectrometry (CI conditions) has revealed the presence of up to 37 (Schröder *et al.* 1992) and 56 hydrogens (R. G. Cooks, personal communication) attached to C_{60}. Many adjacent sites must be occupied by hydrogen in these derivatives.

(ii) *Fluorine*

Large numbers of fluorine atoms can be added to C_{60} so they must occupy adjacent sites. The major product appears to contain *ca.* 42 fluorine atoms (Selig *et al.* 1991; Holloway *et al.* 1991), and ^{19}F NMR indicated the formation also of a small amount of $C_{60}F_{60}$ (Holloway *et al.* 1991). The fluorinated fullerenes (especially those containing many fluorines), are unstable and eliminate fluorine on standing, and the fluorine lability makes it difficult to obtain reliable mass spectra. The early notion that $C_{60}F_{60}$ would be a good lubricant neglected the strain in the molecule due to the eclipsing interactions; in PTFE such interactions are minimized by twisting of the carbon backbone, very difficult in C_{60}. The C–F bond energy is calculated to be reduced by 14% compared with CF_4 (Scuseria 1991). Some twisting of the fluorines is conceivable so that the symmetry becomes I (the molecule would then be chiral) rather than I_h (Fowler *et al.* 1991), though calculations indicate the latter to be the more stable form (Scuseria & Odom 1992).

The fluorines in fluorinated C_{60} can be displaced by a variety of nucleophiles. Furthermore, fluorinated C_{60} derivatives are likely to be synthetically useful because they are both more reactive, and more soluble than other halogenated derivatives (Taylor *et al.* 1992*b*). They thus react readily with water, which negates their use as lubricants (Taylor *et al.* 1992*a*). Mass spectrometry indicates that the products contain numerous hydroxy groups and epoxide links (probably from elimination of either HF or H_2O from adjacent groups). An addition–elimination mechanism is probably involved since the normal S_N2 process is ruled out because backside attack (Taylor *et al.* 1992*b*) is impossible.

(iii) *Nucleophiles*

C_{60} reacts with various nucleophiles (Wudl 1992), and both C_{60}Ht-Bu and C_{60}HEt have been isolated; the addition of up to six *t*-butyl groups has been detected (Hirsch *et al.* 1992). The water-soluble derivatives $C_{60}H_n(NRR6)_n$, (*n* is mainly 6, but up to 12 in minor components) have been obtained by reacting amines with C_{60}. The hydrogens on the cage appeared to be undergoing a series of 1,5-sigmatropic shifts, even though this places two double bonds in the pentagonal rings (Hirsch *et al.* 1991).

3. Addition of bulky reagents

(i) *Bromine and chlorine*

Chlorination of C_{60} results in the uptake of either twelve (Tebbe *et al.* 1991) or approximately 24 chlorine atoms (Olah *et al.* 1991*a*). This latter number is particularly significant in view of subsequent bromination results. Like the fluorofullerenes, the halogen in chlorofullerenes can be replaced by methoxy groups and up to 28 groups were detected (Olah *et al.* 1991*a*). This result may not, however, reflect the number of chlorines present since nucleophilic attack on C_{60} itself is possible. On heating the chloro compounds C_{60} is regenerated; likewise no mass spectrometric evidence for the chloro compounds could be obtained because the halogen is labile.

Treatment of C_{60} with neat bromine produces a compound which contains about twenty-eight bromine atoms fullerene cage (Tebbe *et al.* 1991; Birkett *et al.* 1992). The clue as to where these bromines were located came with the discovery that on bromination in selected solvents, the compounds $C_{60}Br_6$ and $C_{60}Br_8$ are obtained. Each of these derivatives, the structures of which were determined by single crystal X-ray spectroscopy (figures 17 and 18), contains approximately two molecules of bromine solvate per cage (Birkett *et al.* 1992). This suggested that the fully brominated material was similarly solvated $C_{60}Br_{24}$, with the bonded bromines spread over the surface in the same relative dispositions as in $C_{60}Br_8$ (figure 19) (Birkett *et al.* 1992). This conjecture was subsequently proved to be correct (Tebbe *et al.* 1992). Each of the bromo derivatives gives C_{60} on heating, and defies detection by mass spectrometry; the Br_6 compound can be converted into the Br_8 compound on heating in a suitable solvent, and a possible mechanism for this rearrangement has been proposed (Birkett *et al.* 1992).

(ii) *Phenyl and methyl groups*

Reaction of bromine, $FeCl_3$, benzene and C_{60} was reported to give attachment, in an unspecified way, of up to six *benzene* rings to C_{60} (Hoke *et al.* 1991). Repetition of this work but with heating of the reagents and work up followed by mass

Figure 17

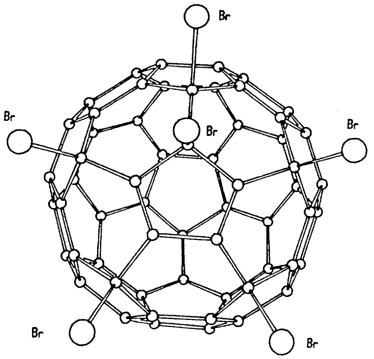


Figure 18

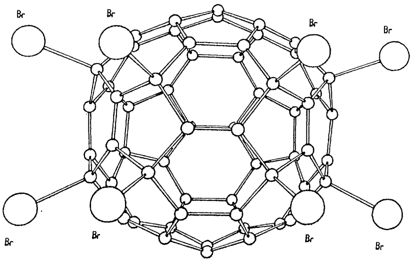


Figure 17. Structure of $C_{60}Br_6$.
Figure 18. Structure of $C_{60}Br_8$.

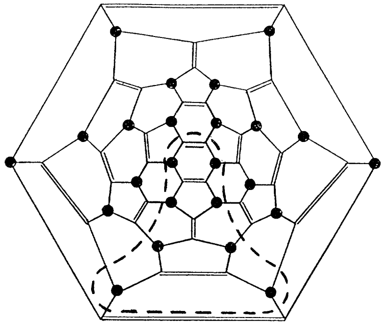


Figure 19. Schlegel diagram for $C_{60}Br_{24}$, where filled circles denote bromine locations; enclosed area shows a $C_{60}Br_8$ subset.

spectrometry showed that up to 16 *phenyl* groups are attached to the cage, ions attributable to species containing six and eight (and to a lesser extent twelve) phenyls being the most intense (Taylor *et al.* 1992*c*). The mechanism must involve electrophilic substitution of benzene by the preformed bromofullerenes, a view supported by the subsequent isolation of some of the corresponding bromofullerenes (§3(i)), which also suggests the location sites of the phenyl groups. Moreover, on reaction of C_{60} anions with methyl iodide, the dominant products also contain six and eight methyl groups (Bausch *et al.* 1991); species with up to 24 methyls were also detected. The reaction of polychlorinated C_{60} with benzene/$AlCl_3$ revealed addition of up to 22 phenyl groups. The reaction of C_{60} with benzene/$AlCl_3$ also indicated the addition of 12 (and to a lesser extent 16) H–Ph groups (Olah *et al.* 1991*b*).

4. Addition of radicals

Alkyl radicals react with C_{60} to give stable products (Krusic *et al.* 1991*b*) and the allylic R_3C_{60} and cyclopentadienyl $R_5C_{60}^{\bullet}$ (figure 20) radicals have been identified; up to 34 methyl groups have been added to C_{60} (Krusic *et al.* 1991*a*). The structure of the cyclopentadienyl radical suggests that a related intermediate may be involved in the formation of $C_{60}Br_6$. More recently, $RC_{60}^{\bullet}$ radicals have been prepared, and the unpaired electron shown to be confined mainly to the 6:6 ring fusion; extensive

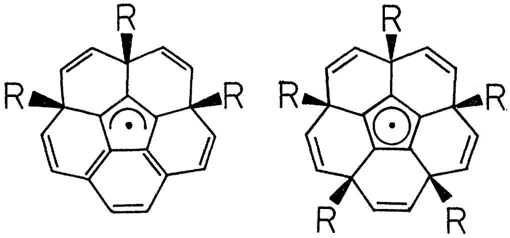


Figure 20. Structures of allylic and cyclopentadienyl radicals formed from C_{60}.

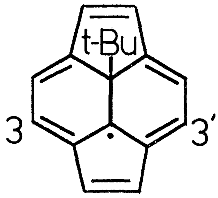


Figure 21. Probable dimerization sites for t-BuC_{60}.

delocalization is absent (Morton *et al.* 1992*b*). The radical signal from t-Bu$C^{\bullet}_{60}$ increases with increasing temperature and vice versa, and the cycle can be repeated several times without significant radical decay. Dissociation of a radical dimer is indicated, and since there is little extensive radical delocalization, head-to-head dimerization is probable, most probably involving the 3- and 3′-sites (figure 21) to minimize steric interactions (Morton *et al.* 1992*b*).

A C_{60}-*p*-xylylene copolymer (-$[C_{60}]_n$-[*p*-xylylene]$_m$-)$_x$, $m/n = 3.4$, has been prepared by reacting the xylylene diradical with C_{60}. The product is thought to be cross-linked, but is not air stable (Loy & Assink 1992).

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Discussion

E. Wasserman (*DuPont Experimental Station, U.S.A.*). One of the particularly exciting things about $C_{60}Br_6$ to us was the unexpected presence of the pair of bromines on adjacent carbons (unlike $C_{60}Br_{24}$). (i) Please comment on the stability of the pairing of bromines compared with $C_{60}Br_8$? (ii) Do they dimerize?

R. Taylor. (i) $C_{60}Br_6$ is unstable; if you warm it in certain solvents it rearranges to $C_{60}Br_8$, and we have suggested a mechanism whereby one of the bromines in the eclipsed pair migrates by a 1–3 shift. In this way three quarters of the $C_{60}Br_8$ structure can be achieved. Of course bromine is present in the cage lattice which can add and complete the conversion. C_{60} is also produced during the recrystallization of $C_{60}Br_6$. It is more soluble and more easy to handle than $C_{60}Br_8$. (ii) The t-butylC_{60} radical dimerizes head-to-head. But the brominated C_{60} are somewhat sterically crowded because of the neighbouring bromines. So far we have no evidence for dimers. We attempted to detect an ESR radical signal during bromination, but were unsuccessful. This does not, of course, preclude a minute concentration of an intermediate.

E. Wasserman. If the dimer is isolated, the new bond formed between two C_{60} molecules should be very interesting; it would be either long and weak or short and strong. It may be shorter because of angle relations, but is could also be long because of conjugation.

R. Taylor. There may be more evidence (of dimers) in P. J. Krusic's work.

R. C. Haddon (*AT & T Bell Laboratories, U.S.A.*). You mentioned that you have managed to add methylene to some of the higher fullerenes. Is this done via diazomethane?

R. Taylor. Our results are based upon byproducts from another reaction and we are retracing our steps to see at what stage it occurred. It is a mystery because we do not think methylating agents were present. Furthermore we cannot be absolutely certain that we have introduced three individual methylenes as opposed to a C_3H_6 chain. The mass spectrum shows the addition of one methylene quite clearly, so that three may have added en route to an octahedral array. Mass analysis shows a CH_2 group, not nitrogen.

H. W. Kroto (*University of Sussex, U.K.*). What is known about hydrogenated C_{60}? It is suggested that it might be responsible for astrophysical spectra, although there is a $C_{60}H_{36}$ result that appears to be suspect. What is the situation?

R. Taylor. We tried the Birch reduction and obtained amino peaks in the IR because amination occurs under the reaction conditions. We tried to get over this problem by hydrogenating over platinum at low pressure, initially in hexane and then in benzene. Benzene must be redistilled first because it contains di-octyl phthalate. Having adopted this precaution, a purple solution was obtained which became bright yellow after 2–3 days. Of course benzene is reduced as well to cyclohexane. Another problem arises because the (hydrogenated) product, although initially soluble in benzene, will not redissolve after removal of the solvent by evaporation. Another curious feature is that the product is insoluble in acetone and in water but dissolves in an acetone/water mixture! Reduction has certainly occurred since the product contains no C_{60}.

R. C. HADDON. What is known about the photochemistry of C_{60}?

R. TAYLOR. In early experiments we UV irradiated C_{60} in hexane, but the amount of decomposition was dependent upon the particular batch of C_{60}. Some decomposed completely within 4 h; others showed little decomposition after 24 h. Therefore we keep C_{60} in the dark. Others have reported that the decomposition of C_{60} may be triggered by an impurity. Indeed deliberate initiation of decomposition has been reported. We have tried halogenation in the light and obtained a product which is different from that isolated under conventional conditions. C_{70} is also photosensitive; it decomposes faster in hexane than in benzene.