# FULLERENES

## 1. Introduction

Fullerenes are closed cage carbon molecules $C_{2n}$ ($n \geq 10$) comprised of a combination of $n$ carbon atoms of $sp^2$ (trigonal) hybridization arranged into 12 pentagons and $(n - 20)/2$ hexagons, and are sometimes referred to as the "third form of carbon" (after diamond and graphite). A notable difference from these other forms is that fullerenes are soluble in many solvents and undergo many chemical reactions. They are formed by various procedures, especially vaporization of graphite either by use of lasers or electric arc discharge in an inert atmosphere, but do not occur naturally because of their instability; they oxidise quite rapidly in air. For a given value of $n$, very many isomers (having a wide range of stabilities) are possible. The number increases geometrically with increasing size of $n$, but only a few are isolable. The most abundant fullerene is the spherical $I_\mathrm{h}$ isomer of $C_{60}$ (there are 1819 other $C_{60}$ isomers, all unstable), which has a diameter of ~10.0 Å. It is axiomatic that stable fullerenes cannot have adjacent pentagons because this introduces too much strain into the cages, and this is known as the "Isolated Pentagon Rule" (1).

The next most abundant fullerene is $C_{70}$, which is shaped like a kiwi fruit; fullerenes containing >70 atoms are known as"higher fullerenes". Those of the latter that have been isolated in quantities sufficient for physical and chemical studies rather than mere characterization comprise $C_{76}$, $C_{78}$ (three isomers) $C_{82}$ and $C_{84}$ (mainly two isomers); $C_{74}$, $C_{80}$, $C_{86}$–$C_{96}$ and other isomers of $C_{84}$ (seven or so are known) have been isolated in single milligram quantities. The geodesic structure of the molecules led to $C_{60}$ being named as Buckminsterfullerene after Richard Buckminsterfullerene who popularized the use of geodesic domes in building construction. This term is now used only rarely, but gave rise to the abbreviation "fullerenes" for this class of molecules.

## 2. Discovery and Synthesis

Evidence for fullerenes was first published in 1984 by a team from the Exxon research laboratories in New Jersey, who used mass spectroscopic analysis of

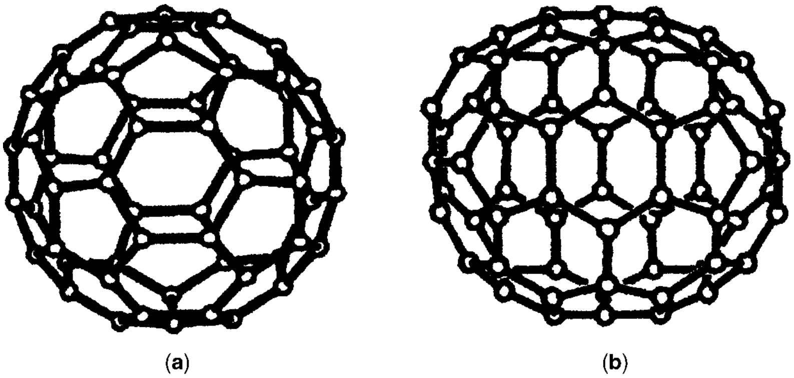

(a) (b)

**Fig. 1.** Structures of (**a**) $C_{60}$ and (**b**) $C_{70}$.

the product from laser-vaporized graphite (2). They found the linear carbon species $C_{4n} - 1$ ($n$ mainly 3–6) and others $C_{2n}$ ($n \geq 10$) for which, however, no interpretation was given. In 1985, a collaborative team from Rice (U.S.)/Sussex (U.K.) universities were carrying out similar experiments, with the intention of forming long-chain carbon molecules thought to be produced in vast amounts by carbon stars. They duplicated the previous results, but found that by manipulation of the reaction conditions, $C_{60}$ appeared as the dominant species, with $C_{70}$ formed also in substantial amounts (3). They deduced that the structure of $C_{60}$ was that of a truncated icosahedral closed cage molecule, consisting of 60 $sp^2$ (trigonal) hybridized carbon atoms (Fig. 1**a**), whereas $C_{70}$ (Fig. 1**b**) contained an additional equatorial band of 10 carbons. In fact, the structure of $C_{60}$ had been conjectured as early as 1970 by a Japanese group (4), and independently in 1973 by Russian theoreticians (5).

The major breakthrough in fullerene research came in 1990, when macroscopic quantities of fullerenes became available. These were produced by arc discharge of graphite rods in an inert atmosphere of helium at 100 Torr (6); argon may also be used but the yield is lower (7). This process produces a fullerene-containing soot (fullerene content ~5%) from which the fullerenes may be extracted with solvents such as toluene, chloroform, etc (7). Subsequent column chromatography yielded $C_{60}$ and $C_{70}$ as magenta and port-wine red solutions, respectively, in either benzene or toluene (7). Very thin films of these fullerenes are correspondingly mustard yellow and red, but thicker films of each appear black (7). $C_{60}$ comprises ~75% of the extract, $C_{70}$ ~24%, and larger (higher) fullerenes 1%. The structures of the two main fullerenes were proved by $^{13}C$ NMR spectroscopy, $C_{60}$ giving just one line (all the carbon atoms are equivalent), whereas $C_{70}$ gives five lines in a 1:2:1:2:1 ratio (Fig. 2), due to the presence in this ratio of the five distinct carbons (labeled a–e) (7).

It is important to exclude all traces of oxygen from the arc-discharge process (which may use either ac or dc current) otherwise significant amounts of fullerene oxides are produced. Other methods of fullerene formation include burning of benzene in oxygen-deficient flames (8) and pyrolysis of aromatic hydrocarbons such as naphthalene (9), but to date the arc-discharge process is the one used

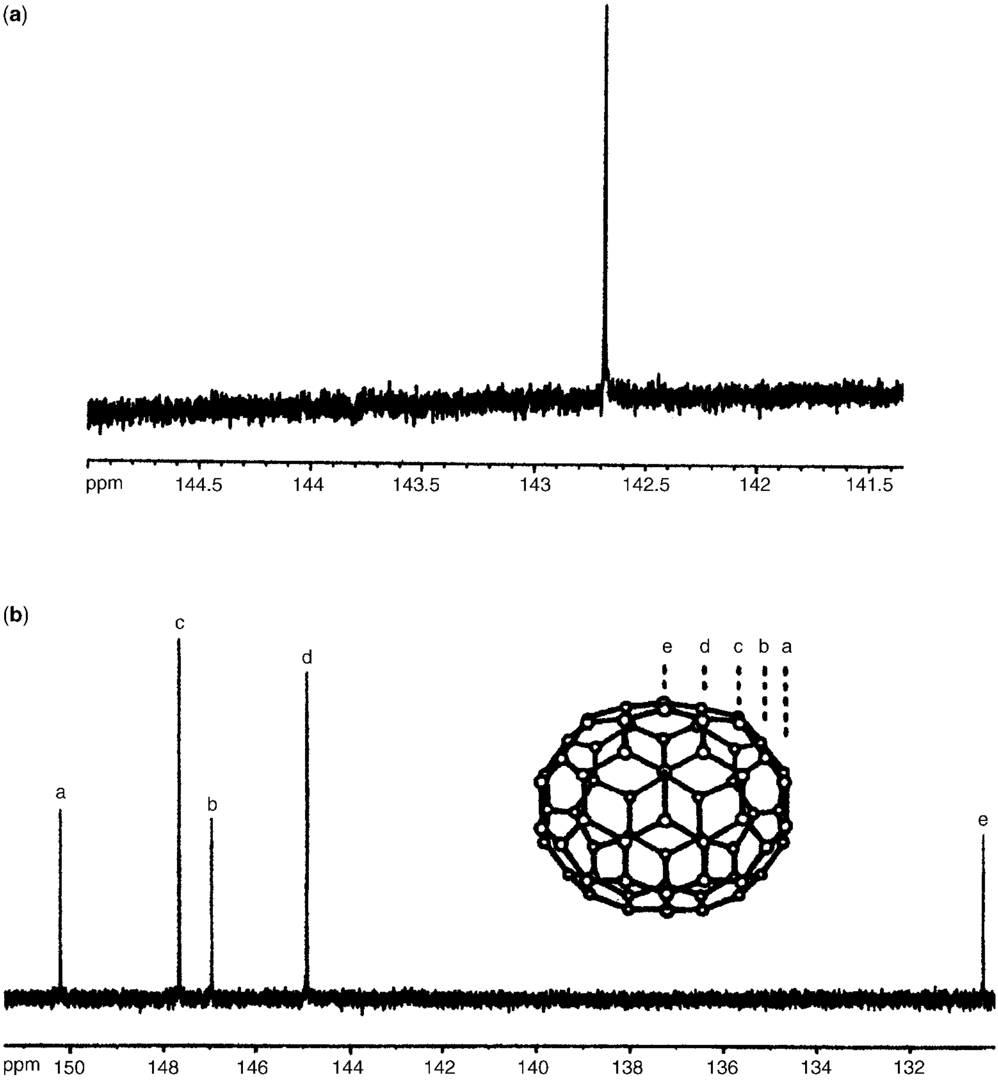


**Fig. 2.** $^{13}C$ NMR spectra of $C_{60}$ (**a**) and $C_{70}$ (**b**).

most widely. When dc is used, large quantities of nanotubes are deposited on the cathode (10).

A number of books describe the discovery of the fullerenes and their main properties (3,11,12).

### 2.1. Endohedral or *Incar*fullerenes.

Fullerenes with elements or molecules trapped inside them are known as either endohedral or *incar*fullerenes (this latter being the IUPAC term). They are generally prepared by filling hollow graphite rods with, eg, either a metal, metal carbide, or metal oxide, which on arc-discharge produces fullerenes with the element trapped inside (14), but the yields are very low (~0.1%); typical elements are La, Y, Sc, Ce, Eu, etc. The particular fullerene produced depends on the element and reaction conditions, and is usually one that is obtained either in low yield or not at all for empty fullerenes. More than one atom can be incarcerated, eg, three lanthanums (14), but the *incar*fullerenes tend to be air unstable so that both physical and chemical research on them is difficult. By contrast, derivatives of ammonia such as $Sc_3N$ can be incarcerated (15), and these derivatives are perfectly air stable, leading to the expectation of a rich chemistry of such compounds. Proof that the elements are inside can be obtained by photofragmentation (which all fullerenes undergo) resulting in progressive $C_2$ loss (sometimes termed “shrink wrapping”) and eventually at a given minimum cage size, the cage bursts apart. The *incar*fullerenes fragment at a larger cage size, which is the minimum that can contain the incarcerated element (14). More recently, the presence of a metal inside a fullerene cage has been demonstrated through the use of synchrotron X-ray powder diffraction (16). Noble gases have also been incarcerated (17) and even atomic nitrogen (18).

The incarcerated element transfers electrons to the cage surface, making it an electron donor, but paradoxically the molecules are also overall better electron acceptors than the empty cages. This latter can be understood in terms of the electrons on the surface being diffused over a wide area whereas the core charge is concentrated. There is thus a parallel with the increase in electronegativities of elements on traversing a given period of the Periodic Table, the addition of an orbiting electron being insufficient to compensate for the charge of the additional core proton.

**2.2. Multiwall or Nested Fullerenes.** Nested fullerenes were first observed in graphitized carbon particles before fullerenes were known (19). The sizes of the $C_n$ cages that can be accommodated one within the other so as to leave acceptable intermolecular distances between them follow the series $n = m^2 60$, where $m$ is an integer, ie, $n = 60$, 240, 540, 960. Nested fullerenes can be produced by electron-beam irradiation of carbon nanoparticles (19), by laser melting of carbon under high pressure, by shock wave treatment of soot, by the high temperature annealing of nanodiamonds, and by hydrocarbon combustion (20). The distances between the layers reduces toward the center of the nest, which creates huge internal pressures such that electron-beam irradiation of the cage at 700°C converts the inner layers to diamond, which is less space demanding (21).

**2.3. Heterofullerenes.** In these fullerenes, one or more carbon atoms are replaced by other elements (thus far either boron, nitrogen, or phosphorus). Borafullerenes are obtained by arc discharging between carbon rods packed with boron nitride, and can only be detected spectroscopically (14,22). Azafullerenes are derived from the corresponding fullerene by a synthetic procedure (23). Since nitrogen has one more electron than carbon, azafullerenes are radicals that can either dimerize to give, eg, $(C_{59}N)_2$ (23) or add hydrogen to give $C_{59}NH$ (24). The different electronic structure produces a different chemistry compared to the corresponding fullerenes. Figure 3 shows the structure of the $C_{59}N$ radical; in solution this dimerizes to $(C_{59}N)_2$.

Phosphafullerenes $C_{59}P^\bullet$ and $C_{69}P^\bullet$ have been made by coevaporating carbon and phosphorus in a radiofrequency furnace (25). The structures have not been determined but may be assumed to be isostructural with the corresponding azafullerenes.

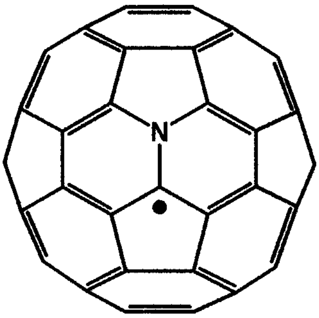


**Fig. 3.** Structure of $C_{59}N^{\bullet}$.

The production and chemistry of azafullerenes have been reviewed recently (26).

**2.4. Opened Fullerenes.** Holes have been made in fullerenes by various procedures, the objective being to incorporate molecules within the cages by the use of high pressure. While this is achievable in principle, the statistical ratio of internal/external volumes means that even at 3000 bar, only 0.1% of molecules will enter the cage, so that this not a feasible procedure from the preparative viewpoint. Useful incorporation of molecules will only be achieved by chemical procedures, yet to be devised. Opened fullerenes are described in a recent review (27).

**2.5. Elongated Fullerene or Nanotubes.** The discovery of these tube-like carbon structures (28) has created much interest and research activity. They are effectively greatly elongated fullerenes, and may either be single-wall nanotubes (SWNT) (paralleling empty fullerenes) or multi wall nanotubes (MWNT) (paralleling nested fullerenes). Single-wall tubes are of greatest interest and are formed by dc arc discharge of carbon rods containing either cobalt or iron/nickel (29). Nanotubes can also be formed during combustion (30) and pyrolysis (31) of hydrocarbons, and when finely divided metals are used as catalysts under the latter conditions, the tubes are frequently spiraled (32).

**2.6. Quasifullerenes.** Although fullerenes are usually considered as being comprised only of 12 pentagons and any number of hexagons, it is feasible to have fullerenes containing a seven-membered ring, in which case an additional pentagon is required to close the cage. Although there are as yet no

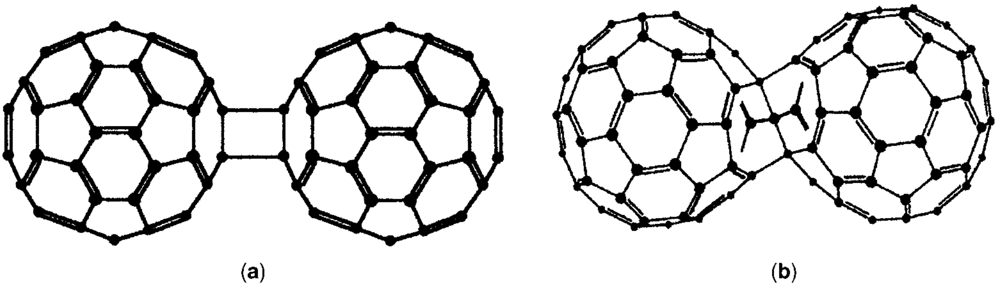


**Fig. 4.** (**a**) $C_{120}$ and (**b**) $C_{119}$.

characterized examples of parent *quasi*fullerenes, derivatives are known having seven-membered rings and in these cases the presence of adjacent pentagons (forbidden with normal fullerenes) becomes possible.

**2.7. Dimeric and Fused Fullerenes.** Fullerenes may also be joined together by pairs of bonds to give dimeric fullerenes or they can be fused together. Examples of each type ($C_{120}$ and $C_{119}$) are shown in Figure 4 **a** and **b** (33).

## 3. Physical Properties

**3.1. Bond Lengths and Structure.** $C_{60}$ has $I_h$ symmetry while that of $C_{70}$ is $D_{5h}$. $C_{60}$ exists at room temperature as a face-centred cubic structure (fcc, lattice constant 14.17 Å) (34) with a mass density of 1.72 g $cm^{-3}$ (35), and a phase transfer to a simple cubic structure occurs <260 K (36). At room temperature, the molecules in the lattice rotate at a rate of $\sim 1 \times 10^{10}$ $s^{-1}$ (37). This limits single-crystal X-ray determination of structure either to fullerenes possessing heavy addends, or to those that have solvent interactions that slow the rotation.

The bonds in fullerenes fall into groups each of differing lengths. The lower the symmetry of the cage the higher the number of groups . The differences arise because it is unfavorable to have double bonds in the pentagonal rings (Fig. 5) as this increases strain (38). In $C_{60}$, the most symmetrical fullerene, the bond lengths are 1.45 Å (within a pentagon, known as a 6:5 bond because it is common to a six- and a five-membered ring) and 1.40 Å (connecting two pentagons, known as a 6:6 bond because it is common to two six-membered rings) (39). The double-bond character of the latter results in addition reactions taking place readily across this bond. This is the basis of most of the chemistry of $C_{60}$. For other fullerenes, addition also takes place across the shortest bonds, ie, those with the highest π-electron density. It follows from the above that delocalisation of electrons in fullerenes is relatively weak, therefore they are not very "aromatic" molecules. This finding has an important bearing on their reactivities and addition patterns (described under the Section Additions).

The cage–cage (center) distances are 10.02 Å for $C_{60}$ (35) and 10.61 Å for $C_{70}$ (40).

The number of isomers that can exist theoretically for a fullerene $C_n$ increases at least geometrically, the higher the value of $n$. The number of isomers for some values of $n$ are 1,812 (*60*); 8,149 (*70*); 19,151 (*76*); 24,109 (*78*); 51,592

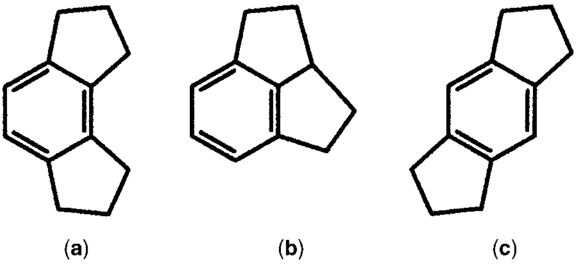


**Fig. 5.** Favorable (**a**) and unfavorable (**b, c**) bond locations in pentagonhexagon combinations.

(*84*).In practise, only a few isomers are stable enough to be isolated, these numbers being for *n* values: 1 (*60*); 1 (*70*); 1 (*76*); 3, (*78*); 2 main and 7 minor isomers (*84*). The structures of the isomers are determined by $^{13}$C NMR (nuclear magnetic resonence) spectroscopy, but for larger fullerenes the numbers and intensities of the spectral lines usually reduce the number of possibilities to a handful of the same symmetry, but further definitive characterization is not possible.

**3.2. Solubility.** The solubility $C_{60}$ in various solvents (mg mL$^{-1}$) is approximately hexane, 0.04; dichloromethane, 0.26; carbon tetrachloride, 0.4; benzene, 1.7; toluene, 2.8; carbon disulfide, 6.5; 1,2-dichlorobenzene, 27; 1-methylnaphthalene, 33; it is virtually insoluble in acetone, ethers, and alcohols. The solubility of fullerenes decreases with increasing size, and, for example the solubility of $C_{70}$ in the above solvents is very roughly 50% of the values for $C_{60}$ (41). The water solubility is greatly increased by the addition of hydroxyl groups either to the cage (giving fullerenols) or having them present in addends such as tris malonate adducts, $C_{60}[C(CO_2H)_2]_3$ (42).

**3.3. Stability.** The heats of formation of $C_{60}$ and $C_{70}$ are ~10.0 and 9.3 kcal mol$^{-1}$ per atom, respectively (43), so that they are each less stable than either diamond or graphite for which the respective values are 0.4 and 0 kcal mol$^{-1}$. The values above show $C_{70}$ to be the more stable, and a general rule of thumb is that the larger the fullerene, the less reactive it is. The reactivity is due partly to the curvature of the surface that weakens the bonds since orbital overlap is poorer. This contributes to the explanation of the lower reactivity of the larger fullerenes since with increasing size their surfaces become more planar. The heats of sublimation also increase with increasing fullerene size, but the differences in values are too small to permit effective separation of fullerene via sublimation (44).

Fullerenes are unstable in air, especially when in the form of thin films that increases greatly the surface to volume ratio; $C_{60}$ can absorb up to 4% by weight of oxygen (45). The oxidative degradation, which is ultraviolet (UV) catalyzed, leads within a few days to the formation of $C_{120}O$ (Fig. 6). This compound is present in all bulk samples of $C_{60}$ unless they are freshly purified and kept under an inert gas (46). The involvement of ozone (47) is implicated since ozonolysis of fullerenes leads to formation of various oxides (48).

Fullerenes decompose at elevated temperatures, eg, >750°C for $C_{60}$ (49).

**3.4. Electron Affinities and Electrochemistry; Oxidation and Reduction.** Fullerenes have substantial electron affinities, and the (gas-phase) values increase fairly regularly from 2.65 and 2.73 eV for $C_{60}$ and $C_{70}$, respectively, to 3.39 eV for $C_{106}$ (50). However, there is a sharp discontinuity

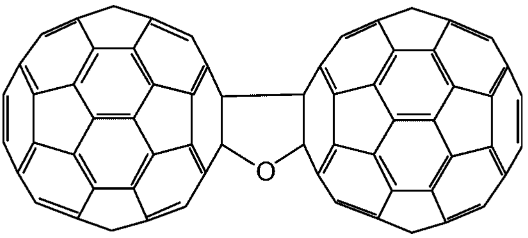


**Fig. 6.** $C_{120}O$.

for $C_{72}$ and $C_{74}$ (fullerenes that are difficult to isolate) that have respective values of 3.09 and 3.28 eV, for reasons that are presently unclear. The electron affinities are increased by electron-withdrawing addends, eg, the value for $C_{60}F_{48}$ is 4.06 eV (51).

The electron affinities are also manifest in fullerenes having energetically low-lying lowest unoccupied molecular orbitals (LUMO). They are thus readily reduced and can easily accept electrons (up to six in the case of $C_{60}$) reversibly under electrochemical conditions (52). It becomes increasingly difficult to add each successive electron, so that the electrochemical potentials for each addition are successively more negative. These values are dependant on temperature, solvent, and supporting electrolyte, but some representative ones for $C_{60}$ ($-10$ °C, PhMe/MeCN solvent, tetra-*n*-butylammonium tetrafluoroborate) are $-0.98$, $-1.37$, $-1.87$, $-2.35$, $-2.865$, and $-3.26$ V (vs $Fe/Fe^+$) (53). The first reduction potentials of $C_{60}$, $C_{70}$, $C_{76}$, and one isomer each of $C_{78}$ and $C_{84}$ correlate linearly with the electron affinities.Just as addition of an electron to the cage makes the reduction potentials more negative for the subsequent additions, so the presence of electron-supplying groups on the cage produce similar effects. The ease of reduction of fullerenes means that they readily form hydrides and such is the oxidizing ability of $C_{60}$ that it will even oxidize $H_2S$ to sulfur (54).

Electron removal (oxidation) is by contrast difficult because (for $C_{60}$) the highest occupied molecular orbital (HOMO) is calculated to be energetically low lying, with the ionization potential estimated as 7.8 eV (55). One-electron reversible oxidation waves have been observed at 1.26 V for $C_{60}$, 1.20 V for $C_{70}$, and 0.81 for $C_{76}$ (56) so that ease of oxidation increases along this series.

A major difficulty with regard to derivatizing fullerenes is that the strong electron withdrawal by the cages makes reaction of them with positive species unfavorable. However, this can be circumvented by converting the cages to anions with varying degree of charge (achieved by control of the electrochemical potential), so that reaction with the desired number of positive species occurs rapidly. Thus far, this technique has been used to make alkylated fullerenes (57).

**3.5. Spectroscopic Properties.** The higher the symmetry level of a fullerene, the fewer lines that are observed in the infrared (ir), Raman, and $^{13}C$ NMR spectra. $C_{60}$ has the highest symmetry of all of the fullerenes (and indeed of any molecule) and thus gives 4 ir and 10 Raman bands, and only 1 line in the $^{13}C$ spectrum (7,58). By contrast, for $C_{70}$, these numbers become 12, 27, and 5, respectively (7,58). $^{13}C$ NMR is used generally to identify the structure of a particular fullerene and derivatives.

The uv–vis spectrum for $C_{60}$ comprises peaks at 213, 230 (shoulder), 257 (main) 329, and 406 nm. $C_{70}$ gives two main peaks at 214 and 236 nm (shoulder at 255 nm) with weaker peaks at 331, 360, and 378 nm. Weaker bands in the 420–700 nm region arise from forbidden singlet–singlet transitions that result in the magenta and red colors of $C_{60}$ and $C_{70}$, respectively (7,59). One of the most common reactions of $C_{60}$ involves 1,2-addition across a 6:6 bond, and derivatives (independent of the nature of the addends) give a peak at ~435 nm (60); the less common 1,4-addition produces a band at 448 nm (61), so these spectroscopic features are structure diagnostic tools.

**3.6. Superconductivity in Fullerenes.** Some fullerenes become superconducting when doped with alkali metals, with transition temperatures up to

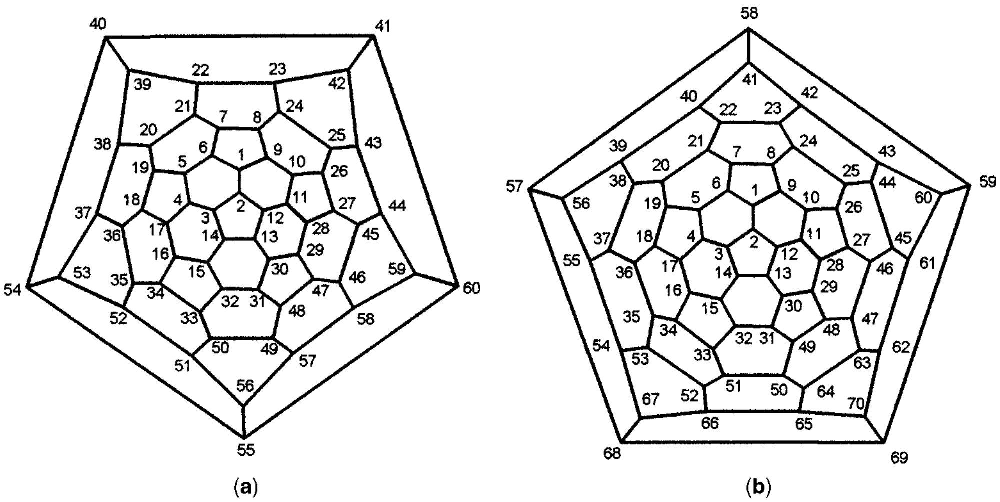
33 and 40 K being observed for $RbCs_2C_{60}$ and $Cs_3C_{60}$, respectively (62). Numerous other combinations of alkali metal and fullerenes have been examined, but these give lower transition temperatures. It is unclear whether this development will have any long-term potential given that the doped materials are pyrophoric.

## 4. Chemical Reactivity

Before describing the chemistry of fullerenes, the method of displaying a fullerene as a two-dimensional diagram (Schlegel diagram) is shown. The need for these diagrams arises when there are many groups (addends) attached to the cages, hence it is not possible to show clearly where these addends are on the far side of the cage. Figure 7 shows the Schlegel diagrams for (**a**) $C_{60}$ and (**b**) $C_{70}$, respectively, together with the numbering schemes that are used to denote positions on the cages.

It is also necessary when describing their derivatives, to adopt a nomenclature for the fullerenes that follow the existing rules of organic chemistry. Thus $C_{60}$ is [60]fullerene and $C_{70}$ is [70]fullerene.

Chemistry has been carried out on those isolated fullerenes described in the introduction, but mostly on $C_{60}$, much less on $C_{70}$, and very little on the higher fullerenes. This reflects not only the respective availabilities of the fullerenes but also their solubilities and reactivities, which decrease with fullerene size. A further complication concerns their symmetries. Thus $C_{60}$ gives only one mono-addition product, $C_{70}$ can give up to five, while some higher fullerenes can in principle give very many more. Note that in any addition, two bonds must be formed to the cage, so that two groups must add (either $X_2$ or XH); $X_2$ can be the components of a cyclic group. In the case of radical addition, which involves one group attaching to the cage, the resultant fullerenyl radical becomes



(a) (b)

**Fig. 7.** Schlegel diagrams for (**a**) $C_{60}$ and (**b**) $C_{70}$, respectively.

stabilized either by abstraction of hydrogen from the surroundings, or if steric conditions permit, through dimerisation. Reactions can take place either at 6:6 bond or less commonly at 6:5 bond (see the Sect. on Bond Lengths and Structure).

A substantial problem when studying the chemistry of fullerenes is that polyaddition can occur to give, in principle, many thousands of isomers. In practice, electronic and steric constraints usually limit these numbers to single figures, nevertheless separating these isomers from each other, and from isomers of derivatives of different addition levels is a formidable task. The technique that is most widely used in high pressure liquid chromatography (HPLC), but the columns that are particularly useful for separating fullerene derivatives are very expensive. Moreover, the solubilities of the derivatives, though usually greater than the parent fullerenes, are not high. Thus only small quantities of compounds can be produced in this way. A further problem is to decide where the addends have become attached to the cage, and for this NMR (proton, carbon, and fluorine) is widely used. Interpretation of these data in terms of possible structures is daunting with considerable intuition being required in many cases. When large enough crystals can be grown (this is not often the case), single-crystal X-ray analysis can provide definitive structures. Unfortunately, many of the crystals of suitable size do not diffract sufficiently for the acquisition of meaningful data. The information that can be obtained by these structural studies often reveals considerable information about the electronic and steric effects that operate in the cages.

Fullerenes are electron deficient, used this deficiency arising from the presence of the electronegative $sp^2$-hybridized carbon atoms. This electronegativity is increased also by strain. Reaction occurs primarily with electron-rich species (nucleophiles). Strain due to the cage curvature also causes poor overlap of adjacent C−C bonds, thereby facilitating reaction. It follows therefore that the larger fullerenes are less reactive since the cage curvature is less.

As noted in the Section on Bond Lengths and Structure, there is considerable bond fixation in fullerenes, which may be regarded as "superalkenes" rather than aromatic compounds. However, there is some delocalization of electrons. This is most clearly demonstrated by patterns that occur upon addition, as shown below. The sites of reactivity are therefore the localized double bonds, and for both $C_{60}$ and $C_{70}$, the 1,2 bonds (see Fig. 7 **a** and **b**) are the most reactive; for $C_{70}$ the next most reactive bond is the 5,6 bond. These are the sites connecting two pentagons. There are only 12 pentagons present whatever the size of fullerene or nanotube, and for the latter, these are located at the ends of the tube, an area that constitutes less or much less than one-thousandth of the overall molecule. Consequently, nanotube chemistry is effectively precluded by the virtual impossibility of obtaining meaningful spectroscopic evidence for reaction products.

A majority of current chemical studies are devoted toward forming derivatives in which there is potential for the transfer, under light stimulation, of electrons from an electron-rich addend to the electron-deficient cage, (usually [60]fullerene since this is the most electron-deficient fullerene). This electroactive process, sometimes referred to as light-harvesting, is seen as a potential electricity-generating application of fullerenes. Detailed accounts of the processes involved and some promising compounds have been published recently (63).

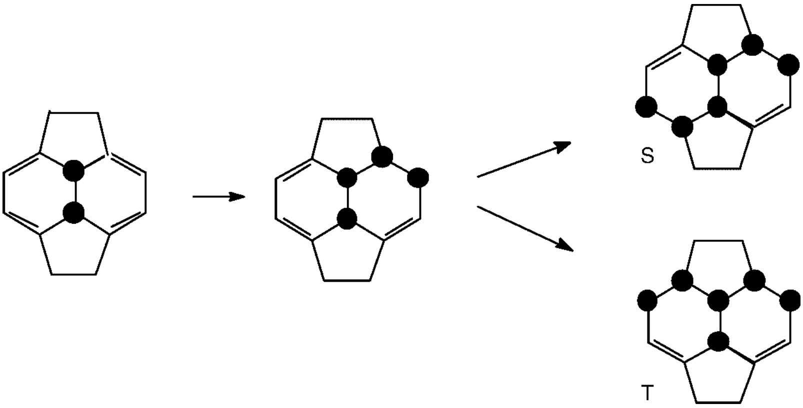


**Fig. 8.** Motif demonstrating contiguous addition of sterically undemanding groups to [60]fullerene (● = H, F).

**4.1. Types of Reactions.** These comprise additions, cycloadditions, reactions with electrophiles and nucleophiles, reaction of anions with electrophiles, formation of radicals, organometallic derivatives, and of polymers.

*Additions.* The two most representative reactions are hydrogenation and halogenation, which involve radical (atomic) addition. Because hydrogen and fluorine have a size that does not cause significant steric hindrance when they are attached to adjacent carbons, the addition patterns, produced in each hydrogenation and fluorination, and based upon sequential 1,2-addition, are identical. Thus each gives $C_{60}X_2$, $C_{60}X_4$, $C_{60}X_{18}$, and $C_{60}X_{36}$ as characterised products (X = H, F) (64). The general underlying principle involves addition to a double bond on the cage. Since there is some delocalization of electrons on the cage (albeit weak), the addition causes increased localisation of the remaining electrons in the addended hexagon. The resultant higher $\pi$ density in the addended

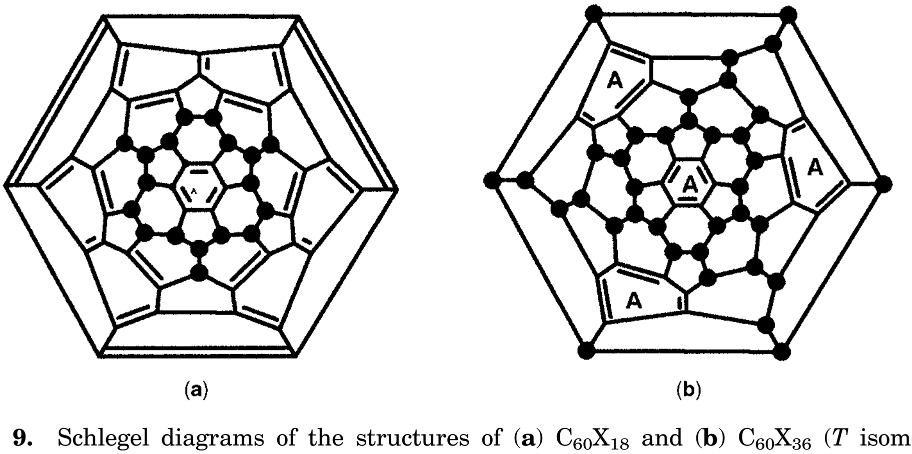


**Fig. 9.** Schlegel diagrams of the structures of (**a**) $C_{60}X_{18}$ and (**b**) $C_{60}X_{36}$ (*T* isomer) (● = addend).

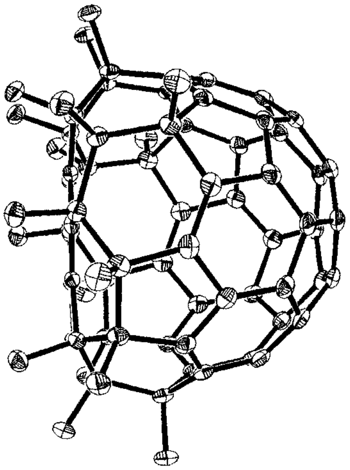


**Fig. 10.** Single crystal X-ray structure of $C_{60}F_{18}$.

hexagon favors further addition there. This process continues so that either an S or T pattern of addition ensues (Fig. 8 shows a motif that is part of the cage) (65). The process is not yet properly established for addition to the other fullerenes, though [70]fullerene hydrogenates to give mainly 1,2- and 5,6-dihydro[70]fullerenes and then 1,2,3,4- and 1,2,5,6-tetrahydro[70]fullerenes (66).

Further addition first gives $C_{60}X_{18}$ and then $C_{60}X_{36}$ (which consists of three isomers of $T$, $C_3$, and $C_1$ symmetry) with the preferential formation of these compounds arising from the formation of fully delocalized aromatic (benzenoid) rings due to loss of strain on conversion of the surrounding $sp^2$ carbons to $sp^3$ (Fig. 9; the aromatic rings are marked with an A). This demonstrates a general feature of fullerene chemistry that is the drive, upon addition, to form structures that are more aromatic.

The aromatic rings are planar as shown by the example of the central ring of $C_{60}F_{18}$ in which the bond lengths are also equal as shown by single-crystal X-ray crystallography Figure 10 (67).

Further addition gives $C_{60}F_{48}$ as a stable derivative that exists as a pair of enantiomers, one of which is shown in the Schlegel diagram (Fig. 11) (68). The

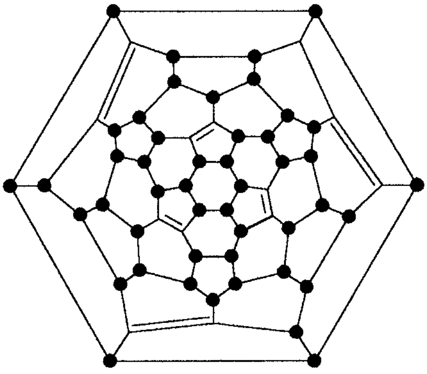


**Fig. 11.** Schlegel diagram of the SS isomer of $C_{60}F_{48}$.

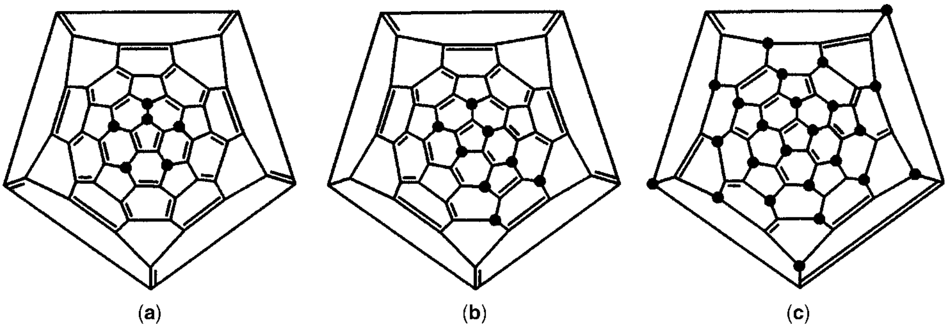


**Fig. 12.** Schlegel diagrams of the structures of (**a**) $C_{60}Br_6$, (**b**) $C_{60}Br_8$, and (**c**) $C_{60}Br_{24}$ (● = Br).

single-crystal X-ray structure shows compression of the double bonds due to the surrounding fluorines (69); similar compression of the central benzenoid ring occurs in $C_{60}F_{18}$.

Addition of chlorine and bromine follows a different pattern because of the larger size of the adding atoms, making 1,2-addition unfavorable. The 1,4-addition becomes preferred. For example, addition of bromine to [60]fullerene gives $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$ (70) shown as Schlegel diagrams in Figure 12; chlorination also gives $C_{60}Cl_6$ (71) and $C_{60}Cl_{24}$ (72). The disadvantage compared to 1,2-addition is that in each derivative, a double bond is located in a pentagon, thereby increasing strain and decreasing stability. Thus addition here involves a balance between steric strain through interaction of the addends and strain in the cage.

Methylation, although not a radical reaction, also gives the $C_{60}X_6$ and $C_{60}X_8$ patterns (● = Me) (73), showing that there is an fundamental mechanistic feature that creates these patterns; benzylation also shows 1,4-addition (74).

1,4-Addition is also involved in chlorination of [70]fullerene (75), whereby 10 chlorines are added to give $C_{70}Cl_{10}$ (Fig. 13). This is a precursor for derivatives

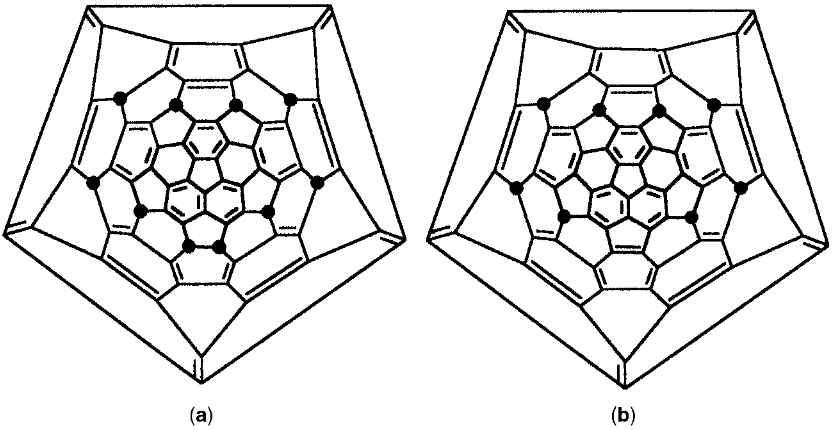


**Fig. 13.** Schlegel diagrams showing addend locations in (**a**) $C_{70}Cl_{10}$ (● = Cl), and (**b**) $C_{70}Me_8$ (● = Me).

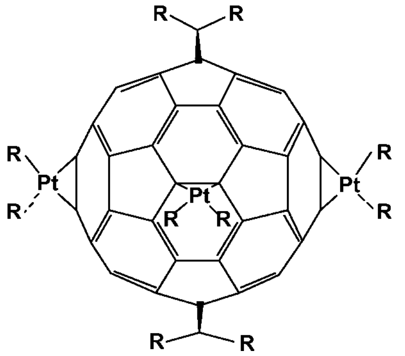


**Fig. 14.** Product of sixfold addition of $Pt(PPh_3)_2$ (R = $PPh_3$) to the octahedral sites of [60]fullerene (the addend at the back of the cage cannot be seen).

having either 10 or 8 addends, the loss of the two adjacent chlorine atoms evidently being facile because of steric hindrance. For example, methylation produces $C_{70}Me_8$ (76). A further example is given under the Section Nucleophilic Substitution: Halogenofullerenes as Electrophiles.

*Cycloadditions.* These are the most studied of fullerene reactions because they tend to give a single product that is relatively easy to isolate and purify. Additions of the [4 + 2], [3 + 2], [2 + 2] and [1 + 2] type are all known, and involve reaction between an electron-rich addend and an electron-deficient “double bond” of the cage. 1,2-Addition across the double bonds is facilitated here since there is no steric effects because the two adding functions are connected. If an excess of reagent is used, then further addition may take place at remote sites on the cage, the preferred sites in [60]fullerene being octahedral because eight hexagonal rings of increased aromaticity are produced on the cage surface (77). A typical reaction is that between $Pt(PPh_3)_2$ and the octahedral sites of [60]fullerene, which gives rise to the structure shown in Figure 14. The location of the cycloaddend is shown as a Schlegel diagram (Fig. 15); in each figure the rings of increased aromaticity are denoted by a B.

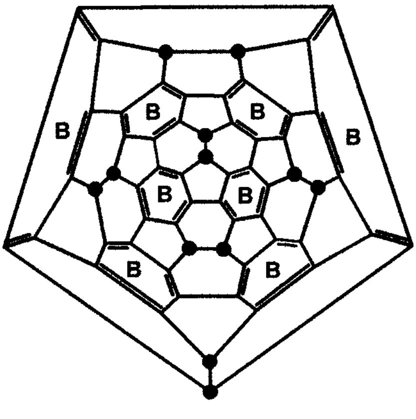


**Fig. 15.** Schlegel diagram showing the octahedral addition sites (denoted by •); rings marked B have enhanced aromaticity.

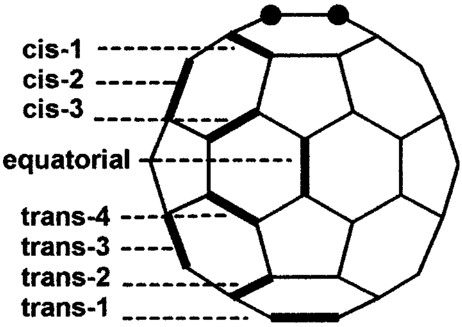


**Fig. 16.** Nomenclature system used to denote the sites of bis-addition to [60]fullerene.

Most cycloadditions do not continue until the hexa-adduct stage, and the majority of studies concern just the mono- and bis-addition products. For the latter, a nomenclature system has been devised to describe the eight derivatives (or nine if the addend is itself unsymmetrical). This system is shown in Figure 16, where the black circles indicate the first addition site (78).

Because cycloadditions are very numerous, only a few representative examples are shown:

1. **[1 + 2] Cycloadditions**. The most ubiquitous example here is the formation of epoxides that occur spontaneously. Because of the traces of oxygen in the arc-discharge apparatus used to make fullerenes, epoxides such as $C_{60}O$ (Fig. 17**a**) (79) are always present in the products.

   Nitrogen and carbon may also be added across a 6:6 bond giving the basic structures shown in Figure 17**b** and **c** (80,81), known as epimino- and methano-fullerenes, respectively. A wide range of compounds involving different R groups have been synthesized, and derivatives of other fullerenes are known.

   By different synthetic procedures, it is possible to obtain the corresponding compounds in which oxygen, nitrogen, and carbon have inserted into 6:5 bonds (Fig. 18**a–c**), and these are known as oxahomo-, azahomo-

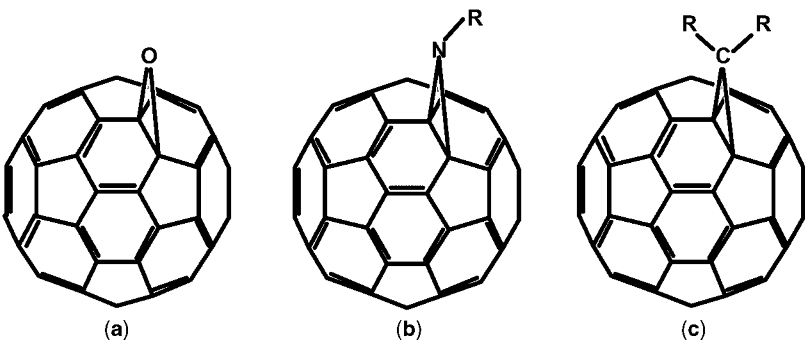


**Fig. 17.** Basic structures of (**a**) oxa-, (**b**) epimino- and (**c**) methano-[60]fullerenes.

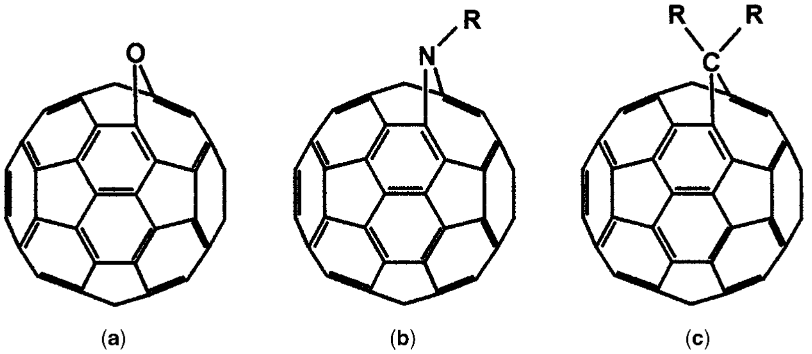


**Fig. 18.** Basic structures of (**a**) oxahomo-, (**b**) azahomo- and (**c**) homo-[60]fullerenes, respectively.

and homo-[60]fullerenes, respectively (82–84). Some of these derivatives of [70]fullerene are also known.

An important feature of the azahomofullerenes is that they are the starting materials for insertion of nitrogen in place of carbon in the cage to give an azafullerene; both aza[60]fullerene (Fig. 3) and two aza[70]fullerene isomers are known (85).

A particularly useful [1 + 2]cycloaddition is the Bingel reaction between a fullerene and a bromomalonate ester in the presence of a base (Fig. 19). The anion, formed by abstraction of hydrogen from the methylene group, attacks the cage, and this is followed by loss of bromine to give a methano[60]fullerene derivative, eg, that is shown in Figure 20 (86). This reaction has been very widely used for forming various derivatives, especially those in which substituted alkyl groups are directed toward carrying out further reactions at specific sites elsewhere on the cage; these are known as tether-directed reactions (87). In one unique case involving $C_{60}F_{18}$, the anion formed following hydrogen abstraction carries out nucleophilic replacement of fluorine, producing the only known example of an all-*trans* annulene; this contains 18π electrons in the annulene chain thereby conferring additional (aromatic) stability (88).

2. **[2 + 2] Cycloadditions**. These are the least common of the cycloadditions and being 4π electron processes are photocatalysed. A typical example

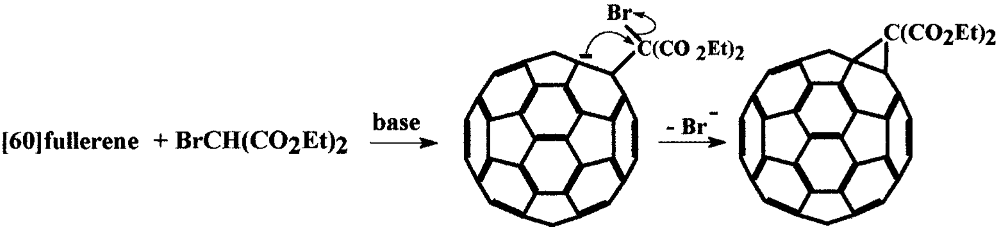


**Fig. 19.** Mechanism of the Bingel reaction.

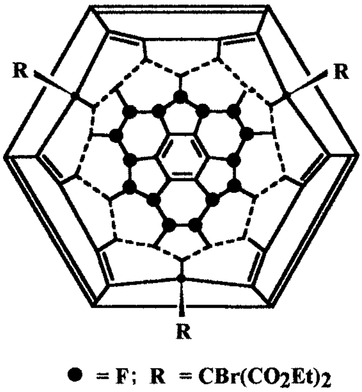


**Fig. 20.** Schlegel diagram of $C_{60}F_{15}[CBr(CO_2Et)_2]_3$; the dotted line denotes the 18 $\pi$ *trans*-annulene chain.

involves addition of electron-rich alkenes or alkynes to the cage (89); four-membered rings behave as incipient double bonds because of strain and these can likewise add (90). Figures 21 and 22 show an example of each type.

3. **[3 + 2] Cycloadditions**. This constitutes a very large class of reactions. One of the most extensively studied is the Prato reaction involving preformation *in situ* of an azomethine ylide ($CH_2{=}N^+R'CHR^-$, prepared from an aldehyde RCHO and an amino acid R'NH · $CH_2CO_2H$ (aminoacids $NH_2$-$CHRCO_2H$ may also be used), giving pyrrolidinofullerenes such as that shown in Figure 23 (91). Various other precursors, such as aziridines etc, can be used to form pyrrolidinofullerenes. These derivatives have been used in particular in investigations of potential light harvesting fullerenes.

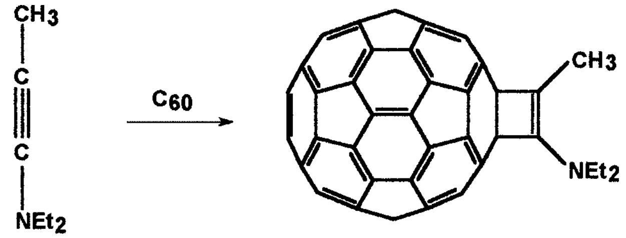


**Fig. 21.** Addition of an electron-rich alkene to [60]fullerene.

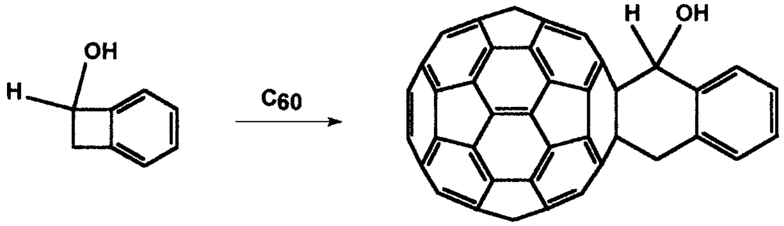


**Fig. 22.** Addition of a strained four-membered ring compound to [60]fullerene.

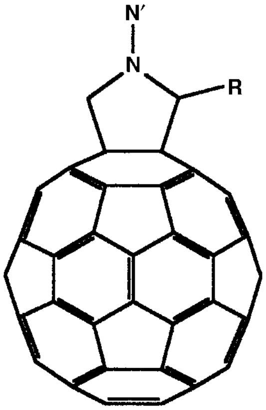


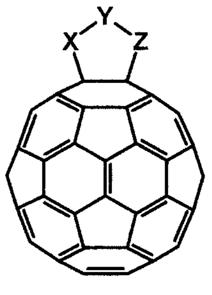
**Fig. 23.** A pyrrolidino[60]fullerene formed between an azomethine ylide and a [60]fullerene.

A wide range of compounds of the general type shown in Figure 24 have been made; these include pyrrolo-, pyrazolo-, isoxazolo-, oxazolo-, isothiazolo-, thiazolo-, furano-, and triazolo[60]fullerenes (92).

4. **[4 + 2] Cycloadditions**. This is another large class of reactions, which are basically Diels-Alder reactions. Simple examples include reaction with anthracene, bicyclopentadiene, and buta-1,3-dienes to give the compounds shown in Figure 25 (93); numerous derivatives have been made with different substituents in the addend group.

Many [4 + 2] cycloaddition products are formed through the use of *o*-quinodimethane intermediates obtained either by HBr loss from 1,2-bis(bromomethyl) arenes or by sulfur dioxide loss from either sulfones or sultines (Fig. 26**a–c**, respectively) (94). Some representative products are shown in Figure 27.

*Addition of Electrons (Reduction).* The ability of fullerene cages to accept electrons (to give radical anions) was noted in the Sect. Electron Affinities and Electrochemistry: Oxidation and Reduction. They are thus readily reduced by metals (95) and by organic donors (96), and may also be electrochemically



| X | Y | Z |
|---|---|---|
| O | N | C |
| O | C | N |
| C | N | C |
| N | N | C |
| C | S | N |
| N | C | S |
| C | O | C |
| N | N | N |

**Fig. 24.** Various heterocyclic derivatives that have been made by [2 + 3]cycloaddition; bonds between X, Y, and Z are variously double.

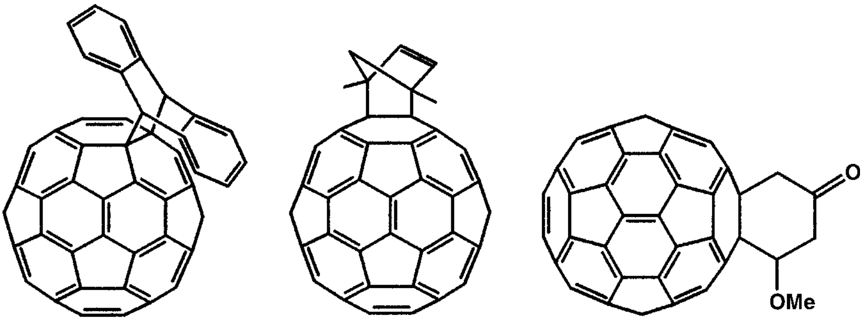


**Fig. 25.** Some derivatives of [60]fullerene, produced by [4 + 2]cycloaddition.

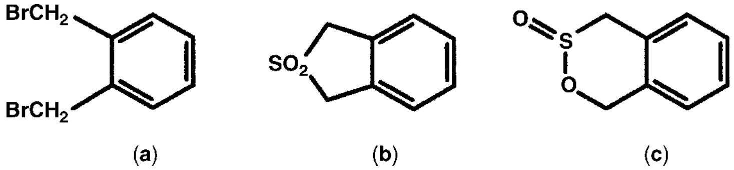


**Fig. 26.** Some precursors used in the preparation of [4 + 2]cycloadducts of [60]fullerene.

reduced (97). The number of electrons added can be controlled by varying the stoichiometric concentrations of the reagents or, in the case of electrochemical reduction, the reduction potential. In contrast to the parent fullerenes, the radical anions are soluble in tetrahydrofuran (THF) and are stable in this solvent for many days, which facilitates handling and subsequent reaction.

*Addition of Neutral Nucleophiles and Anions.* Among neutral nucleophiles, only amines are sufficiently nucleophilic to react with fullerenes. There are many examples of such additions. Typical examples are the reaction of 1,2-diamines to give derivatives such as those shown in Figure 28 (98).

As expected, negatively charged nucleophiles (anions) react more readily with fullerenes, and in particular organometallic reagents such as organolithiums and Grignard reagents; numerous of this kind reactions (which tend to give multiples of 10 addends attached to [60]fullerene) are known (99). A notable example is the reaction between lithium 9-fluorenide and [60]fullerene to yield the anionic product (Fig. 29), which is particularly stable because of the

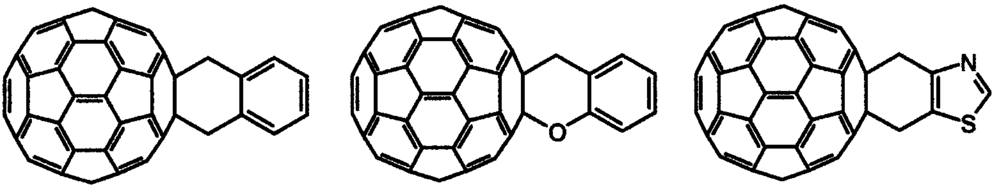


**Fig. 27.** Some [4 + 2]cycloaddition products from *o*-quinodimethane precursors.

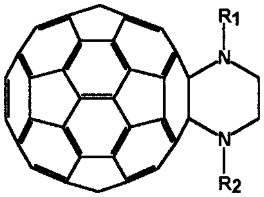


**Fig. 28.** 1,2-Diamino derivatives formed from [60]fullerene and 1,2-diamines.

presence of the central aromatic 6π pentagonal ring; a proton adds to the pentagon on reaction with acid (100).

Radical anions formed both by reduction and intermediate addition of negatively charged nucleophiles also may be reacted with electrophiles (such as alkyl cations), and this overcomes the problem that electrophiles are generally unreactive toward fullerenes. In this way, polyalkylated fullerenes have been isolated and characterized (101).

*Hydroxyfullerenes (Fullerenols).* Fullerenols are of particular interest because they are water soluble, and therefore have the potential to be used in biological applications of fullerenes. For example, they are potent scavengers of radicals, especially the superoxide radical anion $O_2^{\bullet -}$ (102) and show both DNA cleaving ability and toxicity toward tumor cells (103). Unusually, they are more soluble in acid solution than in base, and this may be due to tautomerism giving rise to hemiketals, etc.

Although they can be formed by reaction of the fullerene with hydroxide ion in the presence of *tert*-butylammonium hydroxide (104), the usual procedure involves nucleophilic substitution, and in particular the replacement of initially attached nitro and sulfonic acid groups by hydroxy groups (105), which leads to polyhydroxyfullerenes. Halogens can also be replaced, but generally less extensively.

A convenient method of making fullerenols is *via* hydroboration, and although this should lead to the addition of adjacent H and OH groups, the propensity for hydrofullerenes to oxidize to hydroxyfullerenes means that the reaction, if carried out in air, produces just polyhydroxyfullerenes (106).

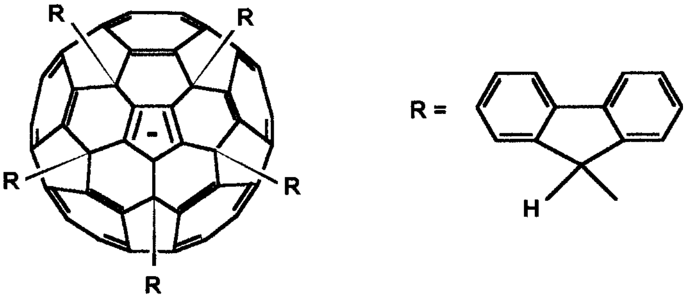


**Fig. 29.** The stable aromatic anion formed from [60]fullerene and lithium 9-fluorenide.

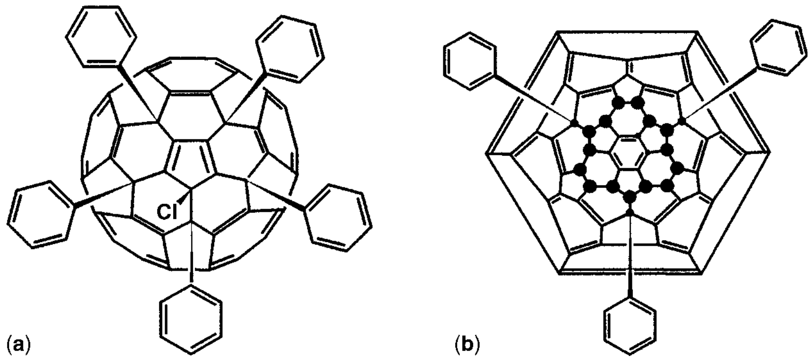


**Fig. 30.** (**a**) $C_{60}Ph_5Cl$; (**b**) Schlegel diagram of $C_{70}F_{15}Ph_3$ (● = location of F).

Progress has been made recently in isolating characterized 1,2-diols such as the 1,2-$(OH)_2C_{60}$, 1,2-$(OH)_2C_{70}$, and 5,6-$(OH)_2C_{60}$ and isomers of $C_{70}Ph_8(OH)_2$ (107).

*Nucleophilic Substitution; Halogenofullerenes as Electrophiles.* The electron-withdrawing property of fullerenes makes them good electrophiles. They will react with aromatics in the presence of Lewis acid catalysts, in the same way that alkenes in the presence of these catalysts produce alkylaromatics (108). However, this leads to lack of control of site location. The reaction with halogenoaromatics is preferred, since substitution occurs at the site occupied by the halogen. The electrophilicity of the cage is also increased by the halogen. Fluoro- and chloroaromatics have mostly been used, because they are reasonably soluble in aromatic solvents; bromofullerenes are very insoluble, but they can be used if generated *in situ* using a mixture of bromine, fullerene, and aromatic (109).

These feature among the most studied of fullerene reactions and in principle a very large range of derivatives can be made. A notable example is $C_{60}Ph_5Cl$ (Fig. 30**a**), made from the precursor $C_{60}Cl_6$ by reaction with benzene/$FeCl_3$ (110). The most hindered chlorine remains unsubstituted, though it can be replaced under more forceful conditions. A similar reaction of $C_{60}F_{18}$ yields $C_{60}F_{15}Ph_3$ (triumphene), which is shown as a Schlegel diagram in Figure 30**b** (111). in this diagram, it is the most accessible halogens that are replaced.

[70]Fullerene readily chlorinates to $C_{70}Cl_{10}$ and on reaction with benzene/$FeCl_3$ it yields a mixture mainly of $C_{70}Ph_{10}$ (Fig. 31**a**) and $C_{70}Ph_8$ (Fig. 31**b**) (112), but derivatives with fewer aryl groups and with one or more halogens replaced by hydroxy groups have also been isolated (113).

*Formation of Cations.* As noted in the Section Electron Affinities and Electrochemistry: Oxidation and Reduction, the strong electron withdrawal by the fullerene cages makes removal of electrons to form cations relatively difficult to achieve. It becomes easier with fullerenes that possess multiple addends, since the $sp^3$ hybridized carbons are less electronegative than the $sp^2$ carbons they replace. Since the aryl groups in the electrophilic aromatic substitutions described occupy the same site as the departing halogen, the intermediate formation of a carbocationic species is inferred, and is aided by the presence of the aryl

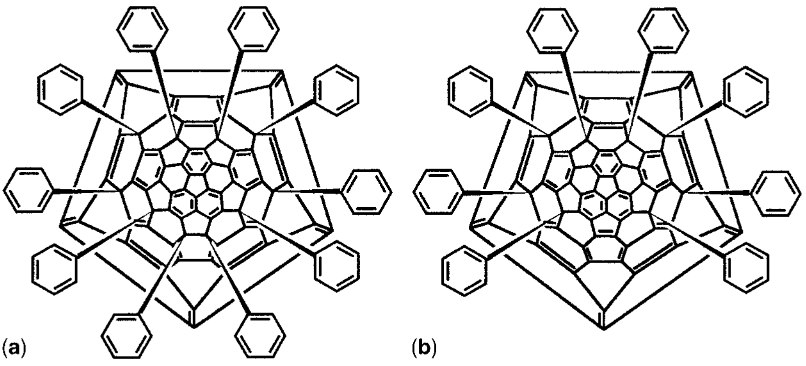


**Fig. 31.** (**a**) Schlegel diagram of $C_{70}Ph_{10}$; (**b**) Schlegel diagram of $C_{70}Ph_8$.

groups. One such species has been isolated from the reaction of $C_{60}Ph_5Cl$ with $AlCl_3$ and was characterized by $^{13}C$ NMR spectroscopy (114).

Radical cations (produced by removal of one electron from a double bond on the cage by oxidizing reagents) have also been obtained under various conditions. One has been isolated ($C_{76}^{\bullet+}$) by using an extremely unreactive nucleophilic counterion ($CB_{11}H_6Br_6^-$), so that recombination and destruction of the cation is unfavorable (115).

*Organometallic Derivatives.* Numerous derivatives of fullerenes have been made through combination with a metallic or organometallic group. In this way, derivatives have been made involving the elements osmium, iridium, rhodium, cobalt, platinum, palladium, nickel, iron, ruthenium, molybdenum, vanadium, tantalum, rhenium, and thallium. Most of these derivatives are unstable, but a major reason for their preparation is a desire to obtain single-crystal X-ray structures of the parent fullerenes. This is difficult in the absence of the heavy metallic addend because of disorder arising from the high speed of rotation of the fullerenes in the solid state (see the Section Bond Lengths and Structure). In some cases, the uses of organometallic fullerenes as hydrogenation catalysts have been explored briefly.

Some remarkable structures can result from the way in which the complexes pack in the crystal lattice. An example (Fig. 32) is that formed between

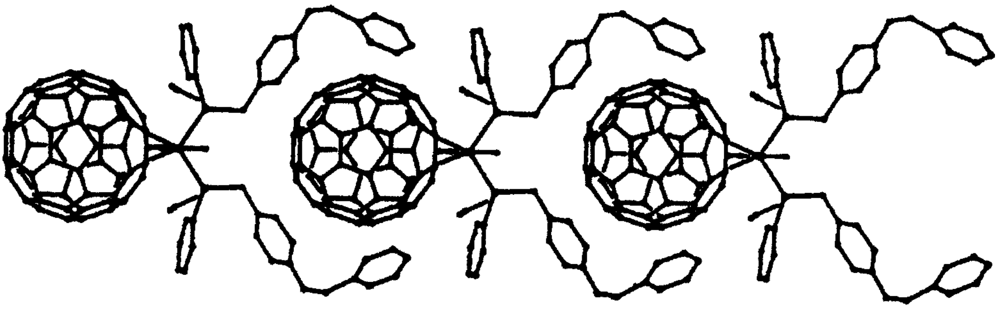


**Fig. 32.** Crystal lattice packing between [60]fullerene and a Vaska complex (see text).

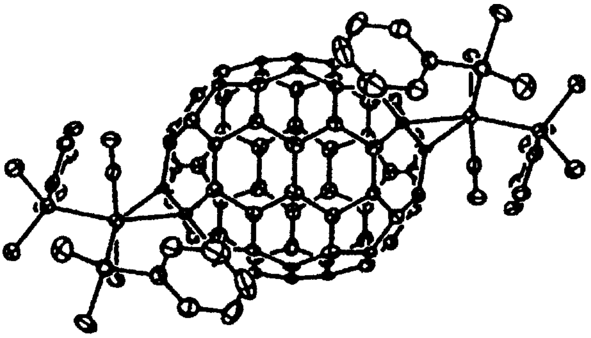


**Fig. 33.** Single-crystal X-ray structure of [70]fullerene$[IrCoCl(PMe_2Ph)_2]_2$.

a Vaska complex $[IrCOCl(PPh_2CH_2C_6H_4OCH_2Ph)_2]$ and [60]fullerene (116). Multiple additions are observed in many cases where this is not precluded by the size of the addend. An example involving addition of $IrCOCl(PMe_2Ph)_2$ to [70]fullerene is shown in Figure 33 (117).

The derivatives involve $\eta^-$-coordination to a double bond of the fullerene cage, with the exception of one example, which involves $\eta^{\pm}$-coordination between molybdenum tricarbonyl and the planar aromatic ring of $C_{60}F_{18}$ (118).

*Formation of polymers.* Polymers formed from fullerenes are superficially attractive because of the large number of sites on the cages to which chains may be attached, and the fullerene structures lend themselves to cross-linking. This latter perceived advantage can, however, also be a disadvantage because of the extreme insolubility that may result. Due to the high cost of fullerenes, all polymer research to date has been carried out with [60]fullerene only. The importance of cross-linking is seen on the addition of small amounts (1∼5 wt.%) of [60]fullerene to polyamides that produce an increase in viscosity, sheer modulus, and tenacity, reduction in the maximum elongation at the breaking load, and better resistance to breakage. The loading is, however, limited by the solubility of the fullerenes in the polymer melts (119).

Fullerene polymers are of three general types, and involve either:

1. Direct linkage between the fullerene cages (possibly together with a small spacer and in some cases with a two-bond linkage) eg, Figure 34. The example shown is one dimensional but may be either two or three dimensional giving *net* and *lattice* polymers, respectively. Because of the high cost

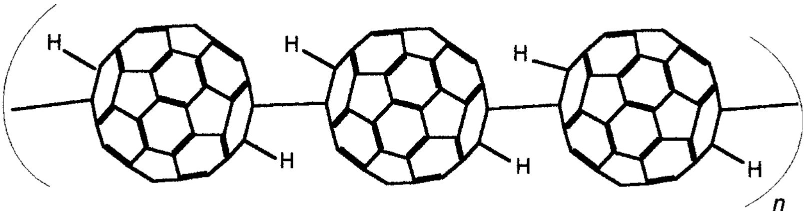


**Fig. 34.** Hypothetical “pearl necklace polymer” possessing single-bond linkages.

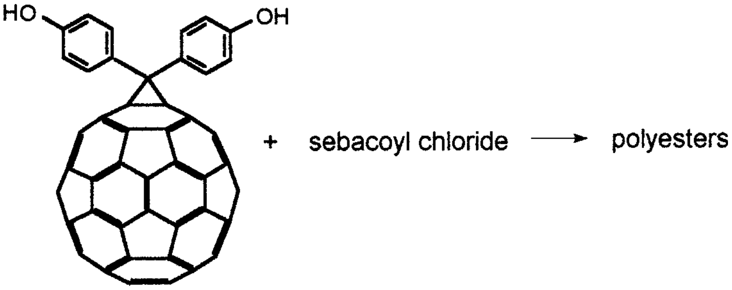


**Fig. 35.** Formation of a pendant chain polymer by condensation.

of fullerenes, there is little realistic prospect of such fullerene polymers becoming useful products. Moreover, they are extremely insoluble, and coupled with the difficulty of accurately determining their structures by mass and other spectroscopic techniques, makes it likely that they will remain largely academic curiosities.

2. Attachment of fullerenes along a normal polymer chain to give "pendant chain" polymers. In these, the fullerene may be incorporated either by initial attachment to one of the components that condense to give the polymer (Fig. 35) (120), or it may be substituted into a preformed polymer chain. Amino groups along the chain have been used to facilitate both attachment to the fullerene and improvement of solubility (121); ideally the fullerene should not exceed ~20 wt.% of the total.
3. Participation of the fullerene as a center of a net or lattice polymer in which the arms attached to the fullerene are polymer or copolymer chains that confer solubility. Polyhydroxyfullerenes have provided the central building blocks for some promising compounds of this type that have a narrow polydispersity (122). In these, the fullerene is the center of a "star", but an "inside-out" alternative involves a polymer as the central star, with fullerenes attached to the ends of the arms (123). Schematic representation of these two polymer types is shown in Figure 36.

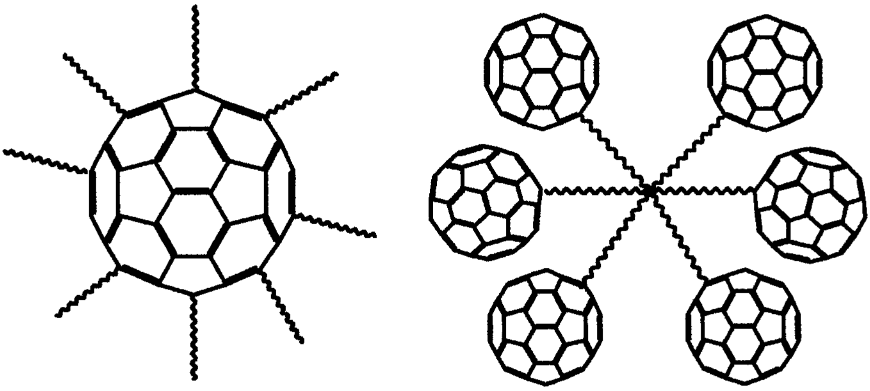


**Fig. 36.** Schematic representation of two types of fullerene star polymers.

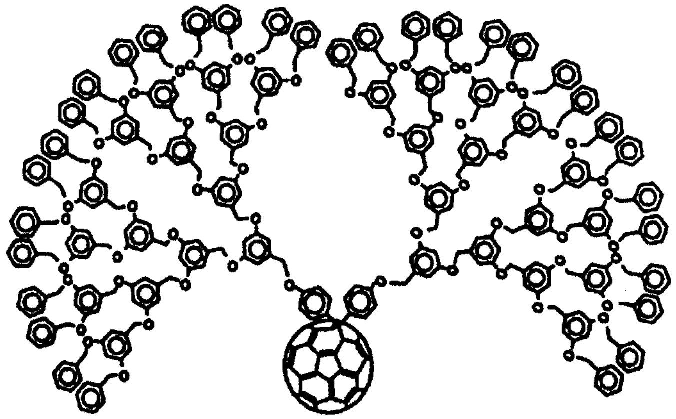


**Fig. 37.** A homofullerene dendrimer.

A close relation of the star polymers are the dendritic polymers or dendrimers. Here also the fullerene cores are unable to associate with each other because of the steric constraints, so that these compounds have good solubility. Furthermore they may be shielded against oxidation, a significant problem with fullerenes and derivatives. Figure 37 shows one such dendrimer (derived from homo[60]fullerene) (124).

*Formation of Dimers, Dumbbells, and Ball and Chains.* Only [60]fullerene has been used in making these structures. The simplest dimers are $C_{120}$ and $C_{120}O$ shown in Figures 4**a** and 6, respectively. Numerous dumbbell structures have been made. Two representative examples are shown in Figure 38**a** and **b** (125); many different spacers between the cages have been employed.

The term "ball and chain" is given to structures in which a chain, often very complex, is attached to one fullerene cage. Some of these have been constructed in order to determine if there is any electronic interaction between the cage and the tail of the chain (63). A typical example is shown in Figure 39 (126).

*Chemistry of Heterofullerenes.* This chemistry is confined mainly to reactions of aza[60]fullerene. Reduction of $(C_{59}N)_2$ by tributyl tin hydride gives $C_{59}NH$ (24), fluorination by $K_2PtF_6$ gives $C_{59}NF$ (127), and various aryl derivatives $C_{59}NAr$ have been made by electrophilic substitution of the azafullerene into aromatics (128). The structure of these derivatives is shown in Figure 40**a** (● = H, F, Ar, respectively). Chlorination of $ArC_{59}N$ by ICl (129), hydrogenation

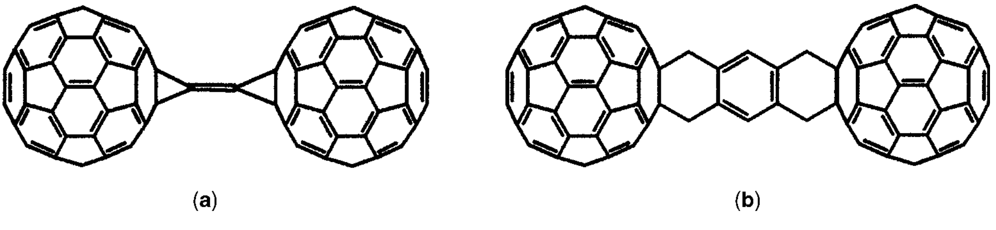


**Fig. 38.** Examples of dumbbells formed from [60]fullerene.

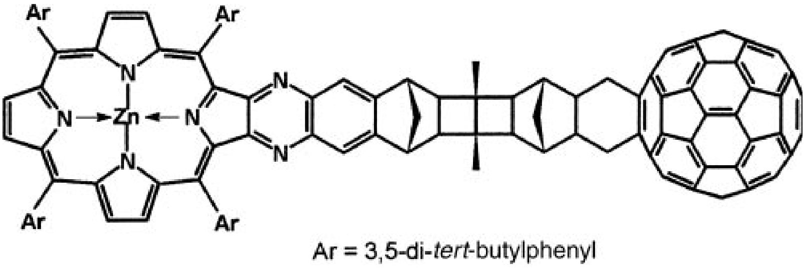


**Fig. 39.** A [60]fullerene ball with a porphyrin tail.

by Zn/HCl, and fluorination by $K_2PtF_6$ (127) yields isostructural $C_{59}NCl_4Ar$, $C_{59}NH_5$, and $C_{59}NF_5$, respectively [Fig. 40**b** $\bullet = Cl(Ar)$, H, and F]. These latter structures have high stability because a 6π aromatic ring is created by the addition.

More vigorous fluorination yields $C_{59}NF_{33}$, the conjectured structure that is given in Figure 41 (127). This structure is based upon the *T*-symmetry structure for $C_{60}F_{36}$ and is stable because of the 10π aromatic central ring (shown in dotted outline in Fig. 40).

*Chemistry of Incarfullerenes (Endohedral Fullerenes).* The low availability and instability of those compounds that contain metals means that very little chemistry has yet been undertaken. *i*$LaC_{82}$ reacts with diphenyldiazomethane but the nature of the products and also those from reaction with disilirane and digermane are uncertain (130,131).

Fullerenes containing noble gases have been prepared, and those containing $^3He$ are of particular significance because it is then possible to study the $^3He$ NMR of derivatives (132). In general, the chemical shifts of the peaks are related to the location of addends rather than their type. Addition to [60]fullerene generally increase the aromaticity, whereas addition to [70]fullerene decreases it, and the greater the addition level the greater the shift (133). This technique has been used to aid identification of the products of reaction of the corresponding empty fullerenes. It has been used, eg, to show that hydrogenation and fluorination of [60]fullerene yields isostructural products (134) (Fig. 41).

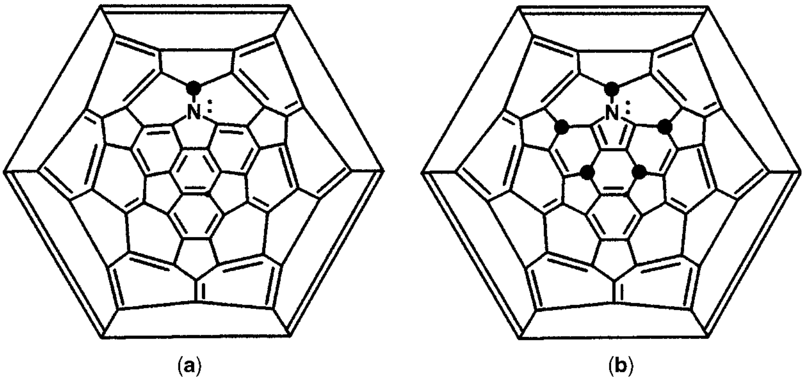


**Fig. 40.** Structures of (**a**) $C_{59}NR$ ($\bullet$ = H, F, Ar) and (**b**) $C_{59}NR_5$ [$\bullet$ = Cl/Ar, H, F) (see text).

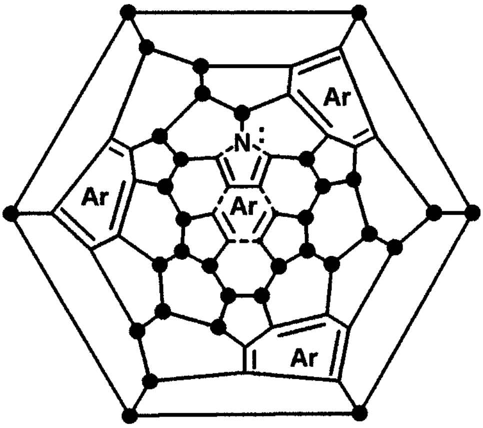


**Fig. 41.** Conjectured structure of $C_{59}$ $NF_{33}$; the five-membered ring containing the N and the adjacent hexagon comprise a 10 π aromatic system.

## CITED PUBLICATIONS

1. T. G. Schmalz, W. A. Seit, D. J. Klein, and G. E. Hite, *J. Am. Chem. Soc.* **110**, 1113 (1988); H. W. Kroto, *Nature (London)* **329**, 529 (1987).
2. E. A. Rohlfing, D. M. Cox, and A. Kaldor, *J. Chem. Phys.* **81**, 3322 (1984).
3. K. M. Kadish and R. S. Ruoff, eds., *Fullerenes, Chemistry, Physics and Technology*, John Wiley, & Sons, Inc. Chichester, U.S., 2000.
4. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature (London)* **318**, 162 (1985).
5. E. Osawa, *Kagaku* **25**, 654 1970; Z. Yoshida, and E. Osawa, *Aromaticity*, Kagakudojin, Kyoto, 1971, pp 174, 175.
6. D. A. Bochvar and E. G. Gal'pern, *Proc. Acad. Sci. USSR* **209**, 239 (1973).
7. W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. Huffman, *Nature (London)* **347**, 354 (1990).
8. R. Taylor, J. P. Hare, A. K. Abdul-Sada, and H. W. Kroto, *J. Chem. Soc., Chem. Commun.* 1423 (1990).
9. J. B. Howard, J. T. McKinnon, Y. Makarovsky, A. L. Lafleur, and M. E. Johnson, *Nature (London)* **352**, 139 (1991).
10. R. Taylor, G. J. Langley, H. W. Kroto, and D. R. M. Walton, *Nature (London)* **366**, 729 (1993); R. Taylor, and G. J. Langley, *Proc. Electrochem. Soc.* **24**, 68 (1994).
11. T. W. Ebbesen and P. M. Ajayan, *Nature (London)* **358**, 220 (1992).
12. J. E. Baggott, *Perfect Symmetry*, OUP, (1994); H. Aldersley-Williams, *The Most Beautiful Molecule*, Aurum, London, 1995; M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Nanotubes*, Academic Press, New York, 1996.
13. R. Taylor, *Lecture Notes on Fullerene Chemistry; A Handbook for Chemists*, Imperial College Press, London, 1999.
14. Y. Chai and co-workers, *J. Phys. Chem.* **95**, 7564 (1991).
15. M. M. Olmstead and co-workers, *J. Am. Chem. Soc.* **122**, 12220 (2000).
16. M. Takata and co-workers, *Nature (London)* **377**, 46 (1995).
17. M. Saunders and co-workers, *Science* **271**, 1693 (1996).
18. B. Pietzak and co-workers, *Chem. Phys. Lett.* **279**, 259 (1997).
19. D. Ugarte, *Nature (London)* **359**, 707 (1992).

20. K. Yamada, H. Kunishige, and A. B. Sawaoka, *Naturwissenschaften* **78**, 450 (1991); N. Hatta, and K. Murata, *Chem. Phys. Lett.* **217**, 398 (1994); V. L. Kuznetsov and co-workers, *Chem. Phys. Lett.* **222**, 343 (1994); K. D. Chowdhury, J. B. Howard, and J. B. Van der Sande, *J. Mater. Res.* **11**, 341 (1996).
21. F. Banhart and P. M. Ajayan, *Nature (London)* **382**, 433 (1996).
22. T. Guo, C. Jin, and R. E. Smalley, *J. Phys. Chem.* **95**, 4948 (1991); B. Cao and co-workers, *Fullerene Sci. Technol.* **6**, 639 (1998).
23. J. C. Hummelen and co-workers, *Science* **269**, 1554 (1995); B. Nuber, and A. Hirsch, *Chem. Commun.*, 1421 (1996).
24. M. Keshavarz-K and co-workers, *Nature (London)* **383**, 147 (1996).
25. C. Moschel and M. Jansen, *Z. Anorg. Allg. Chem.* **625**, 175 (1996).
26. A. Hirsch and B. Huber, *Acc. Chem. Res.* **32**, 795 (1999); F. Hauke and A. Hirsch, *Tetrahedron* **57**, 3697 (2001).
27. Y. Rubin, *Chem. Eur. J.* **3**, 1009 (1997).
28. S. Iijima, *Nature (London)* **354**, 56 (1991).
29. S. Iijima, and T. Ichihashi, *Nature (London)* **363**, 603 (1993); D. S. Bethune, and co-workers, Nature (London) **363**, 603 (1993); T. Guo and co-workers, *Chem. Phys. Lett.* **243**, 49 (1995).
30. K. D. Chowdhury J. B. Howard, and J. B. Van der Sande, *J. Mater. Res.* **11**, **341** (1996).
31. M. Endo and co-workers, *Carbon* **33**, 873 (1995).
32. S. Amelinckx and co-workers, *Science* **265**, 635 (1994).
33. G.-W. Wang, K. Komatsu, Y. Murata, and M. Shiro, *Nature (London)* **387**, 583 (1997); A. Gromov and co-workers, *Chem. Phys. Lett.* **267**, 460 (1997).
34. A. R. Kortan and co-workers, *Nature (London)* **355**, 529 (1992).
35. P. W. Stephens and co-workers, *Nature (London)* **351**, 632 (1991).
36. A. Dworkin and co-workers, *Compt. Rend. Acad. Sci. Series II* **312**, 979 (1991); **313**, 1017 (1991).
37. C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, and J. R. Salem, *J. Phys. Chem.* **95**, 9 (1991); R. Tycko and co-workers, *J. Phys. Chem.* **95**, 518 (1991).
38. R. Taylor, *Tetrahedron Lett.* 3731 (1991); *J. Chem. Soc., Perkin Trans. 2*, 3 (1992).
39. C. S. Yannoni and co-workers, *J. Am. Chem. Soc.* **113**, 437 (1991); W. I. F. David and co-workers, *Nature (London)* **353**, 147 (1991); K. Hedberg and co-workers, *Science* **254**, 410 (1991).
40. G. B. Vaughan and co-workers, *Science* **254**, 1350 (1991); M. A. Verheijen and co-workers, *Chem. Phys.* **166**, 287 (1992).
41. M. K. Korobov and A. L. Smith in Ref. 3, pp. 53–90.
42. I. Lamparth and A. Hirsch, *J. Chem. Soc., Chem. Commun.* 1727 (1994).
43. H.-D. Beckhaus and co-workers, *Angew. Chem. Intl. Edn. Engl.* **33**, 996 (1994); H. P. Diogo, *J. Chem. Soc., Faraday Trans.* **89**, 3541 (1993).
44. V. Piacente, C. Palchetti, G. Gigli, and P. Scardala, *J. Phys. Chem.* **101**, 4303 (1997), and references therein.
45. T. Arai and co-workers, *Solid State Commun.* **84**, 827 (1992).
46. R. Taylor, M. P. Barrow, and T. Drewello, *Chem. Commun.* 2497 (1998).
47. R. Taylor and co-workers, *Nature (London)* **351**, 277 (1991).
48. R. Malhotra, S. Kumar, and A. Satyam *J. Chem. Soc., Chem. Commun.* 1339 (1994); D. Heyman, and L. P. F. Chibante, *Recl. Trav. Chim. Pays-Bas* **112**, 531, 639 (1993).
49. I. Gilmour, J. P. Hare, H. W. Kroto, and R. Taylor, *Lunar Planet Sci. Conf. XXII* 445 (1991); M. Gevaert, and P. M. Kamat, *J. Chem. Soc., Chem. Commun.* 1470 (1992); H. S. Chen, A. R. Kortan, R. C. Haddon, and D. A. Fleming, *J. Phys. Chem.* **96**, 1016 (1992).
50. O. V. Boltalina, E. V. Dashkova, and L. N. Sidorov, *Chem. Phys. Lett.* **256**, 253 (1996).

51. R. Hettich, C. Jin, and R. N. Compton, *Int. J. Mass Spectrosc. Ion Proc.* **138**, 26 (1994).
52. Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.* **114**, 11004 (1992).
53. Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.* **114**, 3978 (1992).
54. A. D. Darwish, H. W. Kroto, R. Taylor, and D. R. M. Walton, *Fullerene Sci. Technol.* **1**, 571 (1993).
55. R. C. Haddon, L. E. Brus, and K. Raghavachari, *Chem. Phys. Lett.* **125**, 459 (1986).
56. Y. Yang and co-workers, *J. Am. Chem. Soc.* **117**, 7801 (1995).
57. R. Subramanian and co-workers, *J. Phys. Chem.* **100**, 16327 (1996).
58. J. P. Hare and co-workers, *J. Chem. Soc., Chem. Commun.* 412 (1991); R. Taylor and co-workers, *Spectrochim Acta* 1289, **47A**, (1991).
59. J. P. Hare, H. W. Kroto, and R. Taylor, *Chem. Phys. Lett.* **177**, 394 (1991); Z. Gasyna and co-workers, *Chem. Phys. Lett.* **183**, 283 (1991); S. Leach and co-workers, *Chem. Phys.* **160**, 451 (1992).
60. A. Hirsch, T. Grösser, A. Siebe, and A. Soi, *Chem. Ber.* **126**, 1061 (1993).
61. T. Kitagawa, T. Tanaka, Y. Tanaka, and K. Komatsu, *J. Org. Chem.* **60**, 1490 (1995); R. González and co-workers, *J. Org. Chem.* **61**, 5837 (1996).
62. R. M. Fleming and co-workers, *Nature (London)* **352**, 787 (1991); K. Tanigaki and co-workers, *Nature (London)* **352**, 222 (1991); T. T. M. Palstra and co-workers, *Solid State Commun.* **93**, 327 (1995).
63. N. Martin, L. Sánchez, B. Illescas, and I. Pérez, *Chem. Rev.* **98**, 2527 (1999); J. L. Segura and N. Martin, *J. Mater. Chem.* **10**, 2403 (2000); D. M. Guldi, *Chem. Commun.* 321 (2000); D. M. Guldi and M. Prato, *Acc. Chem. Res.* **33**, 695 (2000).
64. P. W. Fowler, J. B. Sandall, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2* 419 (1997); O. V. Boltalina and co-workers, *J. Chem. Soc., Perkin Trans. 2.* 1475 (1999); 251 (2002) O. V. Boltalina, A. Yu. Lukonin, J. M. Street, and R. Taylor, *Chem .Commun.* 1601 (2000).
65. R. Taylor, *Lecture Notes on Fullerene Chemistry; A Handbook for Chemists*, Imperial College Press, 1999, pp. 42–44.
66. A. G. Avent and co-workers, *J. Chem. Soc., Perkin Trans. 2*, 15 (1994).
67. I. S. Neretin, *Angew. Chem., Int. Ed. Engl.* **39**, 3273 (2000).
68. A. A. Gakh and co-workers, *J. Am. Chem. Soc.* **116**, 819 (1994).
69. S. I. Troyanov and co-workers, *Angew. Chem. Int. Ed. Engl.* **40**, 2285 (2001).
70. P. R. Birkett and co-workers, *Nature (London)* **357**, 479 (1992); F. N. Tebbe and co-workers, *J. Am. Chem. Soc.* **113**, 9900 (1991); *Science* **256**, 822 (1992).
71. P. R. Birkett and co-workers, *J. Chem. Soc., Chem. Commun.* 1230 (1993).
72. G. A. Olah and co-workers, *J. Am. Chem. Soc.* **113**, 9385 (1991).
73. H. Al-Matar and R. Taylor, *Recent Ad. Chem. Phys. Fullerenes Related Mater.* **7**, 163 (1999); H. Al-Matar and co-workers *J. Chem. Soc., Perkin Trans. 2*, 53 (2002).
74. X. Gao, E. van Caemelbecke, T. Suenoba, and S. Fukuzumi, *J. Am. Chem. Soc.* **122**, 563 (2000).
75. P. R. Birkett and co-workers, *J. Chem. Soc., Chem. Commun.* 683 (1995).
76. H. Al-Matar and co-workers, *J. Chem. Soc., Perkin Trans. 2*, 1251 (2002).
77. R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1667 (1992) P. W. Fowler, D. J. Collins, and S. J. Austin, *J. Chem. Soc., Perkin Trans. 2*, 275 (1993).
78. A. Hirsch, I. Lamparth, and H. R. Karfunkel, *Angew. Chem. Intl. Ed.* **33**, 437 (1994).
79. K. M. Creegan and co-workers, *J. Am. Chem. Soc.* **114**, 1103 (1992).
80. A. B. Smith, and H. Tokuyama, *Tetrahedron* **52**, 5257 (1996); G. Schick, T. Grösser, and A. Hirsch, *J. Chem. Soc., Chem. Commun.* 2289 (1995).
81. T. Suzuki, Q. Li, K. C. Khemani, F. Wudl, and Ö. Almarsson, *Science* **254**, 1186 (1991).
82. O. V. Boltalina, *Chem. Commun.* 1325 (2000).

83. M. Prato, Q. C. Li, F. Wudl, and V. Lucchini, *J. Am. Chem. Soc.* **115**, 1148 (1993).
84. A. B. Smith and co-workers, *J. Am. Chem. Soc.* **115**, 5829 (1993).
85. B. Nuber and A. Hirsch, *Fullerene Sci. Technol.* **4**, 715 (1996); C. Bellavia-Lund and F. Wudl, *J. Am. Chem. Soc.* **119**, 943 (1997).
86. C. Bingel, *Chem. Ber.* **126**, 1957 (1993); C. Bingel and H. Schiffer, *Liebigs Ann. Chem.* 1551 (1995).
87. J. Nierengarten, V. Gramlich, F. Carullo, and F. Diederich, *Angew. Chem. Intl. Ed. Engl.* **35**, 2101 (1996).
88. X.-W. Wei and co-workers, *Angew. Chem. Intl. Ed.* **40**, 3077 (2001); *J. Chem. Soc., Perkin Trans. 2*, 41 (2002).
89. X. Zhang, A. Romero, and C. S. Foote, *J. Am. Chem. Soc.* **115**, 11024 (1993); X. Zhang, A. Fan, and C. S. Foote, *J. Org. Chem.* **61**, 5456 (1996).
90. X. Zhang and C. S. Foote, *J. Org. Chem.* **59**, 5235 (1994).
91. M. Maggini, G. Scorrano, and M. Prato, *J. Am. Chem. Soc.* **115**, 9798 (1993); M. Prato and co-workers, *Tetrahedron* **52**, 5221 (1996).
92. Ref. 65, pp. 172–176.
93. J. A. Schleuter and co-workers, *J. Chem. Soc., Chem. Commun.* 972 (1993); K. Komatsu and co-workers *Tetrahedron Lett.* **34**, 8473 (1993); B. Kräutler and M. Puchberger, *Helv. Chim. Acta* **76**, 1626 (1993); L. S. K. Pang and M. A. Wilson, *J. Phys. Chem.* **97**, 6761 (1993); V. M. Rotello and co-workers, *Tetrahedron Lett.* **34**, 1561 (1993).
94. P. Belik, A. Gügel, J. Spickermann, and K. Müllen, *Angew. Chem. Intl. Edn. Engl.* **32**, 78 (1993); M. Walter and co-workers, *Fullerene Sci. Technol.* **4**, 101 (1996); B. M. Illescas and co-workers, *Tetrahedron Lett.* **36**, 8307 (1995); *J. Org. Chem.* **62**, 7585 (1997).
95. J. W. Bausch and co-workers, *J. Am. Chem. Soc.* **113**, 3205 (1991); P. Boulas and co-workers, *J. Electrochem. Soc.* **140**, L130 (1993); M. Wu, X.-W. Wei, L. Qi, and Z. Xu, *Tetrahedron Lett.* 7409 (1996).
96. A. Pénicaud and co-workers *J. Am. Chem. Soc* **113**, 6698 (1991); J. Stinchcombe and co-workers, *J. Am. Chem. Soc.* **115**, 5212 (1993).
97. D. Dubois, K. M. Kadish, S. Flanagan, and L. J. Wilson, *J. Am. Chem. Soc.* **113**, 7773 (1991); Y. Ohsawa and T. Saji, *J. Chem. Soc., Chem. Commun.* 781 (1992); Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.* **114**, 3978 (1992).
98. K. Kampe, N. Egger, and M. Vogel, *Angew. Chem. Intl. Ed. Engl.* **32**, 1174 (1993).
99. F. Wudl in W. E. Billups, and M. A. Ciufolini, eds., *Buckminsterfullerenes*, VCH, 1993; P. Ya. Bayushkin, G. A. Domrachev, V. L. Karnatsevich, and R. Taylor, unpublished work; A. Hirsch, A. Soi, and H. S. Karfunkel, *Angew. Chem. Intl. Ed. Engl.* **31**, 766 (1992); P. J. Fagan and co-workers, *J. Am. Chem. Soc.* **114**, 9697 (1992).
100. Y. Murata, K. Komatsu, and T. S. M. Wan, *Tetrahedron Lett.* **37**, 7061 (1996); Y. Murata, M. Shiro, and K. Komatsu, *J. Am. Chem. Soc.* **119**, 8117 (1997).
101. C. Caron and co-workers, *J. Am. Chem. Soc.* **115**, 8505 (1993); K. M. Kadish and co-workers, *J. Am. Chem. Soc.* **122**, 563 (2000); S. Miki, M. Kitao, and K. Fukunishi, *Tetrahedron Lett.* **37**, 2049 (1996).
102. L. Y. Chiang, F. Lu, and J. Lin, *J. Chem. Soc., Chem. Commun.* 1283 (1995).
103. E. Nakamura and co-workers, *Bull. Chem. Soc. Jpn.* **69**, 2143 (1996).
104. J. Li and co-workers, *J. Chem. Soc., Chem. Commun.* 1784 (1993).
105. L. Y. Chiang and co-workers, *J. Chem. Soc., Chem. Commun.* 1791 (1992); *J. Org. Chem.* **59**, 3960 (1994); L. Y. Chiang, R. B. Upasani, and J. Swirczewski, *J. Am. Chem. Soc.* **114**, 10154 (1992).
106. N. S. Schneider and co-workers, *J. Chem. Soc., Chem. Commun.* 463 (1994).
107. P. R. Birkett and co-workers, *J. Chem. Soc., Perkin Trans. 2*, 68 (2001); M. S. Meier and J. Kiegiel, *Org. Lett.* **3**, 1717 (2001).

108. R. Taylor, *Electrophilic Aromatic Substitution*, John Wiley & Sons, Inc., Chichester, U.K., pp. 202–203.
109. S. H. Hoke and co-workers, *Rapid Commun. Mass Spectr.* **5**, 472 (1991).
110. A. G. Avent and co-workers, *J. Chem. Soc., Chem. Commun.* 1463 (1994).
111. O. V. Boltalina, J. M. Street, and R. Taylor, *Chem. Commun.* 1827 (1998).
112. A. G. Avent and co-workers, *Tetrahedron* **52**, 5235 (1996).
113. P. R. Birkett and co-workers, *Chem. Commun.* 1231 (1996); *J. Chem. Soc., Perkin Trans. 2*, 68 (2001).
114. A. G. Avent and co-workers, *Chem. Commun.* 2153 (1998).
115. R. D. Bolskar, R. S. Mathur, and C. A. Reed, *J. Am. Chem. Soc.* **118**, 13093 (1996).
116. A. L. Balch, V. J. Catalano, J. W. Lee, and M. M. Olmstead, *J. Am. Chem. Soc.* **114**, 5455 (1992).
117. A. L. Balch, J. W. Lee, and M. M. Olmstead, *Angew. Chem. Intl. Ed Engl.* **31**, 1356 (1992).
118. M. Francis, O. V. Boltalina, J. F. Nixon, and R. Taylor, unpublished work.
119. S. Shi, K. C. Khemani, Q. Li, and F. Wudl, *J. Am. Chem. Soc.* **114**, 10656 (1992).
120. Y. Wang, *Nature (London)* **356** (1992) 585; Y. Wang and co-workers, *The Chemical Physics of Fullerenes 10 (and 5) Years Later*, W. Andreoni, ed., *NATO ASI Series* **316**, (1995), p. 329.
121. N. Manalova, I. Rashkov, F. Beguin, and H. van Damme, *J. Chem. Soc., Chem. Commun.* 3850 (1993); K. E. Geckeler and A. Hirsch, *J. Am. Chem. Soc.* **115**, 3850 (1993); A. O. Patil, G. W. Schriver, B. Carstensen, and R. D. Lundberg, *Polym. Bull.* **30**, 187 (1993).
122. L. Y. Chiang and co-workers, *J. Chem. Soc., Chem. Commun.* 2675 (1994); L. Y. Chiang, L. Y. Wang, and C. Kuo, *Macromolecules* **28** (1995) 7574; S. Tseng and co-workers, *Fullerene Sci. Technol.* **5**, 1313 (1997).
123. E. Cloutet, Y. Gnanou, J. Fillaut, and D. Astruc, *Chem. Commun.* 1565 (1996).
124. K. L. Wooley and co-workers, *J. Am. Chem. Soc.* **115**, 9836 (1993).
125. J. Osterodt and F. Vögtle, *Chem. Commun.* 547 (1996); P. Belik, A. Gögel, J. Spikermann, and K. Müllen, *Angew. Chem. Intl. Ed. Engl.* **32**, 78 (1993).
126. M. G. Ranisinghe and co-workers, *Tetrahedron Lett.* **37**, 4797 (1996).
127. R. Taylor and co-workers, *Recent Adv. Chem. Phys. Fullerenes Related Mater.* **7**, 462 (1999); **10**, 0000 (2002).
128. B. Nüber and A. Hirsch, *Chem. Commun.* 405 (1998).
129. U. Reuther and A. Hirsch, *Chem. Commun.* 1401 (1998).
130. T. Suzuki and co-workers, *J. Am. Chem. Soc.* **117**, 9606 (1995).
131. T. Akasaka and co-workers, *Nature (London)* **374**, 600 (1995); *J. Chem. Soc., Chem. Commun.* 1343 (1995); *Tetrahedron* **52**, 5015 (1996).
132. M. Saunders and co-workers, *J. Am. Chem. Soc.* **116**, 2193 (1994); M. Saunders, H. A. Jiménez- Vázquez, R. J. Cross, and R. J. Poreda, *Science* **259**, 1428 (1993).
133. A. B. Smith and co-workers, *J. Am. Chem. Soc.* **116**, 10831 (1994); M. Saunders and co-workers, *Science* **271**, 1693 (1996); R. J. Cross and co-workers, *J. Am. Chem. Soc.* **118**, 11454 (1996); M. Rüttiman and co-workers, *Chem. Eur. J.* **3**, 1071 (1997).
134. O. V. Boltalina and co-workers, *J. Chem. Soc., Perkin Trans 2.* 1475 (1999).

ROGER TAYLOR
University of Sussex