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The fullerenes — new allotropic forms of carbon: molecular and electronic structure, and chemical properties

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Contents

I.	Introduction	419
II.	Topological and metric characteristics of polyhedral carbon clusters	420
III.	Quantum chemistry of the fullerenes	421
IV.	Mechanism of formation of the fullerenes and of endohedral complexes	428
V.	Classification of the forms of carbon with a regular structure	429
VI.	Chemical properties of carbon clusters	430
VII.	Conclusions	433

Abstract. In the early 1970s Osawa (and also Bochvar and Gal'pern) theoretically discussed the possibility of the existence of polyhedral carbon clusters, and predicted some of their properties. In 1985 it was established by spectral methods that carbon clusters containing an even number of atoms (mainly C_{60} and C_{70}) are formed under certain conditions when graphite is evaporated under the influence of laser radiation. These discoveries stimulated extensive studies of the synthesis of polyhedral carbon clusters of various molecular masses, and descriptions of their molecular and electronic structure and of their chemical properties. The most important results achieved in these areas of research are reviewed. The bibliography contains 194 references.

I. Introduction

A remarkable discovery in the chemistry of one of the best known of all the elements (carbon) was reported during the late 1980s. A group of workers, including Kroto (UK, Sussex University) and Heath, O'Brien, Curl, and Smalley (USA, Rice University),[1] studied the mass spectra or graphite vapour obtained by laser irradiation of a solid sample and observed peaks corresponding to masses 720 and 840. They suggested that these peaks correspond to the individual molecules C_{60} and C_{70}, and that the C_{60} molecule is a truncated icosahedron with an I_h symmetry while C_{70} is a more extended structure with an ellipsoidal (D_{5h}) symmetry type (Figures 1 and 2). This paper was followed by a report[2] of the observation of a peak with $m/e = 859 = (720 + 139)$ in the mass spectrum of the vapour of graphite doped with La atoms, from which it was concluded that the internal cavity of the spheroidal C_{60} molecule can incorporate a lanthanum atom with formation of the endohedral La @ C_{60} complex. Both these hypotheses were subsequently confirmed quite unambiguously.

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Polyhedral carbon clusters were called fullerenes [and their prototype, C_{60}, buckminsterfullerene (BF)] from the name of the distinguished American architect Richard Buckminster Fuller (1895–1983).† The publication of these results stimulated wide-ranging studies of the spectroscopic and other physical properties of the structure of fullerene[3] clusters.

The next step forward was taken in 1990 by Krätschmer, Lamb, Fostiropoulos, and Huffman,[4] who developed a method of preparing gramme quantities of carbon clusters by burning graphite electrodes in an electric arc in a helium atmosphere at an optimised (subatmospheric) pressure. In a study of the preparative conditions of carbon clusters in specific assemblies it was shown that the deposited soot contains a mixture of these clusters, which can be separated by extraction. As reported,[5–7] the content of carbon clusters can vary between 3% and 44%. The most selective method of separating the carbon clusters is by successive extraction with different solvents.[5] The clusters isolated in this way included molecules containing up to 200 carbon atoms. The ratio of the main components (C_{60}/C_{70}) is usually $(80 \pm 5)/(20 \pm 5)$. Approximately 1% of the graphite black consists of the heavier clusters. Other workers[6,7] detected even heavier carbon clusters in graphite black, as well as the oxide $C_{60}O$.

The most laborious part of the process is the separation of the components, since as a result of the very small structural differences between the components the properties of the various polyhedral carbon clusters such as solubility and adsorbability are also very similar. Separation can be achieved only by column or liquid chromatography methods, which are time-consuming as well as requiring large amounts of solvents.[8,9] These methods can separate some of the higher fullerenes as well as C_{60} and C_{70}.[10] However, some important technical improvements have now been introduced into the processes: these offer a faster separation, a better yield of pure products, and a more modest consumption of solvents.[11–14].

The detection of polyhedral carbon clusters in the soot deposits formed by burning benzene and other hydrocarbons[15] was unexpected. The ratio of the main components varies according to the combustion conditions, and the proportion of C_{70} can be as high as 85%. However, it has not yet been established whether this method is of preparative value.

† The C_{60} cluster, of icosahedral I_h symmetry, has the shape of a truncated icosahedron, similar to a football. Therefore this cluster has also been called carbo-*s*-icosahedron, footballene, or soccer ball.

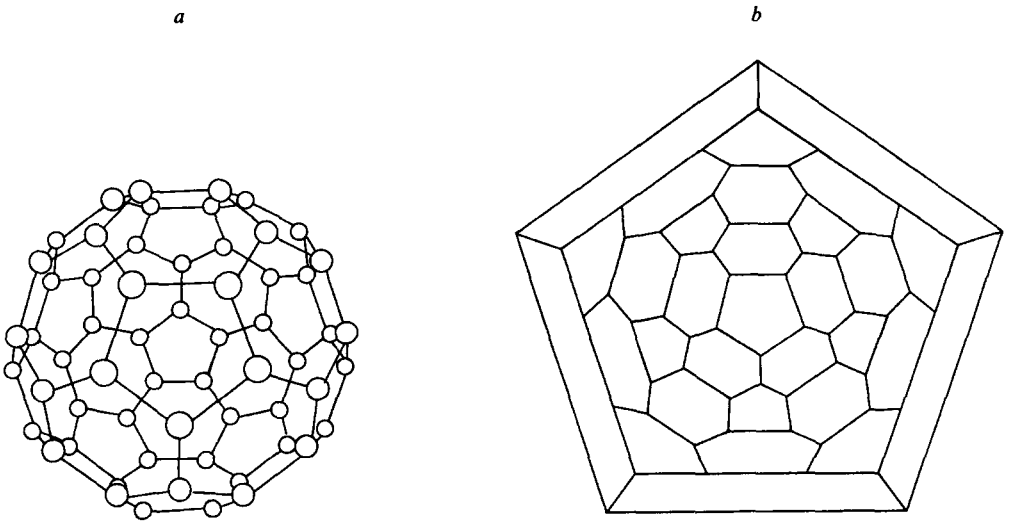


Figure 1. I_h-C_{60} carbon cluster (*a*) and its molecular diagram (*b*).

These methods of preparative synthesis of carbon clusters made a substantial number of fullerenes available to researchers and made possible the detailed study of their physical and chemical properties. Various derivatives of the fullerenes were also produced. Papers describing the synthesis of crystalline samples of C_{60} and of doped systems of the A_nC_{60} type attracted special attention. The salts of BF with alkali metals (n = 3) have superconducting properties at T_c = 18 K (A = K) and at T_c = 28 K (A = Rb).[16,17] Some reports of the preparation of superconducting doped fullerenes with higher values of T_c have not been confirmed. The highest adequately reproducible critical temperature T_c so far reported for the fullerene series is 33 K (for the caesium–rubidium salt Cs_2RbC_{60}).[18]

The main aim of the present review is to assess the current state of research on the molecular and electronic structure and on the chemical properties of the fullerenes (with the use of information available up to the second half of 1992). Because of the wide scope and of the rapidly increasing number of publications on this topic the review cannot claim to be exhaustive. Several reviews of the fullerenes have already appeared,[19,20] but it is difficult to disagree with the statement[21] that any such review should be treated as out of date even on the day of its publication unless transmitted by electronic mail. However, the conceptual and the analytical parts of recent publications should be of more lasting value.

II. Topological and metric characteristics of polyhedral carbon clusters

Various convex polyhedra are used to model the structure of carbon clusters. The topological characteristics of the clusters, defined by systems of two-centre carbon–carbon bonds, are described in terms of these polyhedra. However, it follows from the theory of valency that not all polyhedra are equally suitable for describing the carbon skeleton. The most successful for this purpose[22] are the polyhedra with faces consisting of five-, six-, seven-, or possibly eight-membered rings.‡

We shall call F the number of faces of the polyhedron, V the number of vertices, and E the number of edges. A simple relationship, known as Euler's theorem, exists between these quantities: $V+F-E = 2$. According to the theory of valency each carbon atom in the polyhedral cluster should have either three or two neighbours. It follows that in the topological method of modelling these structures the choice of polyhedra can be confined to figures in which all the vertices have an order of three. These polyhedra can be represented as planar uniform molecular diagrams of order three. By placing new vertices on some of their edges we obtain molecular diagrams which describe the topology of carbon clusters containing atoms with a coordination number of two.[23] Polyhedra with a greater number of vertices are difficult to represent clearly as three-dimensional figures. Therefore planar images (Schlegel diagrams) are used to describe the higher fullerenes. Two diagrams of this type are shown in Figures 1 and 2 for the clusters C_{60} (truncated icosahedron) and C_{70}. We shall denote as n_i the number of faces having i angles. In this case the following equality applies to polyhedra of this class:

$$3n_3 + 2n_4 + n_5 = 12 + n_7 + 2n_8 + 4n_{10} + \ldots$$

It follows directly from this formula that if the faces of a convex polyhedron in which all the vertices are of order three consist exclusively of five- and six-membered rings we must have n_5 = 12. In other words any polyhedron of this type [(5,6)-polyhedron] has not less than 20 vertices, and contains 12 five-membered rings.§ Furthermore the following formulae, which apply to the system, can be useful for discussing the topology of the clusters:

$$2E = 3V, \quad 2E = \sum jn_j, \quad n_6 = \tfrac{1}{2}V - 10 - 2n_7$$

(for polyhedra with faces consisting of five-, six-, and seven-membered rings respectively).

(5,6)-Polyhedra in which none of the pentagonal faces are contiguous are of special interest from the chemical point of view. The truncated icosahedron has the smallest number of vertices among the polyhedra of this class (V = 60).

The other criteria used in the selection of polyhedra and useful for describing the carbon skeletons are based on an analysis of their metric characteristics, consistent with the topology of the polyhedron. These characteristics include the length of the edge and the angles between the edges and between the faces. The values of these parameters, calculated for polyhedra with an ideal geometry, are used to determine the size of the corresponding carbo-polyhedra and to infer the degree of strain of their σ-frame, defined in terms of the distortions of the bond angles from their ideal values.[25–31] Table 1 shows the geometric characteristics of three polyhedra: the dodecahedron, the *s*-octahedron, and the *s*-icosahedron.

‡ We know that in some polyhedra all of the faces are regular polygons. If all these polygons are equal the resulting polyhedron is called Platonic or regular. If some of the faces are different, though formed by regular polygons, the polyhedron is called Archimedean or semiregular.[24]

§ The dodecahedron is the simplest member of the family of (5,6)-polyhedra, with n_6 = 0 six-membered rings.

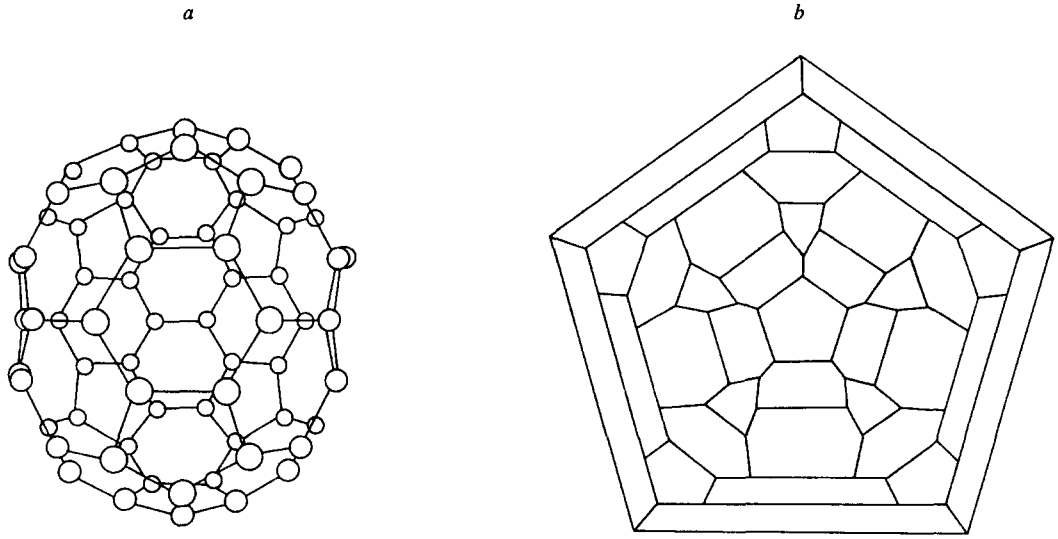


Figure 2. D_{5h}-C_{70} carbon cluster (*a*) and its molecular diagram (*b*).

We shall now examine in more detail some of the methods of constructing polyhedra to be used in the molecular modelling of the structure of carbon clusters.

The triangulation method.
Methods of designing carbon clusters of icosahedral symmetry have been discussed in several papers.[27,29,32,33] These clusters are conveniently generated by the triangulation of a sphere circumscribed about the icosahedron. The first stage is the triangulation of each face of the regular icosahedron, which divides it into small equilateral triangles. This procedure is described in terms of two integers b and c, with $b \geqslant c \geqslant 0$, and leads to a triangulation of the sphere containing V vertices: $V = 20(b^2+bc+c^2)$. Among these vertices 12 have a degree of five, and the remainder have a degree of six. If $b = c$, or $bc = 0$, the deltahedron¶ corresponding to this sphere has the I_h symmetry group. In other cases the polyhedra have the I symmetry group. Furthermore by joining the centres of adjacent faces we convert the deltahedron into a dual polyhedron: a (5,6)-polyhedron of icosahedral symmetry. In this way we can model the structures of giant fullerenes of icosahedral form. The method can also be used to model the structure of clusters of tetrahedral and even lower symmetry groups.[33] Figure 3 shows the self-repeating fragments of some of the icosahedral clusters with a large number of vertices.

The method based on the triangulation of a sphere is widely used in geodesy and in architecture. The general principles governing the application of this approach to the construction of geodesic domes were formulated by R Buckminster Fuller. The structure of the C_{60} cluster can be interpreted as the combination of two hemispheres covered with a network of five- and six-membered rings.

The leapfrog method.
The method of constructing carbo-polyhedra now known as the leapfrog method was proposed by Fowler.[34] Its application involves starting, for example, from a (5,6)-polyhedron with a relatively small number of vertices. A new vertex is then inserted at the centre of each face of the polyhedron, and connected (by new edges) to the nearest existing vertices. The next stage produces a dual polyhedron. This procedure yields a polyhedron with a number of vertices three times greater than in the original polyhedron. The essential features of the leapfrog method are illustrated in Figure 4.

¶ The term deltahedron denotes a polyhedron in which all the faces are triangular.

The petal method.
This method of constructing polyhedra was proposed for the modelling of structures having an axis of symmetry of fairly high order (5, 6, or 7). It relies on the construction of a self-repeating fragment consisting of several condensed rings. The fragments (or petals) are then interconnected to form new faces (Figure 5). The petal method has also been used in the design of chiral and of polar carbo-polyhedra.[28,29,35]

The spiral method.
This method relies on representing the structure of a polyhedron as a planar diagram in which the vertices lie on concentric circles. In this case the structure of the polyhedron can be coded as a sequence of numbers denoting the size of the rings met along a spiral path which begins at the central ring and then passes in turn through the faces of the neighbouring rings.[36] A path of this type for the C_{60} cluster is illustrated in Figure 6. To progress from the topological description of the carbon clusters to a more detailed analysis of their structure and to a prediction of their physicochemical properties we must apply physicochemical methods such as those of quantum chemistry and of molecular mechanics.

III. Quantum chemistry of the fullerenes

The quantum-chemical models of carbon clusters of the polyhedral type described in papers published up to 1985 were based on classical convex polyhedra (the dodecahedron and the truncated icosahedron).[25,37,42] The π-electron model, known to be a convenient method of describing planar conjugated hydrocarbons and their hetero analogues,[43] has been applied to the C_{20} (carbo-dodecahedron) and C_{60} (carbo-*s*-icosahedron) carbon clusters. Strictly speaking a π electron system cannot exist in a polyhedral molecule, which is non-planar and has an approximately spherical surface. However, the bonds in a carbo-polyhedron can be described by the following procedure, which is used in classical (planar) conjugated systems: each carbon atom contributes three hybrid orbitals and three electrons to the formation of three two-electron (localised) σ-bonds with neighbouring atoms. The fourth electron is placed in a hybrid ρ-orbital orthogonal to the three σ-orbitals oriented along the bonds to the neighbouring atoms.[25,29,31] Bochvar et al.[25,38,39] discussed the structure of the ρ-electron system by using the Hückel approximation in conjunction with the concepts adopted in that theory to describe the classical π-electron systems.

Table 1. Some geometric characteristics of polyhedra.[30]

Characteristic	Dodecahedron	*s*-Octahedron	*s*-Icosahedron
Number of vertices	20	24	60
Number of faces	12 pentagons	6 quadrangles + 8 hexagons	12 pentagons + 20 hexagons
Diameter of inscribed sphere (for a CC bond length of 1.40)	3.118	3.429	6.348
Angle between edges and radius vector/°	110.90	108.26	101.65

Some relevant aspects of the Hückel theory should be stressed in order to make clear the significance of the results obtained in the many calculations of carbo-polyhedra in the ρ approximation published in the last 5–7 years. We should note first of all that the Hückel method is essentially topological. In its simplest variant it merely takes account of the nature of nearest neighbours (i.e. of the presence of chemical bonds) and ignores the metric characteristics of the molecule. Two empirical parameters are used in the Hückel method: the Coulombic (α) and the resonance integral (β). These quantities are used to describe the Hamiltonian for the π-electron system and to calculate the one-electron energy levels ε_i as the linear functions

$$\varepsilon_i = \alpha + x_i\beta,$$

where x_i are the characteristic numbers of the molecular diagram which describes the σ skeleton of the carbo-polyhedron. Energy levels with $x_i > 0$ are called bonding, and those with $x_i < 0$ are called antibonding. The energy level $\varepsilon_i = \alpha$ is called nonbonding. A similar terminology is used for the molecular orbitals (MO).

The fundamental concept of the Hückel theory is the formation of closed electron shells. This property is found in systems in which all the bonding MO are doubly occupied in the ground state, and the nonbonding and antibonding energy levels are vacant. If the molecule in the ground state possesses unoccupied as well as doubly occupied bonding orbitals the system is said to have a pseudo-closed shell. The presence of a closed electron shell denotes a kinetically stable system. The stability usually increases with the width of the energy gap $\Delta\varepsilon$ which separates the antibonding from the bonding energy levels. The systems which contain unoccupied bonding energy levels can have an increased tendency towards the formation of anions. The presence of occupied antibonding energy levels stabilises the oxidised forms. The case of an occupied nonbonding level usually requires a more detailed analysis.

Various form of resonance energy are used, in addition to the delocalisation energy, to calculate the stabilisation of the ρ-electron systems of carbo-polyhedra: these include the topological resonance energy,[29,44,45] the resonance energy of Hess and Schaad,[46] calculated by the fused rings method,[47] and some other similar characteristics. All these quantities are commonly used to determine the degree of aromaticity of classical conjugated hydrocarbons. However, these calculations have also been used[27–29,48,49] to establish the relative stability of unsaturated polyhedral carbon clusters.

Since 1985, when the original paper by Kroto et al.[1] was published, the fullerene problem has stimulated increasing theoretical interest. Many studies by quantum-chemical methods in various approximations of the electronic structure of footballene (I_h-C_{60}) were published, as well as studies of its isomers, anions, cations, and of polyhedral carbon clusters with different numbers of atoms, including the higher fullerenes. Calculations were made in the restricted and the expanded Hückel,[26–34,36–39,42,48–64] MNDO,[64–71] and AMI methods,[72–74] in the nonempirical MO LCAO SCF method in different basis sets,[71,73,75–77] in the CNDO[30,39,78] and INDO methods,[79] and in the Pariser–Parr–Pople method allowing for configuration interaction,[80–82] the X_α method,[83,84] and the methods of molecular mechanics with estimates of the vibration frequencies.[83–89] We shall examine in some detail some of these papers, highlighting those which appear to have played a dominant role in our understanding of the special features of the chemical structure of polyhedral carbon clusters.[29,36,66,69]

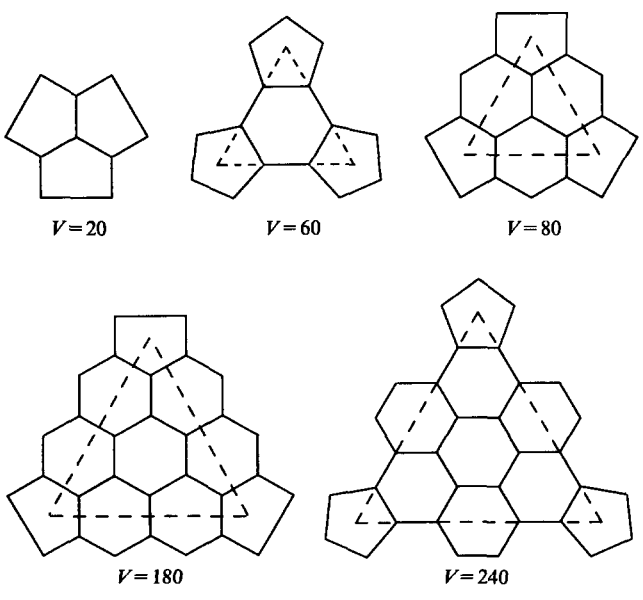


Figure 3. Self-repeating fragments of some icosahedral clusters.

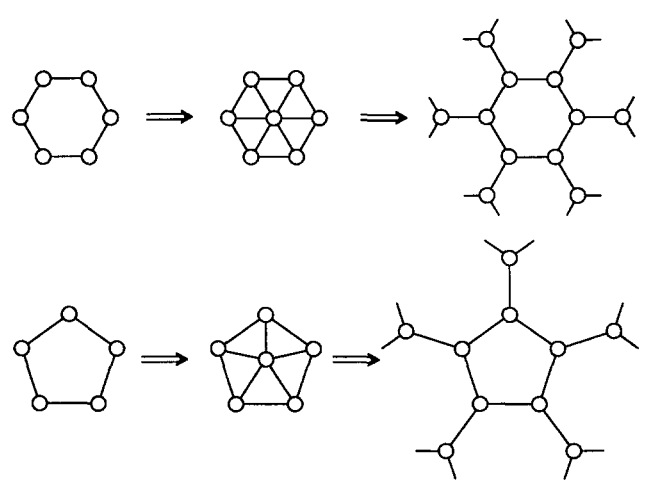


Figure 4. Scheme illustrating the construction of the higher fullerenes by the addition of one corner at the centre of each face of the initial (5,6) polyhedron.

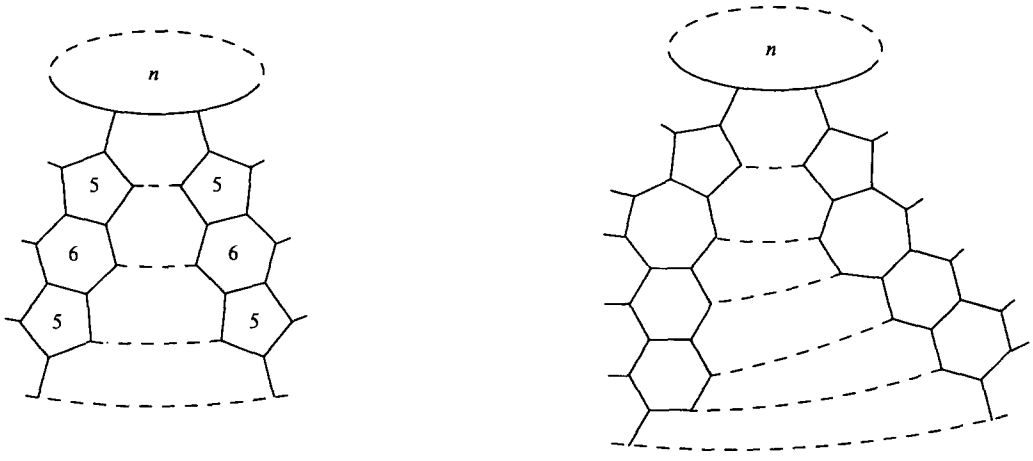


Figure 5. Examples of the basic fragments used in the design of carbon clusters with 5th- and 6th-order symmetry axes.

Schmalz and coworkers[29] developed a simple method of designing polyhedral structures with the D_{nd} and D_{nh} symmetry groups and used it to model the electronic structure of more than 30 carbon clusters of that type in the topological approximation. An analysis of their results[29] led to the formulation of several rules governing the stabilisation of polyhedral structures. The following are the most important:

1. Stable carbon clusters are polyhedra in which each carbon atom has a coordination number of 3.
2. The carbo-polymers containing only five- and six-membered rings are the most stable.
3. The most symmetric carbon clusters are the most stable.
4. Five-membered rings in the polyhedra should be isolated.
5. The shape of the carbo-polymers should be approximately spherical.

Some corollaries of these rules should be noted. For example, it follows from the first rule that the number of vertices in the cluster should be even (odd clusters of larger size have not been reported), and from the second rule we conclude that any polyhedron in this class should contain exactly 12 pentagons. No limit is placed on the number of hexagons. Footballene (I_h-C_{60}) is the smallest cluster which satisfies the fourth rule.

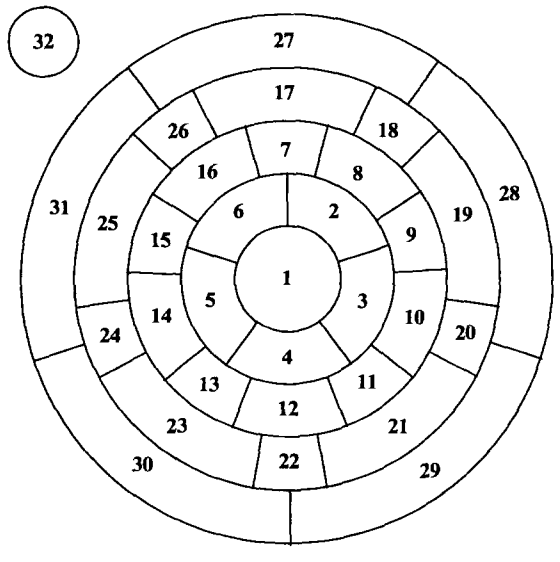


Figure 6. Structures of the I_h-C_{60} cluster coded with a system of concentric rings. Faces numbered clockwise in a spiral path. The code for the I_h-C_{60} cluster is 566 666 565 656 565 665 656 565 656 666 65. The first number of this code is the number of sides of the ith face. The last number corresponds to the infinite face of the molecular diagram [D E Manolopoulos, J C May, S E Down *Chem. Phys. Lett.* **181** 105 (1991)].

The number of isomers of the polyhedral C_n structures should increase rapidly with the number of atoms, even if only the (5,6)-polyhedra are considered. The C_{20} carbododecahedron has no isomers in this class of polymers, but (for example) in the polymer with $n = 78$ we find 21 822 isomers. Therefore the listing of all possible polyhedral structures with a given number of atoms is not an easy problem. The problem becomes even more complex when *a priori* estimates of the energetic and of the spectral characteristics of these structures are required. Hückel's topological approximation is often used as a rapid method of analysis, and the most probable structures are identified as a result of these calculations and studied in more detail. Papers in which Hückel's method is used account for a substantial proportion of the theoretical publications on the electronic structure of carbon clusters. Therefore it is natural to ask to what extent the Hückel approximation is suitable for solving problems in the structural chemistry of the fullerenes.

Let us consider, in this context, the results of some studies which are not only of intrinsic interest but also confirm the usefulness of the Hückel method for analysing the properties of carbon clusters. We note first of all that in the case of the most widely studied cluster (C_{60}) all the higher-level methods of calculation give a scheme of one-electron energies similar to that given by the Hückel method.[20]

Newton and Stanton[66] reported calculations on footballene and on some other carbon clusters by the MNDO method. In the case of C_{60} the authors[66] analysed the structure of the frontier orbitals and established that the HOMO are functions consisting (to within 97%) of the radial p-orbitals of the carbon atoms.

Bakowies and Thiel[69] studied approximately 30 carbon clusters of very different structure: clusters of icosahedral and of tetrahedral symmetry, and spherical or barrel-shaped clusters with groups of D_{nd} and D_{nh} symmetry. The choice of the systems was largely dictated by the results of MNDO calculations with full optimisation of the geometry. The structures examined included a giant C_{540} cluster of icosahedral symmetry. Schmalz et al.[29] determined the geometric characteristics and the heats of formation of the clusters. They found that the heats of formation of some of these carbon superclusters are directly proportional to the energy of delocalisation calculated by the Hückel approximation, which includes corrections for the resonance integrals (associated with the deviation of the cluster structure from a spherical form).

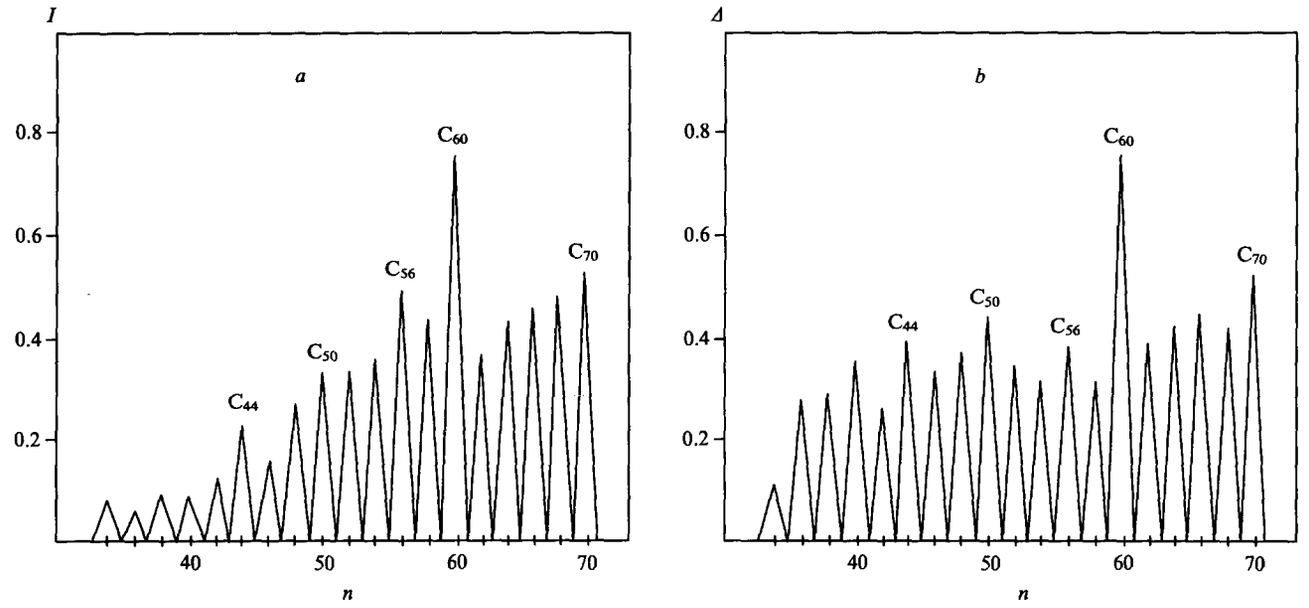


Figure 7. Relative intensities in the mass spectra of the C_n carbon clusters for $34 \leqslant n \leqslant 70$ (*a*). Energy gaps separating the filled from the empty energy levels (in the ground state) of the C_n clusters (*b*). The width Δ of these energy gaps was calculated in the topological approximation by the Hückel method and expressed in units of the resonance integral β.

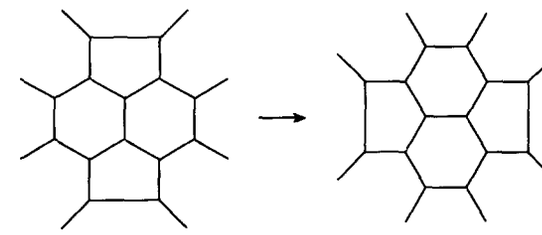
An interesting paper by Manolopoulos et al.[36] reports a correlation between the intensities of the mass spectra of the ions obtained from C_n^+ carbon clusters, where $34 \leqslant n \leqslant 70$, produced by laser evaporation of graphite, and the values of the energy gap $\Delta\varepsilon$ in the ρ-electron spectra calculated by the simple Hückel method for the corresponding fullerenes (Figure 7). Among all the possible isomers of the C_n clusters they chose those with the largest energy gap $\Delta\varepsilon$.

It is clear from this brief analysis that in systems of the polyhedral type with an almost spherical form it is convenient to use the Hückel approximation, since this method gives valuable information on the electronic properties of the systems. Let us examine in greater detail some of the characteristics of the geometry and of the electronic structure of the C_{60} and C_{70} clusters and of carbo-polyhedra with a greater number of atoms, and also of endohedral complexes.

1. C_{60} clusters

Many isomers can be constructed from 60 carbon atoms: one of these is the I_h-C_{60} cluster. Its geometric characteristics were established by electron diffraction[92] and X-ray structural analysis† (the structure of the osmium derivatives has been reported[93]), and calculated by various quantum-chemical methods.[49, 54, 66, 68, 72, 73, 75, 76] Bonds of two types are found in the I_h-C_{60} cluster: r_1, specific to the five-membered rings, and r_2, common to the pentagonal and the hexagonal faces. All the methods of calculation indicate an alternation of the two bond lengths (r_1 and r_2), in keeping with the experimental results (r_1 = 1.401, r_2 = 1.456 Å).[92, 93] The C_{60} isomers can be constructed in different ways. For example, from the dodecahedral C_{20} structure a new structure (C_{60}) consisting of three-membered and ten-membered rings can be obtained by truncating the vertices. A series of C_{60} isomers was generated by the petal method.[29] Isomers of the fullerene type can be obtained from I_h-C_{60} as a result of Stone–Wales regrouping in the pyracyclene fragments.[63] However, this operation leads to the appearance in the new isomer structures of adjacent five-membered rings (pentalene fragments), which destabilise the carbon cluster.

† H B Burgi, E Blanc, D Schwarzenbach, S Liu, Y Lu, M M Kappes, J A Ibers *Angew. Chem.* **104** 667 (1992).



It follows from the results of extensive theoretical studies that the icosahedral BF structure is the most stable of the polyhedral C_{60} isomers. The stability of the I_h-C_{60} footballene is usually attributed to the presence of 12 equivalent (partially overlapping) corannulene structural fragments, each containing a five-membered ring surrounded by five hexagons, which ensure that the pentagons are mutually isolated. Qualitative considerations indicating instability of structures containing adjacent five-membered rings are confirmed by calculations[71] by the semiempirical MNDO method and by the nonempirical MO LCAO SCF method in the two-exponential 3-21G basis, applied to C_{60} isomers containing two, three, and four pairs of adjacent five-membered rings. It was established that the most stable isomer of this type has a C_{2v} symmetry and an energy 2 eV higher than the energy of the I_h-C_{60} isomer. Each pair of adjacent five-membered rings makes approximately the same contribution (1.0 ± 0.2 eV) to the destabilisation energy of the I_h-C_{60} structure.

The effect of the pentalene fragments on the stability of the C_{60} isomers was discussed by Stanton[70] in relation to the photodissociation reactions of the C_{60} cluster, and also of some other carbon clusters studied by O'Brien et al.[94] MNDO calculations of the equilibrium geometry, of the heats of formation, and of the ionisation potentials of several carbon clusters (C_{62}, C_{60}, C_{58}, C_{56}, C_{54}, C_{52}, and C_{50}) have also been reported.[70] Estimates of the heats of isomerisation of these polyhedral clusters by the Stone–Wales mechanism have been obtained, as well as estimates of the heats of elimination of the C_2, C_4, and C_6 fragments from footballene (C_{60}) and from the C_{62} cluster. These calculations also confirm the conclusion that the presence of pentalene fragments destabilises the carbon clusters. It was found that the elimination of C_2 from the C_{62} cluster is strongly endothermic (ΔH = 99 kcal mol^{-1}), but the heat of this

reaction is much smaller than that of the reaction $C_{60} \rightarrow C_{58} + C_2$ (ΔH = 273 kcal mol^{-1}). We also note that the same workers[70] described the structure of one of the most stable polyhedral isomers of C_{30}.

These results indicate that the structure of footballene is more stable than that of its polyhedral isomers. However, under certain conditions other isomers can also exist as metastable high-energy species. It has been shown[95] that a series of C_{60} isomers is present in the flame produced by the combustion of benzene.

2. Aromaticity of the C_{60} fullerene

The Japanese workers Yoshida and Osawa[37] have proposed a definition of a new class of conjugated molecules, which they called superaromatics. They assigned to this class of compounds molecules of polyhedral form which contain electrons in molecular orbital delocalised on the surface of a three-dimensional structure having an almost spherical symmetry.‡ They suggested as an illustration the hypothetical C_{60} molecule with the structure of a truncated icosahedron. This C_{60} molecule possesses a system of mobile electrons which contributes additional stabilisation to the polyhedron, as in the benzene molecule. Independently of the work of Yoshida and Osawa[37] polyhedral analogues of the classical aromatic systems (containing only carbon) were discussed by Bochvar and Gal'pern.[25,38] They produced[25] the first quantitative estimates of the resonance energy (or delocalisation energy) for this unusual type of conjugated molecule. It was concluded[25] that the C_{60} cluster has a greater resonance energy than the benzene molecule, and that in keeping with the quantum-mechanical criterion of aromaticity the C_{60} molecule should be assigned to a new class of aromatic systems.

We should stress the fact that the term 'aromaticity' has long been used in organic chemistry. It is associated with the presence of a large group of physicochemical properties (listed, for example, by Vol'pin[90]). However, the use of the term aromaticity has always been ambiguous to some extent, depending on whether the main stress of the argument lay on the chemical properties or on the molecular and the electronic structure (compare, for example, the definitions of this term given in Refs 90 and 91).

An analysis of the chemical properties of footballene shows that this molecule cannot be classified as an aromatic compound. Indeed, most of the known derivatives of footballene were prepared by addition reactions at multiple bonds (see Section VI).

However, according to the physical criteria the C_{60} molecule can be assigned to the group of aromatic systems [for example, the C–C bond lengths in C_{60}, though different for the (6, 6) and the (6, 5) bonds, are close to the bond lengths in graphite; furthermore the C_{60} system absorbs light at relatively long wavelengths, has a closed electron shell, and its resonance energy is relatively high].

The resonance energy is often used as a measure of the stability of the system relative to some standard structures. Comparative estimates of the resonance energy of C_{60} have been calculated[29] by different methods: Hückel's method, the methods of Hess and Schaad and of Randic, the conjugated rings method, and some others. The results are consistent with the aromaticity of BF in the sense of the quantum-chemical criteria, though according to most of these criteria the aromaticity of BF is lower than that of benzene.

Thus the aromaticity concept developed for the classical conjugated molecules cannot be applied to molecules of the fullerene type. The term 'pseudoaromaticity' gives a more accurate description of the formation of a single delocalised π-electron system, with a definite energy gain. The most important physical properties of BF are listed below.[18]

Structural data

Cubic crystal structure:
- $Fm\bar{3}m$ ($T > 260$ K)
- $Pa\bar{3}$ ($T < 260$ K)

Diameter of carbon cage: 7.1 Å

Bond lengths:
- C=C 1.391 Å,
- C–C 1.455 Å

Nonvalence distance between C_{60} molecules in the crystal: 3.1 Å

Bulk modulus: 18 GPa

Density: 1.65 g cm^{-3}

Spectral characteristics

Electron affinity: 2.6–2.8 eV

Ionisation potential: 7.6 eV

Energy gap: 1.9 eV

^{13}C NMR chemical shift: 142.68 p.p.m.

Vibration frequencies:
- IR: 528, 577, 1183, 1429 cm^{-1}
- Raman: 1250, 1422, 1467, 1573 cm^{-1}

Refractive index: 2.2 (630 nm)

3. The C_{70} cluster

The structure of the C_{70} cluster was determined by electron diffraction[96] and X-ray structural analysis of the iridium derivatives,[97] and calculated by various quantum chemical methods (see, for example, Ref. 77). It was established[96] that the C_{70} cluster has a fullerene structure with an ellipsoidal shape, described by the D_{5h} symmetry group. The C–C bond length varies between 1.37 and 1.47 Å. The shortest bonds are those connecting the vertices of two different pentagons; the longest are found within the five-membered rings. The 'height' of the molecule is 7.8 Å. As reported,[96] the equatorial part of C_{70} has a diameter of 6.94 Å and is narrowed by 0.05 Å. The lengths of the C–C bonds found by the XSA method for the iridium derivative of C_{70}[97] agree on the whole with the values obtained[96] by electron diffraction.

Formally the D_{5h}-C_{70} cluster can be obtained from two halves of the C_{60} cluster by inserting five pairs of carbon atoms in the equatorial plane.

The D_{5h}-C_{70} cluster, like the I_h-C_{60}, contains only isolated five-membered rings. In the spheroidal I_h-C_{60} molecule the carbon atoms are equivalent: they can be readily divided into pairs contributing to the formation of bonds between adjacent five-membered rings, which are equivalent in pairs. The I_h-C_{60} structure can also be described in terms of pyracyclene fragments or fragments of the corannulene type, which are structurally equivalent in pairs. However, the ellipsoidal D_{5h}-C_{70} structure cannot be described in terms of the fragments of a single type defined above. In the D_{5h}-C_{70} molecule corannulene and pyrene structural units can be distinguished in addition to the pyracyclene fragments.

The nonequivalence of the carbon atoms in the C_{70} molecule results in different values of the chemical shifts in the ^{13}C NMR spectra. Five types of atoms are present in the C_{70} molecule, with a corresponding number of signals. The following interpretation of the chemical shifts in the D_{5h}-C_{70} cluster has been proposed:[98] the signal at 130.8 p.p.m. is assigned to the carbon atoms of the ten pyrene fragments, the signals which appear in the range of 147.8–150.8 p.p.m. are assigned to the three different carbon atoms of the pyracyclene fragments, and the signal at 144.4 p.p.m. is assigned to the corannulene carbon atoms.

This interpretation of the chemical shifts in the D_{5h}-C_{70} cluster was used in subsequent work to model the structure of higher fullerenes in terms of their NMR spectra.[10]

‡ An English translation of part of the relevant paper,[37] kindly supplied by Professor Osawa, was used in the preparation of this review.

4. C_n clusters with $n > 70$

As was pointed out above, the number of isomers of the C_n clusters increases rapidly as n increases, even if the analysis is confined to fullerenes containing five- and six-membered rings. However, the number of isomers is greatly decreased if only the clusters which obey the isolated pentagons rule are considered. For C_{78} the number of isomers containing only isolated pentagons is five; for C_{84} it is 24, and for C_{90} it is 46.[55] However, the number of these isomers also increases fairly rapidly as n is increased. Therefore qualitative methods of predicting the structure and the properties of polyhedral clusters containing more than 70 atoms are of interest. One of these methods is based on the Hückel approximation. It was used by Fowler et al.[57,60] to formulate a group of rules analogous to the classical $(4n+2)$ Hückel rule, which must be satisfied by a closed electron shell. The most generally applicable of these rules can be formulated as follows.[60]

Rule 1. The isomers of the C_n clusters with $n = 60+6k$, $(k \geqslant 1)$ include at least one molecule with a closed electron shell for each integral value of k.

Rule 2. The isomers of the C_n clusters having a fifth-order axis of symmetry with $n = 70+30k$ or $n = 84+36k$ include at least one molecule with a closed electron shell for each integral value of $k \geqslant 0$.

Rule 3. The cluster C_{3m} obtained from the cluster C_m by a 'leapfrog' operation has a closed electron shell.

In the presence of a closed electron shell the difference between the HOMO and the LUMO energy ($\Delta\varepsilon$) is often used as a measure of the relative stability of carbon clusters. As was said above, this quantity is sufficiently well correlated with the intensities of the mass spectra of the $C_{34}-C_{70}$ carbon clusters obtained by the laser evaporation of graphite. However, the estimates of the stability of the higher fullerenes based on the width of the energy gap $\Delta\varepsilon$ are not always reliable. Thus, three structures (of D_{6h}, T_d, and D_2 symmetry) have been proposed[60] for the C_{84} cluster. A fourth isomer, of D_{7d} symmetry, was later added to this list.[99] The main parameters of the electronic structure of these four isomers, calculated by Hückel's method, are shown in Table 2.

It can be seen that the energy characteristics of the D_{7d}-C_{84} structure are close to the corresponding values for footballene (C_{60}). Furthermore the energy gap $\Delta\varepsilon$ for D_{7d}-C_{84} differs from the value for footballene by only $0.011\,|\beta|$, and therefore the structure of D_{7d}-C_{84} should be the preferred structure. However, calculations[71] by the MNDO and the nonempirical variant of the MO LCAO SCF method in the 3-21G basis showed that this is not the case. It was established[71] that the three structures of the C_{84} cluster with D_{6h}, T_d, and D_{7d} symmetry actually correspond to local minima on the potential energy surface, and that the D_{6h}-C_{84} structure is more stable than T_d-C_{84} [by 23.4 kcal mol^{-1} (MNDO) or by 18.2 kcal mol^{-1} (*ab initio*)]. Furthermore the energy of the D_{7d}-C_{84} structure is higher by several tens of kcal mol^{-1} than the energy of the T_d-C_{84} structure.

Table 2. Energy characteristics of the C_{84} isomers calculated by the Hückel method.[99]

Cluster	Symmetry	HOMO (β)	LUMO (β)	$\Delta\varepsilon$ ($\lvert\beta\rvert$)[a]	E_d (β)[b]
C_{84}	T_d	0.572	−0.124	0.696	0.559
	D_{6h}	0.529	0	0.529	0.558
	D_2	0.497	−0.117	0.614	0.558
	D_{7d}	0.607	−0.139	0.746	0.556
C_{60}	I_h	0.618	−0.139	0.757	0.553

[a] $\Delta\varepsilon$ is the width of the forbidden band
[b] E_d is the delocalisation energy per electron

This example shows that topological methods can give erroneous results in the comparison of the energy characteristics of the higher fullerenes. However, were it not for the topological approximation there would have been no progress in the search for possible structures, in the detection of isomers, in the interpretation of the NMR spectra, and in some other aspects of the structural chemistry of the fullerenes. A paper by Fowler et al.[100] in which the topological isomers of C_{84} of the fullerene type are characterised is noteworthy in this respect.

The structures of the higher fullerenes with a number of carbon atoms $\leqslant 84$ have also been discussed.[57-59,67] Table 3 shows reported data on the structure of the C_n carbon clusters with $60 \leqslant n \leqslant 78$, which satisfy the isolated pentagon rule and have a closed electron shell. The table also gives the characteristics of the ^{13}C NMR spectra and the heats of formation of the isomers, calculated by the molecular mechanics method.

Table 3. C_n fullerenes with closed and with pseudo-closed electron shells for $60 \leqslant n \leqslant 78$, ^{13}C NMR spectra, and calculated heats of formation.

Structure	Line intensity	ΔH_f°/kcal mol^{-1}
I_h-C_{60}	1(60c)	573.0
D_{5h}-C_{70}	3(10c), 2(20c)	–
D_{6h}-C_{72}	2(24c), 2(12c)	–
D_{3h}-C_{74}	1(2c), 4(4c), 4(12c)	–
D_2-C_{76}	19(4c)	–
C_{2v}-C_{78}	18(4c), 3(2c)	695.7
D_{3h}-C_{78}	13(6c)	697.8
C_{2v}-C_{78}	17(4c), 5(2c)	694.3
D_{3h}-C_{78}	5(12c), 3(6c)	702.3
D_{3h}-C_{78}	5(12c), 3(6c)	697.8

Note. Data for two symmetries (C_{2v} and D_{3h}) are given for the C_{78} fullerene

Fullerenes with a large number of atoms (giant fullerenes), including the extended carbon structures of the fullerene type, have been studied extensively.[59,101-106] Methods of modelling their structure have stimulated most interest. Thus, Kroto[101] proposed using spherical models for the giant fullerenes. The suggested structures are very attractive at first sight. Furthermore quantum-chemical calculations[69] for large clusters suggest that even a giant fullerene of icosahedral symmetry as large as C_{540} may be stable. Nevertheless the formation of hollow giant fullerenes of the spheroidal type seems unlikely, because these molecules must include a large proportion of empty space. It is difficult to believe that in the synthesis of the giant clusters C_n by the evaporation of graphite or by the combustion of benzene the inner cavity of the cluster is not filled by other smaller species formed from carbon atoms, or by other (impurity) atoms. Therefore the possibility that giant fullerenes have a more complex structure cannot be excluded. For example, these clusters may have a structure of the onion bulb type. Some of the giant fullerenes could be cylindrical, or they could have more complex cellular structures. Carbon clusters of these types (capsulenes, barrelenes, tubulenes, kegs, torenes, etc.) have been widely discussed.[31,64,102-108]

Cylindrical structures can be described as homologous series. Thus, Gal'pern et al.[64] have examined the molecular and the electronic structure of barrelenes of general formula C_m ($m = 36+12n$). In the limit, cylindrical carbon clusters can be treated as infinite macromolecules, and their corresponding endohedral complexes (containing linear chains of atoms within the carbon cylinder §) can be treated as molecular conductors.[106]

§ The possible formation of isolated homoatomic chain macromolecules consisting of atoms of the first or of the second period has long been a topic of discussions among specialists.[109] The formation of lead conductors within carbon microtubes up to 2 nm in diameter has recently been reported [P M Ajayan, S Iijima *Nature (London)* **361** 333 (1993)].

The properties of the carbon cylinders depend on the radius and on the character of the end groups. Carbon clusters with a closed electron shell should have the form of cylinders closed at the ends (capsulenes, barrelenes). Open carbon cylinders can have no independent existence, because they include many radical centres at their ends. However, by saturating the free valencies of these radicals we can create cylindrical macromolecules having favourable properties as electronic conductors. Mathematical models of these systems, including their toroidal analogues, were first discussed by Heilbronner[110] in 1954 from the standpoint of a study of the electronic structure of homologous series of polynuclear aromatic hydrocarbons. More recently renewed interest has been shown in the search for new classes of quasi-one-dimensional conductors.[111,112]

The production of filiform carbon crystals, probably composed of microtubulenes, has been reported.[103]

In principle the possible formation of carbon structures with carbon atoms distributed over surfaces of various types should also not be excluded. For example, Lenosky et al.[104] have considered the case of surfaces with a negative curvature.

5. Endohedral fullerene complexes

Let us now turn to inclusion compounds of the $M_n @ C_m$ type. The first results of quantum-chemical calculations on these systems were reported by Bochvar et al.,[38,39] who applied the CNDO/2 method with partial optimisation of the geometry to the system $M^+ @ C_{24}$, with M = Li, Na. In these calculations the C_{24} cluster was assumed to be a truncated octahedron. According to the results the introduction of a Li cation at the centre of the carbo-*s*-octahedron stabilises the C_{24} system, whereas Na^+ has a destabilising effect. This is because in the case of Li the whole of the positive charge is transferred to the carbon skeleton whereas with Na 30% of the charge remains on the metal atom. A high energy barrier has to be overcome in order to extract the M^+ cation through the centre of the hexagonal face. This effect ensures the kinetic stability of $M^+ @ C_{24}$.

Relatively few calculations on endohedral clusters have been published. Special interest was stimulated by detailed calculations on Li^+C_{60} by Bakowies and Thiel,[69] who considered the case of Li^+ present both within and outside the C_{60} cluster. It was found that the formation of the endohedral $Li^+ @ C_{60}$ cluster requires a large consumption of energy (ΔH = 30 kcal mol^{-1}), whereas the formation of an exohedral cluster, with the Li^+ located outside the carbon cage over a pentagonal or hexagonal ring, results in a substantial gain in energy.

The charge on the Li atom is positive varying between 0.5 and 0.8 a.u. The position of the Li cation at the centre of the cage does not correspond to the absolute minimum: the cation can move almost freely within the polyhedron to a point 1.4 Å from the centre. However, as in the case of $M^+ @ C_{24}$, the emergence of the M^+ cation from the carbon cage requires overcoming a high potential barrier (> 75 kcal mol^{-1}), which ensures the kinetic stability of this type of endohedral complex.

Nonempirical calculations of the clusters $X @ C_{60}$ (X = O, F, K, Ca, Mg, Cr, Ba, La, Eu, U) have been reported. Chand et al.[113] used the Hartree–Fock method in conjunction with a relativistic potential for the core electrons. It was assumed that the impurity atom is located at the centre of the carbon cage. Calculations in the approximation of an energy functional dependent on the local electron density[114] were carried out with the exchange-correlation potential proposed by Barth and Hedin.[115] By analysing the Mulliken populations it was established that a charge of $\sim 2.85e$ is retained on the carbon skeleton. The highest occupied energy level corresponds to the MO localised on the carbon atoms.

From the calculations[113] on the $M @ C_n$ inclusion compounds it can be seen that the role of the atom (or ion) within the carbon cage is principally to donate electrons to the ρ-electron shell of the carbon core. The extent of electron transfer and the stability of the system depend on the relative values of the redox properties of the additive atom and of the carbon cluster. Thus the La atom donates two 6*s* electrons to the delocalised system of the carbon cage, occupying two vacant orbitals of the C_{60} clusters, and the third valence electron remains localised on the 5*d*-AO. We may conclude from the results of the calculation[113] that the $La @ C_{60}$ complex should have chemical properties similar to those of fullerene in a triplet excited state. The electronic structure of the endohedral $M @ C_n$ complexes has been discussed also by other workers.[116–119]

The acceptor capacity of the C_n clusters can be evaluated qualitatively at the level of the Hückel approximation. Thus it was shown[56] that the C_n^{2-} dianions with n = 74, 82, and 88 are the most stable of these species. It is stressed that these dianions are convenient structures for the formation of endohedral complexes with metals which donate two electrons to the ρ system of the surrounding cage. In particular, the stability of the C_{3v}-C_{82}^{2-} cluster is specially noted. This conclusion agrees with experimental data indicating the existence of a long-lived $La @ C_{82}$ cluster and defining the charge distribution pattern in the system.[56]

6. Unstable fullerenes

Most of the theoretical papers in which polyhedral carbon clusters are discussed are mainly concerned with structures which satisfy variously defined stability criteria and in particular with clusters having a closed electron shell. The presence of an open electron shell in a polyhedral C_n cluster denotes a fairly high reactivity. Such a cluster is kinetically unstable, and difficult to isolate. However, knowing the geometry of the ground state and the electronic structure of the C_n cluster with an open electron shell it is often possible to make a qualitative estimate of the stable derivatives of such a cluster. Therefore the unstable structures also are of interest, and it is reasonable to treat them as intermediates whose stabilisation under prescribed conditions can lead to the creation of new types of materials.

Let us examine some examples. The simplest member of the fullerene family is the carbododecahedron C_{20}. The earliest calculations on the cluster C_{20}, made first in the Hückel ρ approximation[25] and then by the expanded Hückel method,[38] showed that this fullerene has an open electron shell and that its ground state should be triplet. Recent nonempirical calculations by Parasuk and Almlöf[120] confirmed this conclusion from which it follows that the C_{20} cluster should be a chemically active species. One of the methods of preparing stable, less reactive systems relies on passing from the C_{20} cluster to its carborane derivative $C_{18}B_2$.[25,121]

The D_{6h}-C_{36+12n} family of clusters of the barrelene type has been discussed.[64,122] It was established that these clusters have an open electron shell. However, it appeared that the highest partially occupied doubly degenerate level is a bonding level and that two electrons are not sufficient to fill it. Therefore it was concluded that the D_{6h}-C_{36+12n} clusters can readily form dianions.[64] They can be stabilised in the solid phase by the addition of alkali metal atoms.

Another interesting method of stabilising polyhedral clusters was proposed by Guo et al.[117] It was shown that the most stable C_{28} isomer has a tetrahedral (T_d) type of symmetry (Figure 8). At each corner of the tetrahedron we find a group of three condensed pentagonal rings: the carbon atoms shared by the three rings lie exactly at the corners of the tetrahedron. The electronic ground state of the C_{28} cluster has the $^5A_2$ configuration. One of the four unpaired electrons is located on a molecular orbital of a_1 symmetry, whereas the other three are on orbitals of t_2 symmetry. The tetrahedral C_{28} cluster can be formally treated as a super-atom with a valency of four, able to form compounds analogous to those of the quadrivalent carbon atom in the sp^3 hybridisation state.

Furthermore, calculations[117] by the nonempirical SCF method showed that the $C_{28}H_4$ molecule (of T_d symmetry) should be extremely stable. This molecule could be appropriately called supermethane. However, there is an alternative method of

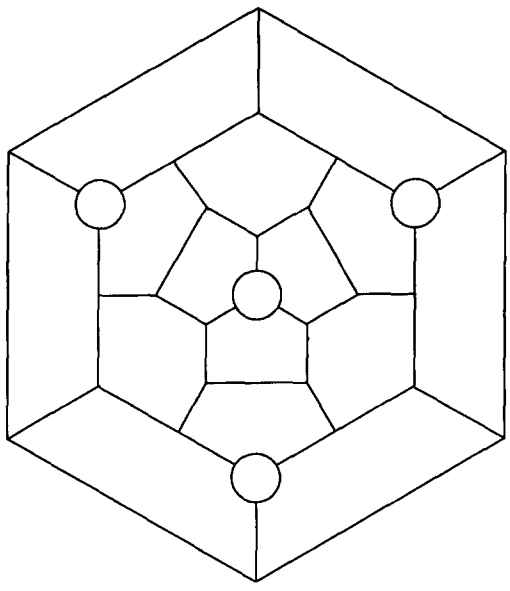


Figure 8. Molecular diagram for the C_{28} cluster of tetrahedral symmetry. The corners denoted by open circles correspond to carbon atoms lying on third-order axes of symmetry.

stabilising C_{28}: by introducing into the inner cavity of the polyhedron a quadrivalent atom such as Ti or U to form endohedral M @ C_{28} compounds. Mass spectral data for samples obtained by laser evaporation of a recently prepared composite (graphite – UO_2) were also reported.[117] These suggest the existence of U @ C_{28} clusters.

We should also point out that by analogy with the carbon atom in the sp^3 hybridisation crystal lattices of the diamond type can be constructed from the C_{28} super-atom, as well as some other lattices. The C_{28} super-atom can find applications in the design of superaliphatic hydrocarbons $[(C_{28}H_2)_m(C_{28}H_3)_n]$.

7. Polyhedral clusters of atoms of other elements

The synthesis of polyhedral clusters of carbon atoms strongly stimulated the search for analogous structures composed of atoms of elements of group IV of the Periodic Table, or of mixed clusters of atoms of elements from groups III and V, For example, Nagase and Kobayachi[123] have discussed the stability of the O_h-Si_{24} cluster, of the icosahedral Si_{60} cluster, and of the endohedral M @ Si_{60} complexes, where M = Ne, F^-, or Na^+. The calculations were carried out by the Hartree–Fock–Roothaan method. A two-exponential basis was used for Si_{60}, and an effective nonempirical potential for the cores of the Si atoms. The structure of the Si_{60} cluster was optimised by postulating the retention of the I_h symmetry group. It was established that bonds of two types are present in the Si_{60} cluster: bonds shared by two hexagons have a length of 2.189 Å, and those shared by a pentagon and a hexagon have a length of 2.266 Å. The highest occupied energy level (−6.5 eV) has a five-fold degeneracy, and the lowest unoccupied level (−2.5 eV) is triply degenerate. The structure of the Si_{60} cluster was found to be stable with respect to certain distortions which lower the symmetry. It was shown that the Na^+ @ Si_{60} complex is much more stable than F^- @ Si_{60}, unlike the X @ C_{60} complexes (X = Na^+, F^-), to which the inverse order of stability applies. The structure of the Si_{24} cluster was calculated on the assumption that the O_h symmetry group is retained. It was pointed out that the total potential energy surface does not contain a local minimum corresponding to this structure.

It should be noted that problems relating to the structure of clusters of silicon atoms have been widely discussed in the literature.[124, 125] The results of mass-spectral analyses suggest that silicon (unlike carbon) tends to form clusters with an odd number of atoms.[124] The greater length of the Si – Si (as compared with the C–C) bond may assist the formation of three-dimensional structures on whose surface partially conjugated Si_m chains are accommodated. This model was constructed for the Si_{45} cluster[125] by the molecular mechanics method. Evidently the structure of the Si_{45} cluster[124] is a reflection of the greater tendency of Si atoms to form single bonds.

We know that the elements of the third period do not form aromatic compounds.[126] Therefore the problem of synthesising the silicon analogue of footballene is of great interest to theoreticians as well as to experimentalists.

The ability of boron atoms to form polyhedral structures of composition C_nB_m is beyond doubt.[121] Similarly, the replacement of some carbon atom in a polyhedral cluster by nitrogen is not incompatible with the general principles of valency theory. However, it is reasonable to ask whether the homonuclear N_n or B_n clusters can exist.

In the former case the clusters could play the role of Lewis superbases, in the latter they could be superacids. The possibility of combining boron and nitrogen atoms within the same molecule has already been established in nature for a small molecule: borazole, a very stable compound of aromatic character.

The study of the possible existence of N_n clusters has a long history, and is directly related to the stability of hexa-azabenzene (the cyclic molecule N_6), which has been discussed extensively (see for example, the work of Gal'pern et al.,[127] and Stankevich et al.[128] and the references quoted in those papers).

It was concluded[127, 128] that the repulsion between the neighbouring unshared electron pairs could be responsible for instability of the cyclic N_6 molecule. In principle this destabilising factor should also be found in polyhedral systems. Chen Cheng et al.[129] reported the results of calculations by the MINDO/3, MNDO, and AMI methods for a dodecahedral N_{20} cluster. The equilibrium geometry was identified, and the heat of formation of the cluster was calculated as well as the heats of the reactions $10N_2 \rightleftharpoons N_{20} \rightleftharpoons 20N$. All three methods lead to the conclusion that a local energy minimum exists for the N_{20} cluster. The following values (in Å) were obtained for the N–N bond lengths: 1.484 (AMI), 1.426 (MNDO) and 1.347 (MINDO/3). The N_{20} cluster was found to be more stable than a system of 20 nitrogen atoms but less stable than a system of 10 nitrogen molecules (AMI, MNDO).

The stability and the electronic structure of polyhedral clusters of the mixed type $(C_nB_mN_k)$ were discussed by Xia et al.,[130] who calculated by the MNDO method the electronic structure of the 60-atom systems C_{60}, B_2C_{58}, N_2C_{58}, BNC_{58}, $C_{12}B_{24}N_{24}$, and $B_{30}N_{30}$, and obtained their heats of formation. It was established that all the mixed systems have a stability close to that of C_{60}. According to these workers[130] it should be easier to synthesise the $B_{30}N_{30}$ than the C_{60} cluster, but no attempt appears to have been made so far to prepare that cluster.¶

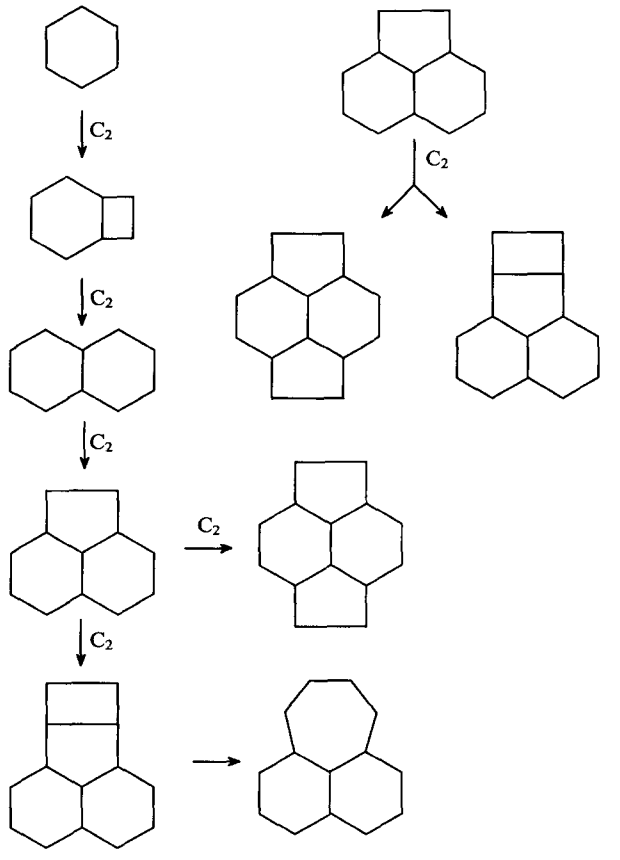
IV. Mechanism of formation of the fullerenes and of endohedral complexes

The mechanism of formation of the fullerenes is not known in detail. There are only some general considerations on the growth of the carbon cluster by the successive addition of C_2 particles, which are thought to be predominant in graphite vapour.[131] Experimental morphological observations (the spiral growth of cylindrical tubes in tubulenes[97]) cannot be extended to the closed molecules of the higher fullerenes.

The main structural difference between the fullerenes and graphite is the presence of pentagons in the former. The first pentagon (surrounded by hexagons) leads to the formation of

¶ Reports of the synthesis of M_8C_{12} systems, where M = Ti, Zr, V, have recently appeared [B C Guo, K P Kerns, A W Gastleman *Science* **256** 515 (1992)]. Dodecahedral structures, with each M atom associated with three C atoms, were assigned to these molecules.

corannulene (a nonplanar structure), and the formation of a heptagon can lead to the same result.[132] The formation of even a single nonhexagonal ring is a prerequisite for the eventual conversion of the structure into a closed figure. The formal scheme described in the next section explains the formation of nonhexagons during the initial stages of the process.



The presence of pentagons is the critical stage in the *de novo* formation of endohedral metal complexes. It should be noted first of all that endohedral complexes have been described only for group III metals (lanthanum, yttrium, and scandium). These metals are characterised by the formation of π-cyclopentadienyl (cp) complexes with η^5 coordination, and π-arene complexes with η^6 coordination are practically unknown in this case. According to the hypothesis formulated by one of us[132] this difference is critical in the formation of endohedral metal fullerenes with the participation of intermediates of the $(\eta^5\text{-}C_5H_5)_nM$ type (n = 1, 2) with a closed fullerene shell. Thus η^5 coordination with several cp ligands is also characteristic of other metals (for example, uranium), and in these transition metals, as in nickel and iron, η^5 coordination is preferred over η^6.

If the $(\eta^5\text{-}C_5H_5)_nM$ intermediates are important in the synthesis of endohedral complexes it may be preferable to introduce into the graphite electrode the already prepared cp_2M-X complex instead of the metal salt (or, indeed, the oxide) in view of the high affinity of the group III metals for oxygen, which may produce an undesirable competition for the metal. The prepared cp–M fragment is stable in an inert gas atmosphere, and it can arrange itself in hexagons during high-temperature dehydrogenation, which favours the formation of endohedral complexes of the fullerenes with other metals possibly in high yields. The *de novo* synthesis of endohedral fullerene complexes thus described, i.e. the synthesis at the instant of the formation of the fullerene spheroid itself, was complemented by another approach different in principle. It was shown mass-spectrometrically[133–137] that when an inert gas is bombarded with a beam of accelerated C_n^+ cation radicals endohedral $X@C_n$ complexes are formed with the inert gases (helium or neon) in an ionised form. A special technique was developed to reduce the $He@C_{60}$ reversibly in the gas phase and to detect it.[137] These studies were recently reviewed by Schwarz.[138]

V. Classification of the forms of carbon with a regular structure

Known forms of carbon with a regular structure are most rationally classified as molecular or covalent crystals. Molecular crystals are composed of individual molecules (carbon clusters) of finite size: the fullerenes. Covalent crystals are characterised by polymeric structures.

The structures of covalent crystals are conveniently described in terms of infinite graphs. In this method of description diamond corresponds to a uniform graph of order 4. By constructing such a graph in three dimensions we can easily represent the diamond structure, which corresponds to the closest packing of carbon atoms.

Graphite is described by a disconnected graph consisting of an infinite number of two-dimensional lattices. Each of these lattices can be realised as a hexagonal grid on a plane. The third allotropic form of carbon (carbyne[139]) is described in terms of an infinite number of simple, rectilinear paths.

The real structures of diamond, graphite, and carbyne suggest a three-dimensional, a quasi-two-dimensional, and a quasi-one-dimensional character for these allotropic modifications of carbon, accurately reflected by the theory of hybridisation.

In addition to the above, there are many other methods of regularly filling a three-dimensional space with carbon atoms. Some of these are described in the monograph by Wells,[24] who used infinite graphs with coordinates. The construction of nets of trigonal carbon atoms has also been described:[140,141] it was shown that in addition to diamond, graphite, and carbyne, which display (in the ideal case) the sp^3, sp^2, and sp hybridisation of the atomic orbitals, crystalline modifications of carbon with an intermediate hybridisation are possible, and also mixed forms of carbon containing tetragonal, corner, and trigonal atoms.

A mechanism allowing the regrouping of several nets of this type into planar graphite layers has been proposed.[142] In the crystals the graphite layers are at a distance of 3.35 Å from each other. This defines the 'thickness' of the graphite layer, i.e. its extent in a direction perpendicular to the plane. Since this is infinitely small in comparison with the size of the graphite plane the three-dimensional structure of the graphite layer can be characterised by the effective dimensionality $2+\varepsilon$ where $0 < \varepsilon \ll 1$. Similarly the van der Waals interaction defines the thickness of the carbyne filament. The three-dimensional structure of the carbyne molecule can be described as $1+\delta$, where $0 < \delta \ll 1$. Obviously, on this scale the effective dimensionality of diamond is described by the number 3, corresponding to that of three-dimensional space.

Let us now consider a fragment of a hexagonal net on a plane, in the shape of an infinite band. This fragment can be rolled into a hexagonal net (tubulene), drawn over the lateral surface of a cylinder, and in this way chiral tubulenes of different size can be produced.

The tubulene form of carbon is intermediate between diamond and the fullerenes. The growth of carbon tubes of different diameter has been observed experimentally by Iijima.[103]

If the network on a plane consists of 5- and 6-membered rings it can be treated as the result of defect formation in an ideal hexagonal system. Toroidal structures (the torenes) can be formed from fragments of this net in the form of an infinite band. A combination of tubulenes can give tubular systems with bifurcations, and also structures whose atoms are located on a surface having a negative curvature.[104]

We should also note that the structures of all the forms listed above can be interpreted as the result of 'grafts' between chain carbon molecules.

Some workers suggest[20] that the mechanism of formation of the fullerenes from carbon vapour includes a process of the grafting type as one of its initial stages.

The classification of the regular carbon structures proposed by one of us[35] is shown in Figure 9.

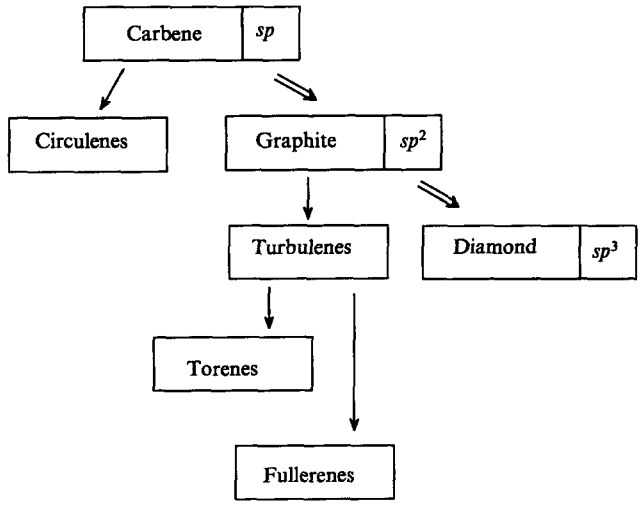


Figure 9. Classification of the regular carbon structures.[35]

VI. Chemical properties of carbon clusters

The unique structural features of the fullerenes, causing unsaturation of all the bonds in the absence of substituents, make only two types of primary reaction possible in this system: the withdrawal of electrons and the addition of electrons or of groups. The replacement of already present groups and their removal are secondary reactions of the derivatives. It follows from the above that the fullerenes are electrophilic and good electron acceptors. They readily undergo addition of nucleophiles, and also of free-radical and of carbenoid species. Nearly all the reactions studied in fullerenes took place on C_{60} or its mixtures with C_{70}. Nothing is known about the chemical properties of the higher fullerenes.

1. Reactivity of C_{60}

a. Addition of hydrogen and halogens

The addition of several hydrogen molecules takes place under the conditions of the Birch reaction in the presence of an alkali metal in ammonia or in an amine, giving $C_{60}H_{36}$ as the main product, from which (as reported[143]) the $C_{60}H_{60}$ fullerene can be obtained. Dihydrofullerene $C_{60}H_2$ was obtained by selective hydrozirconylation of C_{60} followed by hydrolysis.[144]

$$C_{60} + cp_2Zr(H)Cl \longrightarrow C_{60}H(Zr\,cp_2Cl) \xrightarrow{H_2O} C_{60}H_2$$

8% ($\delta_H = 5.07$ p.p.m.)

A theoretical evaluation of all the possible isomers of $C_{60}H_2$ has been reported:[145] many of the isomers are found to be stable.

Buckminsterfullerene adds on some fluorine atoms in the presence of XeF_2, and complete fluorination is observed when solid C_{60} is treated with gaseous fluorine.[146,147] The fullerene $C_{60}F_{60}$ is a colourless crystalline substance soluble in THF and in acetone. Its ^{19}F NMR spectrum contains only one singlet line. The chlorination and bromination reactions are reversible, and iodine undergoes almost no addition. Chlorination and bromination yield a mixture of products containing (on average) 22 chlorine atoms and 28 bromine atoms respectively. Some bromofullerenes have been isolated in a pure form. The halogen atoms in the halogenofullerenes are easily replaced by nucleophilic OH or NH_2 groups.[148-150]

b. Electrochemical reduction

The electrochemistry of the fullerenes has been studied by a few groups of workers. By examining a continuously increasing range of electrolytes and solvents it was shown that 6 electrons can be added sequentially and reversibly to C_{60}.[151] It is interesting to note that no difference was observed between the first ionisation potentials of C_{60} and C_{70}.[152] The C_{60}^{n-} anions are anion radicals for odd values of n, but for even n the spin pairing problem prevents the observation of the ESR spectrum under certain conditions. Some work on the electrochemistry of BF derivatives has been published recently.[153]

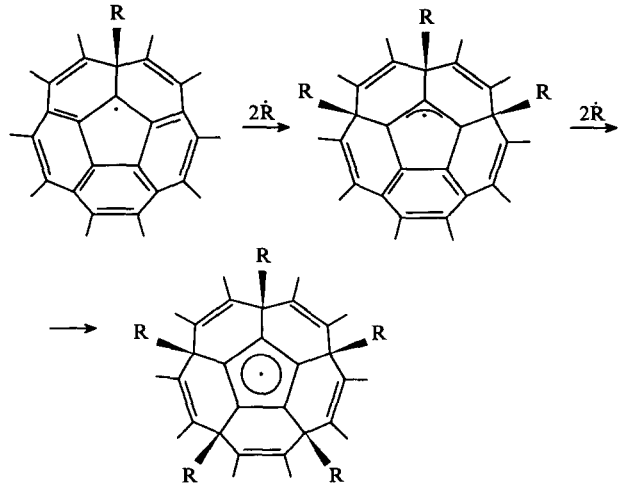
c. Reduction by metals

The transfer of electrons from alkali metals to fullerenes has been studied in reasonable detail both in solutions and in films. The stimulus for this work was the discovery of superconductivity in the M_3C_{60} phase.[17] The highest critical temperature observed for the caesium–rubidium salt Cs_2RbC_{60} was 33 K. We note that the superconducting salts are ion radicals and have a face-centred cubic lattice.[154] Changing from Cs_2RbC_{60} to Cs_3C_{60} produces a different type of lattice, and the superconductivity disappears.

Other metals and their salts can also transfer electrons to the fullerenes. However, these compounds have not been adequately studied. It was recently shown that the C_{60} anion radical is formed during the homogeneous reduction of C_{60} by samarium(II) iodide in THF.[155]

d. Addition of free radicals

Krusic et al.[156] observed the very easy addition to C_{60} of free radicals with their centre over the carbon, oxygen, or sulphur atoms. By using ESR they established the structure of some of the most stable radical products of repeated additions. An analysis of the hyperfine splitting lines showed that the most stable radicals are those of the allyl and cyclopentadienyl type, with three or five benzyl radicals added at the (6, 6) bonds.[157] The benzyl radical used in this work was labelled with the ^{13}C isotope at the methylene group.



We have studied the addition to C_{60} and C_{70} of free radicals in which the spin density was concentrated on an atom which had a magnetic moment (phosphorus, boron, tin, etc.).[158-160] This approach is useful because it allows the hyperfine splitting in the ESR spectra to be observed without introducing an isotopic label. The addition of the phosphoryl radical, conveniently generated by the photolysis and thermolysis of the mercury salt $Hg[P(O)(OR)_2]_2$, was studied in most detail. The spin density in

the phosphoranylfullerenyl radical was almost fully localised on three carbon atoms of the short-range surroundings. We studied the kinetics of the reversible dimerisation of this radical.

$$2C_{60}^{\cdot}-P(O)(OR)_2 \rightleftharpoons [C_{60}-P(O)(OR)_2]_2$$

e. Ion-radical salts

In addition to the salts with alkali metals mentioned above other ion-radical salts have also been described.† The electrolysis of C_{60} in a mixture of THF and CH_2Cl_2 in the presence of tetraphenylphosphinium chloride gave the paramagnetic salt $Ph_4P^+ \ldots C_{60}^{-} \ldots (Ph_2PCl)_2$.[161] The interaction of C_{60} with the electron-donor complex of low-valency chromium **1** in toluene solution gave the salt **2** as a result of electron transfer from **1** to the fullerene.

$$C_{60} + \underset{\mathbf{1}}{(TPP)Cr(II)} \underset{THF}{\overset{PhMe}{\rightleftharpoons}} \underset{\mathbf{2}}{C_{60}^{-}(TPP)Cr(III)^{\cdot+}}$$

The addition of THF causes dissociation of salt **2**. The reaction of BF in toluene solution with a 20-fold excess of tetrakis-(dimethylamino)ethylene produces the salt $C_{60}(TDAE)_{0.86}$. This ion-radical salt undergoes a ferromagnetic transition at 16.1 K, which is the highest reported temperature for an organic ferromagnetic.[163]

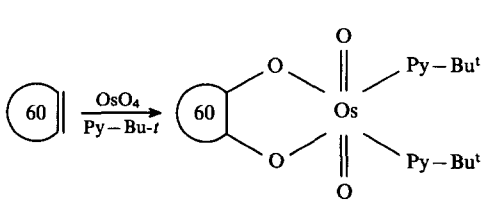
f. Oxidation and reactions with Lewis acids

Buckminsterfullerene C_{60} forms a cation radical under the influence of Lewis acids (for example, SbF_5).[164] However, in order to obtain stable derivatives from these cation radicals it is convenient to use $AlCl_3$, which yields the polyarylated fullerenes $C_{60}H_nAr_n$ ($n \simeq 12$).[165]

$$C_{60} \xrightarrow[AlCl_3]{ArH\ (exc.)} C_{60}H_nAr_n$$

Oxidation with oxygen. Buckminsterfullerene reacts with oxygen only when irradiated:[166] the triplet state of C_{60} is formed first, and energy transfer from this state produces singlet oxygen which reacts directly with the fullerene. Under these conditions some of the carbon–carbon bonds are broken and carbonyl groups are formed, with evolution of CO and CO_2. One direction of the reaction produces the oxides $C_{60}O$ and $C_{70}O$, which are usually found in mixtures of fullerenes.[167]

Oxidation with OsO_4. The oxidation of olefins by osmium tetroxide with opening of the double bond and formation of 1,2-diol ethers is well known. This reaction has been observed with C_{60}.



The conditions needed to produce the pure mono-derivative have been identified, and an X-ray diffraction analysis of the compound has been reported.[87, 168–170] The first experimental data on the geometry of the BF were obtained for this compound.

†A complex with the (+)-DIOP ligand (the first optically active organometallic derivative in the fullerene series) was obtained in a similar way [V V Bashilov et al. *Izv. Ross. Akad. Nauk, Ser. Khim.* 428 (1993)].

g. Fullerenes as ligands

The presence of a continuous 'electron cloud' in a fullerene polyhedron allows us, in principle, to select different numbers of electrons as participants in the bonding to give metal complexes. The formation of the following types of complex can be postulated:

η^1 — a simple complex with a σ bonding at one vertex (an even number of groups can be found in a non-free-radical product),
η^2 — a π-olefin complex at an edge or the geometrically equivalent double σ bonding at neighbouring vertices,
η^3 — a π-allyl complex,
η^4 — a π complex of the trimethylenemethane or 1,3-diene type,
η^5 — a π-cyclopentadienyl complex,
η^6 — a π-arene complex.

The stable complexes so far identified all belong to the first two types. Other types do not appear to have been prepared as yet. The last two types are of special interest because double π complexes of metals with nonadjacent hexagonal faces of C_{60} should be chiral and therefore could occur in an optically active form.[171]

Reactions with low-valency complexes of the transition metals. The analogy between fullerenes and the electron-acceptor olefins is clearly seen in the formation of π complexes with some transition metals. The reaction of C_{60} with ethylene-bis-(triphenylphosphine)platinum results in the addition of between 1 and 6 L_2Pt fragments: the first and the second of these complexes have been characterised by X-ray structural analysis.[172–174] In the $(\eta^1\text{-}C_{60}).(PtL_2)_6$ complex the six L_2Pt groups are disposed octahedrally, forming a molecule with the T_h symmetry. The reaction of C_{60} with tetrakis-(triphenylphosphene)palladium gives the complex $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$,

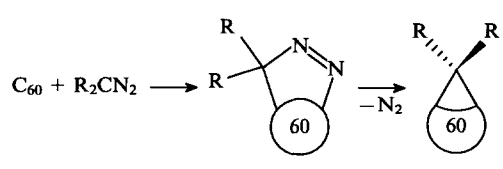
$$C_{60} + (Ph_3P)_4Pd \longrightarrow (\eta^2\text{-}C_{60})Pd(PPh_3)_2\ ,$$

whose structure[175] is very similar to that of its platinum analogue: the only difference is that the coordinated C–C bond is less stretched and has approximately the same length as the corresponding bond in the initial fullerene.‡ The reaction of C_{60} with the zero-valent $Pd_2(dba)_3$ complex yields insoluble oligomeric products of composition $C_{60}Pd_x$.[176]

$$C_{60} + Pd_2(dba)_3 \longrightarrow C_{60}Pd_x + dba\ .$$

In the olefin complexes with Ir(I) the olefin can be removed by buckminsterfullerene, whereas the CO, PPh_3 and $P(OMe)_3$ molecules remove the fullerene from the complex.[177–179]

Reactions with diazo compounds. Fulleroids. A new type of product was obtained by Wudl[180–182] from the reaction between buckminsterfullerene and diaryldiazo compounds. The first stage was probably [3 + 2]-cyclo-addition with formation of pyrazolene. However, after one hour a mixture of products of composition $C_{60}[CR_2]_n$ (where n = 1–6, R = Ar) was precipitated from a toluene solution.



3

‡The electrochemical synthesis of the salt $[(Ph_3P)_2N]^+C_{60}^{-}$ has recently been reported [H Moriyama, H Kobayashi, A Kobayashi, T Watanabe *J. Am. Chem. Soc.* **115** 1185 (1993)]. Single crystals of this salt have been studied by the X-ray structural method.

A remarkable feature of the fullerene structure is the breaking of one C–C bond in the reaction with carbenes, forming a bridge consisting of a tetrahedral carbon atom with two aryl substituents. The structures **3** formed in this way were called fulleroids. This is still the only way so far reported of preparing fullerenes with an odd number of carbon atoms: all the other fullerenes known at present have an even number of carbon atoms.

All the 6 homologous fullerenes with $n = 1-6$ (R = Ph) have been isolated and characterised spectroscopically (and also by X-ray structural analysis in the case of the first homologue). The methanoannulene structure for the compound **3** is suggested by the large distance between the carbon atoms of the pair (1.84 Å) and also by comparing the NMR spectra of this compound with those of the Vogel model compounds.[183]

The addition of the Ar_2C species to the final product takes place at a (6, 6) bond, but it was established that two additional isomers can be formed and then be converted into the main isomer. Surprisingly, in a recent study[184] of the reaction of C_{60} with unsubstituted diazomethane the addition of CH_2 was found to take place on a (6, 5) junction. Thus the regioselectivity of the formation of the fulleroid depends on the nature of the substituents on the carbene carbon (Figure 10).

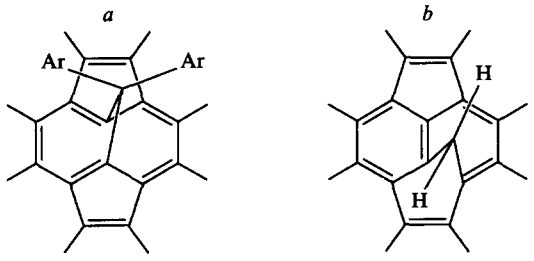


Figure 10. Fragments of the surface of $C_{60}CR_2$ fulleroids. *a* with the carbene added across the (6,6) bond, *b* with the carbene added across the (6,5) bond.

A recent publication[185] suggests that the thermolysis of azides in the presence of C_{60} produces azafulleroids; in one of these, the azide $Me_3SiCH_2CH_2OCH_2N_3$ with the ^{15}N isotopic label, it was shown that the nitrene group breaks a (5, 6) carbon bond.

We should stress the difference in structure between the adducts of C_{60} with a true (carbon) carbene or nitrene and with a platinum (or palladium) carbenoid (see above). Obviously, for carbon and nitrogen the most favourable process is the breaking of the strained cyclopropane fragment, giving two σ bonds, whereas with a transition metal the η^2 coordination is preferred.

2. Reactivity of C_{70}

Studies with C_{60}/C_{70} mixtures failed to detect a significant difference in reactivity between the two. Therefore, since pure C_{70} is more difficult to prepare than pure C_{60} its chemical properties have been less widely studied.

Balch et al.[179] have described the synthesis and the structure of the complex of iridium(I) with C_{70}.

$$Ir(CO)(PPh_3)_2Cl + C_{70} \longrightarrow (\eta^2\text{-}C_{70})Ir(CO)(PPh_3)Cl$$

Precise information on the geometry of fullerene-70 itself was inferred from the structure of this complex. Iridium is added across a (6, 6) edge at the 'sharp' end of the egg-shaped molecule. As reported,[179] the freedom of this end of the molecule from departures from a spheroidal shape favours bond formation. The iridium complex of C_{70} could not be obtained from the η^5-indenyl derivative of iridium.[178]

The reaction of C_{70} with the $^{\bullet}P(O)(OR)_2$ phosphoranyl radicals has been studied by ESR.[160] The primary products were found to be three different phosphoranylfullerenyl radicals corresponding to addition at nonequivalent corners of a nongraphite type (i.e. not at the junction of three hexagons).

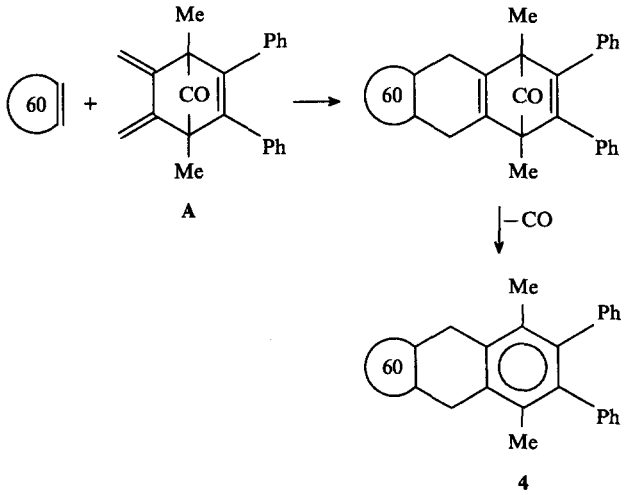
3. Other chemical properties

Inclusion compounds in which hydrophobic fullerenes act as guests for the inclusion of appropriate hosts within molecules or lattices are of special interest. It should be possible to separate the different fullerenes by this method. However, so far only one detailed publication has appeared,[185] describing the structure of the inclusion compound of C_{60} and hydroquinone with a stoichiometry of 1 : 3. The formation of a complex of γ-cyclodextrine with C_{60} has also been reported.[187] However, the formation of the inclusion compound was inferred only from the evidence of the absorption spectrum of a dilute aqueous solution.

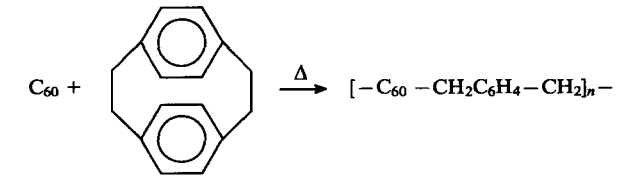
For many reactions of the fullerenes no corroborated data are available, but tentative advance reports can be found in papers on related topics. Thus, we know that fullerenes react with anthracene, cyclopentadiene, phosphines, and amines but only the adduct of C_{60} with morpholine has been described in sufficient detail.[188] A light yellow substance whose analysis indicated the addition of 6 equivalents of the amine was precipitated from a solution of C_{60} in morpholine. The ^1H NMR spectra of this compound suggest the presence of a dynamic process, interpreted as the motion of H atoms over the surface of the spheroid.

Reliable descriptions of two cases of cycloaddition at a double bond of fullerenes in purely carbon systems are available.

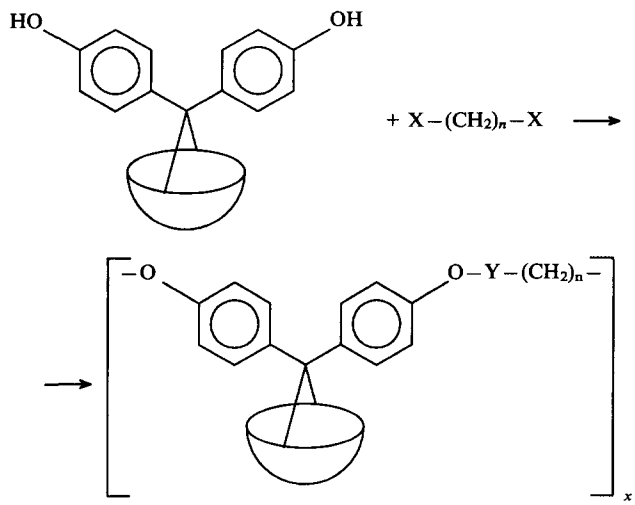
The reaction with dehydrobenzene takes place as a [2+2] cycloaddition, leading to adducts of the biphenylene type.[189] To identify the product of the Diels–Alder [4+2] reaction a special diene was used (structure A), whose adduct with fullerene undergoes partial aromatisation thus preventing the retro-decomposition.[190] The stable end product **4** was characterised by X-ray structural analysis.



The prospects of including fullerenes in polymeric systems have been examined. Thus polydiazo compounds can be converted into polyfullerenes of the 'pendant chain' type.[182] By exploiting the tendency of benzyl radicals to combine with fullerenes a polymer in which the C_{60} spheroids are connected in a chain by xylylene radicals was synthesised: pyrolysis of this material gives [2,2]-paracyclophane.[191]



Clearly, multiple grafting of the chains with formation of net polymers is possible. Polymers of the polyester and polyurethane types have been obtained[192] from a fulleroid containing two *p*-hydroxyphenyl groups and derivatives of dibasic carboxylic acids.



X = –COCl, *n* = 8, Y = –CO–
X = –NCO, *n* = 6, Y = –CO–NH–

Very useful information is given by a quantitative study[193] of the solubility of C_{60}. The best solvent is carbon disulfide, in which the solubility of C_{60} greatly exceeds the solubility in any other solvent. The solvents can be arranged in the following series of decreasing ability to dissolve the fullerenes: carbon disulfide ≫ toluene > benzene > mesitylene ≫ carbon tetrachloride > methylene chloride ≫ tetradecane > dodecane > decane > cyclohexane > dioxan ≈ hexane > isooctane ≈ octane ≫ pentane.

We also have a report[194] of the preparation of mixed polyhedral carbon–lanthanide clusters (C_nLn_m) in a solution of the iron–carbon eutectic.

No information on the biological activity of the compounds of the fullerene series has been published so far. Nevertheless their ability to generate singlet oxygen under UV irradiation justifies the expectation of oxidation catalysis *in vivo*, which implies biological activity.

VII. Conclusions

This review has dealt only with the most interesting and promising directions in the chemistry of the fullerenes. Evidently, during the next few years these areas will be actively developed, and will stimulate increasing interest in both experimentalists and theoreticians.§ These directions include, in particular:

— the development of new cheaper and more convenient methods and schemes for the preparation and separation of the pure C_{60} and C_{70} fullerenes;

— the synthesis of fullerenes containing a greater number of carbon atoms;

— the development of methods of synthesis of heterofullerenes consisting of polyhedra of noncarbon atoms (boron, nitrogen, transition metals, etc.), and the synthesis of new endohedral complexes;

— the development of reliable theoretical methods of predicting the physicochemical properties of carbon clusters and of their hetero-analogues and endohedral complexes;

— the computer modelling of the mechanism of formation of fullerenes, tubulenes, torenes, and other carbon clusters;

— the creation of methods of selective functionalisation (i.e. the preparation or individual fullerene derivatives);

— the preparation of optically active fullerene derivatives and their study by chiro-optical methods;

— the creation of a fund of information on the biological activity of the fullerenes and of their derivatives, and the assessment of the ecological safety of the fullerene derivatives.

§ This expectation is supported by the appearance of a new international and interdisciplinary journal: *Fullerene Science and Technology*. The first issue of this journal was produced in February 1993 by Marcel Dekker.

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