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Parent Fullerenes

1.1 Fullerenes: Molecular Allotropes of Carbon

For synthetic chemists, who are interested in the transformation of known and the creation of new matter, elemental carbon as starting material once played a minor role. This situation changed dramatically when the family of carbon allotropes consisting of the classical forms graphite and diamond became enriched by the fullerenes. In contrast to graphite and diamond, with extended solid state structures, fullerenes are spherical molecules and are soluble in various organic solvents, an important requirement for chemical manipulations.

Fullerenes are built up of fused pentagons and hexagons. The pentagons, absent in graphite, provide curvature. The smallest stable, and also the most abundant fullerene, obtained by usual preparation methods is the I_h -symmetrical Buckminsterfullerene C_{60} (Figure 1.1). Buckminsterfullerene has the shape of a soccer ball. The next stable homologue is C_{70} (Figure 1.2) followed by the higher fullerenes C_{74} , C_{76} , C_{78} , C_{80} , C_{82} , C_{84} , and so on. The building principle of the fullerenes is a consequence of the Euler theorem, which says that for the closure of each spherical network of n hexagons, 12 pentagons are required, with the exception of $n = 1$.

Compared to small two-dimensional molecules, for example the planar benzene, the structures of these three-dimensional systems are aesthetically appealing. The beauty and the unprecedented spherical architecture of these molecular cages immediately attracted the attention of many scientists. Indeed, Buckminsterfullerene C_{60} rapidly became one of the most intensively investigated molecules. For synthetic chemists the challenge arose to synthesize exohedrally modified derivatives, in which the properties of fullerenes can be combined with those of other classes of materials. The following initial questions concerned the derivatization of fullerenes: What kind of reactivity do the fullerenes have? Do they behave like a three-dimensional “superbenzene”? What are the structures of exohedral fullerene derivatives and how stable are they?

The IUPAC method of naming Buckminsterfullerene given below is too lengthy and complicated for general use [1]:

Hentriacontacyclo[29.29.0.0.^{2,14}.0^{3,12}.0^{4,59}.0^{5,10}.0^{6,58}.0^{7,55}.0^{8,53}.0^{9,21}.0^{11,20}.0^{13,18}.0^{15,30}.0^{16,28}.0^{17,25}.0^{19,24}.0^{22,52}.0^{23,50}.0^{26,49}.0^{27,47}.0^{29,45}.0^{32,44}.0^{33,60}.0^{34,57}.0^{35,43}.0^{36,56}.0^{37,41}.0^{38,54}.0^{39,51}.0^{40,48}.0^{42,46}]hexaconta-1,3,5(10),6,8,11,13(18),14,16,19,21,23,25,27,

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29(45),30,32,(44),33,35(43),36,38(54),39(51),40(48),41,46,49,52,55,57,59-triacontane.

Furthermore, the enormous number of derivatives, including the multitude of possible regioisomers, available by chemical modifications requires the introduction of a simple nomenclature. According to the latest recommendation, the icosahedral Buckminsterfullerene C_{60} was named as $(C_{60}-I_h)[5,6]$ fullerene and its higher homologue C_{70} as $(C_{70}-D_{5h})[5,6]$ fullerene [2, 3]. The parenthetical prefix gives the number of C-atoms and the point group symbol; the numbers in brackets indicate the ring sizes in the fullerenes. Fullerenes involving rings other than pentagons and hexagons are conceptually possible (*quasi*-fullerenes [4]). The identification of a well defined and preferably contiguous helical numbering pathway is the basis for the numbering of C-atoms within a fullerene. Such a numbering system is important for the unambiguous description of the multitude of possible regioisomeric derivatives formed by exohedral addition reactions. A set of rules for the atom numbering in fullerenes has been adopted [2, 3]. The leading rule (Fu-3.1.1) is:

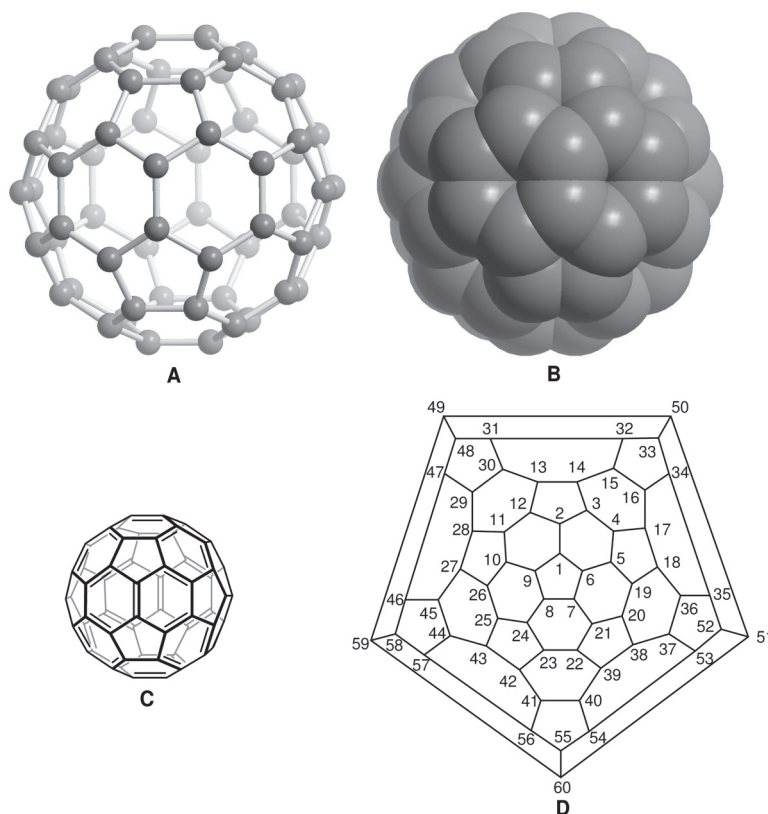


Figure 1.1 Schematic representations of C_{60} . (A) ball and stick model, (B) space filling model, (C) VB formula, (D) Schlegel diagram with numbering of the C-atoms (according to [4]).

Proper rotation axes (C_n) are examined in sequence from the highest-order to the lowest-order axis, until at least one contiguous helical pathway is found that begins in a ring through which a proper rotation axis passes, at the end a bond bisected by a proper rotation axis, or at an atom through which a proper rotation axis passes. Numbering begins at the end of such a contiguous helical pathway, and the corresponding axis is called the “reference axis”.

This system allows also for the indication of the absolute configuration of inherently chiral fullerenes by introducing the stereodescriptors ($^{f,s}C$) and ($^{f,s}A$) (“f” = fullerene; “s” = systematic numbering; “C” = clockwise; “A” = anti-clockwise).

In another nomenclature recommendation it was suggested that fullerenes be named in the same way as annulenes, for which the number of C-atoms is indicated in square brackets in front of the word [4]. For fullerenes the number of C-atoms is accompanied by the point group symmetry and by the number of the isomer (using capital Roman) in cases where there are more than one. This is especially important for higher fullerenes. Thus, for Buckminsterfullerene the full description is

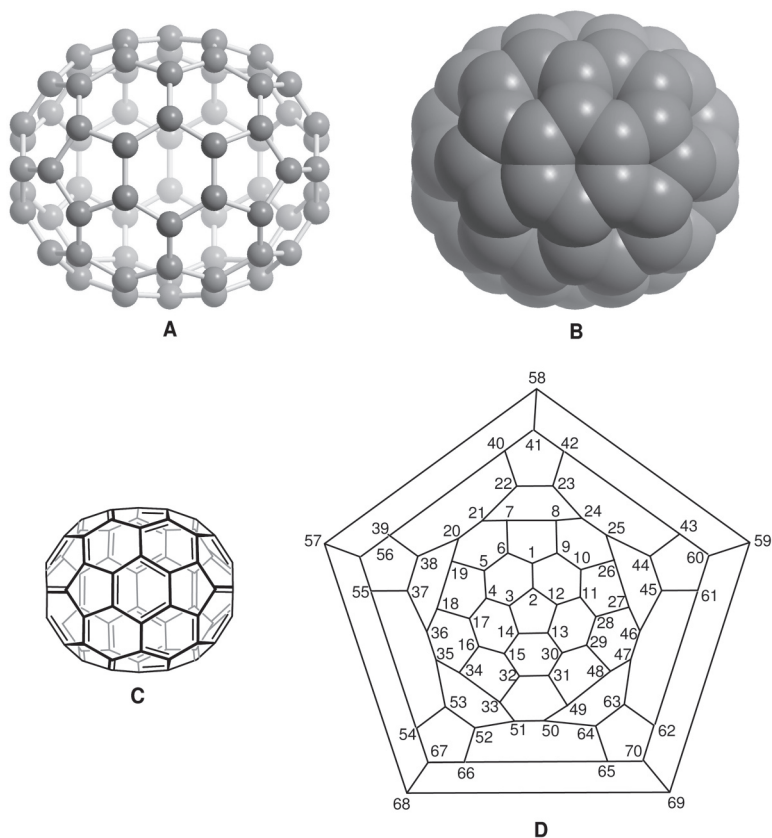


Figure 1.2 Schematic representations of C₇₀. (A) ball and stick model, (B) space filling model, (C) VB formula, (D) Schlegel diagram with numbering of the C-atoms (according to [4]).

[60- I_h]fullerene and for C_{70} (Figure 1.2) [70- D_{5h}]fullerene. In most cases further simplification to [60]fullerene and [70]fullerene or even C_{60} and C_{70} is made, since there are no other stable isomers of these fullerenes. An alternative numbering of C-atoms to that pointed out above [2, 3] is also based on a contiguous spiral fashion but numbers the bond of highest reactivity as 1,2 (Figure 1.1) [4]. For [60]fullerene these are the bonds at the junction of two hexagons ([6,6]-bonds). Since the chemistry of [70]fullerene has many similarities to that of [60]fullerene, it is advantageous if the numbering scheme for [70]fullerene parallels that of [60]fullerenes, which is indeed possible (Figure 1.2) [4].

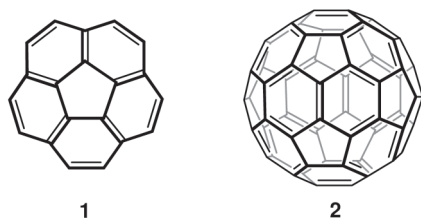
Valence bond (VB) formulas or Schlegel diagrams are useful for simple schematic representations of fullerenes and their derivatives. VB formulas are mostly used for parent fullerenes or for derivatives with a few modifications of the cage structure only. A Schlegel diagram shows each C-atom of the fullerene, which is flattened out in two dimensions. This model is suitable for considering polyadducts, for example, polyhydrofullerenes.

The main type of chemical fullerene derivatizations are addition reactions. Regardless of the relatively many possible reaction sites, addition reactions show a remarkable regioselectivity, especially when the number of addends is small. This is another fulfilled requirement, which makes these molecular spheres exciting objects for synthetic chemists.

1.2

Discovery of the Fullerenes

In 1966 Deady alias D.E.H. Jones considered the possibility of making large hollow carbon cages, structures now called giant fullerenes [5, 6]. This suggestion elicited no reaction from the scientific community. Four years later, in 1970, simulated by the synthesis of the bowl shaped corannulene **1** [7], Osawa first proposed the spherical I_h -symmetric football structure for the C_{60} molecule (**2**) [8, 9]. During his efforts to find new three-dimensional superaromatic π -systems, he recognized corannulene to be a part of the football framework. Subsequently, some theoretical papers of other groups appeared, in which inter alia Hückel calculations on C_{60} were reported [10–13].



In 1984 it was observed that, upon laser vaporization of graphite, large carbon-only clusters C_n with $n = 30$ –190 can be produced [14]. The mass distribution of these clusters was determined by time-of-flight mass spectrometry. Only ions with

even numbers of carbon atoms were observable in the spectra of large carbon clusters ($n \geq 30$). Although C_{60} and C_{70} were among these clusters, their identity was not recognized. The breakthrough in the experimental discovery of the fullerenes came in 1985 [15] when Kroto visited the Rice University in Houston. Here, Smalley and co-workers developed a technique [16] for studying refractory clusters by mass spectrometry, generated in a plasma by focusing a pulsed laser on a solid, in this case graphite. Kroto and Smalley's original goal was to simulate the conditions under which carbon nucleates in the atmospheres of red giant stars. Indeed, the cluster beam studies showed that the formation of species such as the cyanopolyynes HC_7N and HC_9N , which have been detected in space [17, 18], can be simulated by laboratory experiments [19]. These studies found that, under specific clustering conditions, the 720 mass peak attributed to C_{60} , and to a lesser extent the peak attributed to C_{70} , exhibits a pronounced intensity in the spectra (Figure 1.3). Conditions could be found for which the mass spectra were completely dominated by the C_{60} signal. Kroto and Smalley immediately drew the right conclusion of these experimental findings. The extra stability of C_{60} is due to its spherical structure, which is that of a truncated icosahedron with I_h symmetry [15]. This molecule was named after the architect Buckminster Fuller, whose geodesic domes obey similar building principles. Retrospectively, the enhanced intensity of the peak of C_{70} , which is also a stable fullerene, became understandable as well. Although Buckminsterfullerene (C_{60}) was discovered, a method for its synthesis in macroscopic amounts was needed.

This second breakthrough in fullerene research was achieved by Krätschmer and Huffman [20]. Their intention was to produce laboratory analogues of interstellar dust by vaporization of graphite rods in a helium atmosphere [21]. They observed that, upon choosing the right helium pressure, the IR-spectrum of the soot, generated by the graphite vaporization, shows four sharp stronger absorptions,

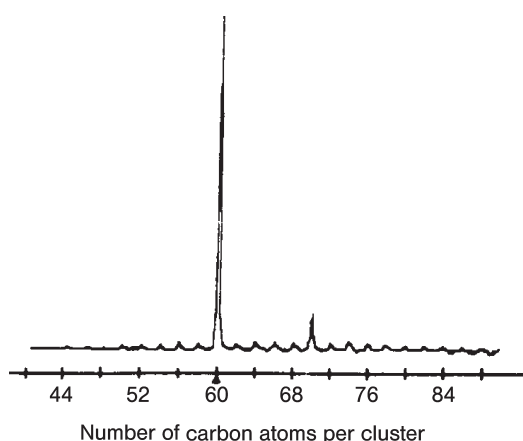


Figure 1.3 Time-of-flight mass spectrum of carbon clusters produced by laser vaporization of graphite under the optimum conditions for observation of a dominant C_{60} signal [15].

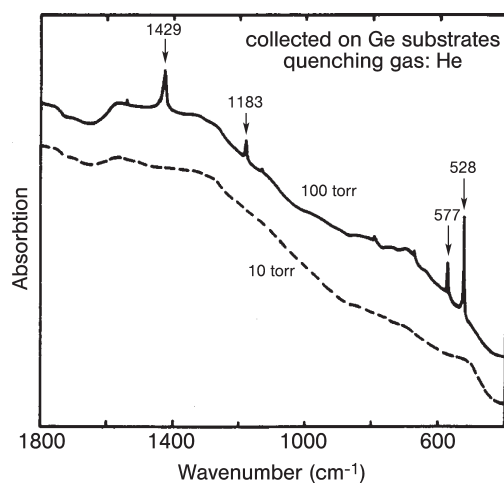


Figure 1.4 IR-spectra of soot particles produced by evaporation of graphite under different helium quenching gas pressures. The occurrence of the four additional sharp peaks at elevated helium pressures turned out to originate from $[60-I_n]$ fullerene (C_{60}) [20].

together with those of the continuum of regular soot (Figure 1.4) [22]. These absorptions were close to the positions predicted by theory for Buckminsterfullerene [23]. The fullerenes were then isolated from the soot by sublimation or extraction with benzene. This allowed the verification of their identity by spectroscopic and crystallographic methods as well as by control experiments with ^{13}C -enriched material. Along with Buckminsterfullerene C_{60} , higher homologues are also obtained by this technique. Fullerenes were then available for the scientific community.

1.3 Fullerene Production

1.3.1 Fullerene Generation by Vaporization of Graphite

1.3.1.1 Resistive Heating of Graphite

Macroscopic quantities of fullerenes were first generated by resistive heating of graphite [20]. This method is based on the technique for the production of amorphous carbon films in a vacuum evaporator [24]. The apparatus (Figure 1.5) that Krätschmer and Fostiropoulos used for the first production of fullerenes consisted of a bell jar as recipient, connected to a pump system and a gas inlet. In the interior of the recipient two graphite rods are kept in contact by a soft spring. Thereby, one graphite rod is sharpened to a conical point, whereas the end of the other is flat. The graphite rods are connected to copper electrodes.

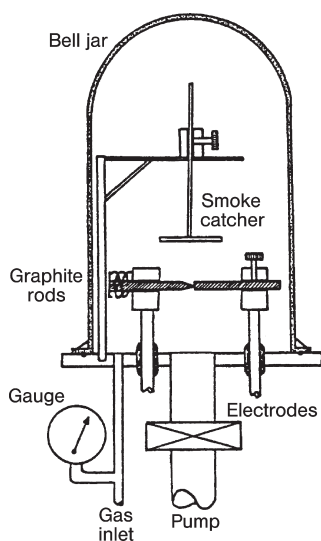


Figure 1.5 Fullerene generator originally used by Krätschmer [20].

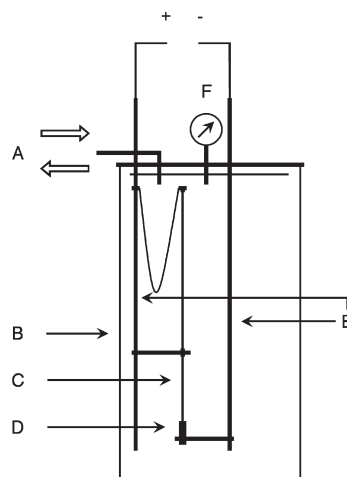


Figure 1.6 Simple benchtop reactor developed by Wudl [27]. Helium supply and connection to a vacuum system (A), Pyrex bell jar (B), graphite rod (3 mm) (C), graphite rod (12 mm) (D), copper electrode (E), manometer (F).

To produce soot, the apparatus is repeatedly evacuated and purged with helium and finally filled with about 140 mbar of helium. After applying a voltage, the electric current passing through the rods dissipates most of its Ohmic power heating at the narrow point of contact. This leads to a bright glowing in this area at 2500–3000 °C. Simultaneously, smoke develops at the contact zone, being transported away by convection and collected on the cooler areas (bell jar and smoke catcher) of the apparatus. The evaporation of the graphite is most efficient at the sharpened end of the rod. After the reaction is over, fullerenes are extracted from the soot, for example with toluene, in about 10–15% yield.

Modifications of this type of fullerene reactor are gravity feed generators [25–27]. The advantage of these generators is their simple construction principle. This, together with their low costs, makes them attractive for synthetic chemists. A schematic representation of such a simple benchtop reactor, developed by Wudl [27] is given in Figure 1.6. A thin graphite rod (3 mm), guided by a copper sleeve, with a sharpened tip is placed on a thick rod (12 mm). A commercially available arc welder serves as power supply. After applying a current (AC or DC) of about 40–60 A, only the material of the thin rod evaporates, whereupon it slips downward, guided by the copper sleeve that keeps the electrical contact. After a few minutes the rod is consumed to the point that it can no longer make contact with the 12 mm rod. The power is then shut off. Based on evaporated graphite, fullerene yields of 5–10% are obtained [27, 28].

The buffer gas cools the plasma by collisions with the carbon vapor. The gas has to be inert, to prevent reactions with smaller carbon clusters or atoms, initially formed by the evaporation. Using N_2 dramatically reduces the yield of fullerenes, presumably due to nitrogen atoms, formed in the hot zone of the generator, reacting with the carbon fragments [28]. The highest yields of fullerenes are obtained if helium is used as buffer gas. Also, the concentration of the buffer gas is important (Figure 1.7), with maximum yields obtained between 140 and 160 mbar [28]. With a very low buffer gas pressure the carbon radicals diffuse far from the hot zone and the clusters continue to grow in an area that is too cool to allow an annealing to spherical carbon molecules. Conversely, if the pressure of the buffer gas is too high, a very high concentration of carbon radical results in the hot reaction zone. This leads to a fast growth of particles far beyond 60 C-atoms and the annealing process to fullerenes cannot compete [29].

During these resistive heating procedures the formation of slag, depositing on the thicker graphite rod, can be observed after some time of evaporation. As long as this vapor-deposited boundary layer remains between the two electrodes in a sufficiently thick and resistive form, the electrical power continues to be dissipated just in this small zone, and carbon vaporization from the end of the thin graphite rod proceeds efficiently [30]. Thus, the formation of such a resistive layer may be an important requirement for the continuation of smoke production. In the beginning of the reaction this was guaranteed by the sharpened thin graphite rod (heat dissipation in this small resistive zone). For graphite rods, with diameters of 6 mm or greater, the resistive layer does not remain sufficiently resistive and the entire length of the graphite rod eventually begins to glow. This causes inefficient evaporation of carbon from the center of the rod. Therefore, only comparatively thin graphite rods can be used for efficient fullerene production by the resistive heating technique.

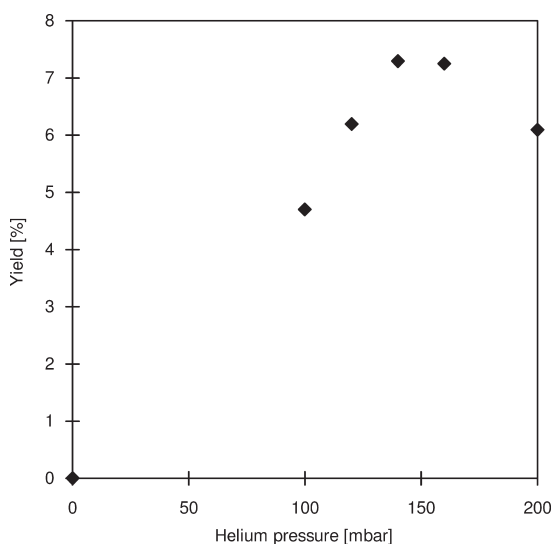
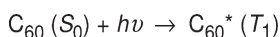


Figure 1.7 Dependence of the fullerene yield on the helium gas pressure in the fullerene generator.

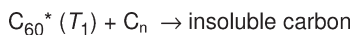
1.3.1.2 Arc Heating of Graphite

An alternative to resistive heating is arc vaporization [29, 31–36] of graphite, first developed by Smalley [31]. If the tips of two sharpened graphite rods are kept in close proximity, but not in a direct contact, the bulk of the electrical power is dissipated in an arc and not in Ohmic heating. In an original generator a spring tension was adjusted to maintain the arc between the nearly contacting graphite electrodes. The most efficient operation occurs when the electrodes are barely touching, which lead to the term “contact-arcing” [31]. This method also allows an efficient evaporation of carbon with somewhat thicker, for example, 6 mm rods. The yield of fullerenes obtained by this technique was found to be about 15%. However, by increasing the rod diameter the yield decreases almost linearly [31], which also prevents an upscaling to very large rod sizes. The reason for the low yields observed by using larger rod-sizes is the fullerenes sensitivity towards UV-radiation. Very intense UV-radiation originates from the central portion of the arc plasma. Newly formed fullerenes moving from the region around the arc are exposed to this intense light flux. The absorption of UV-light produces a triplet state (T_1), which lives for a few microseconds (Scheme 1.1) [37].



Scheme 1.1

In this T_1 state the fullerene is an open shell system and very susceptible to other carbon species C_n . As a result of such a reaction a non-vaporizable insoluble product may be formed (Scheme 1.2) [30].



Scheme 1.2

The effect of increased rod sizes is a larger photochemically dangerous zone. The rate of migration of the newly formed fullerenes through this zone, however, remains constant. Therefore, the yield of fullerenes that migrate through this region without reacting with other carbon species linearly decreases with the rod diameter [30]. A mathematical model for an arc reactor has taken into account (a) cooling and mixing of carbon vapor with buffer gas, (b) non-isothermal kinetics of carbon cluster growth and (c) formation of soot particles and heterogeneous reactions at their surface. This model provided good coincidence of experimental and calculated values both for the fullerene yields and the C_{60}/C_{70} ratio in the reaction products obtained under widely varied conditions [38].

The ratio of C_{60} to higher fullerenes is typically about 8 : 2. The relative yields of higher fullerenes were improved when graphite containing light elements such as B, Si or Al was used and the buffer gas He was mixed with a small amount of N_2 [39, 40]. Fullerenes have also been synthesized by a pulse arc discharge of 50 Hz–10 kHz and 150–500 A, with graphite electrodes and ambient helium (about 80 torr). Instead of graphite, coal was also used as carbon source [41]. Extraction of the corresponding soot with toluene resulted in a 4–6% yield of fullerenes.

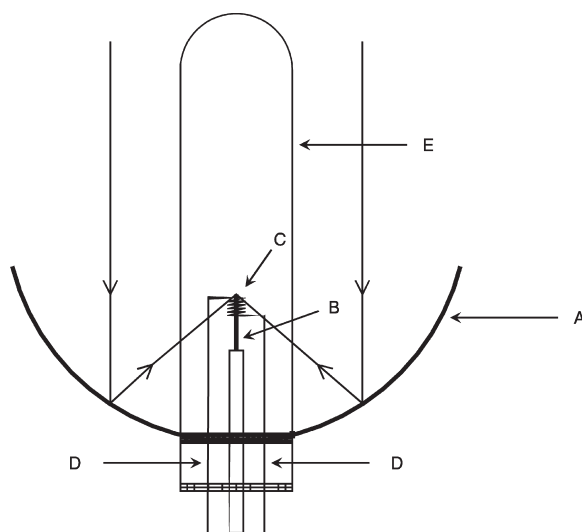


Figure 1.8 “Solar 1” fullerene generator [30].
 (A) Parabolic mirror, (B) graphite target, (C) preheater,
 (D) insulated preheater connectors and (E) glass tube.

1.3.1.3 Solar Generators

The problem of intense UV-radiation is avoided by the use of solar furnaces as fullerene generators [30, 42]. Although sun light is used to evaporate graphite the exposure of generated fullerenes to radiation is far less extensive than with resistive heating or arc vaporization techniques. As an example solar generator, “Solar 1” developed by Smalley [30] will be discussed (Figure 1.8). Sunlight is collected by parabolic mirrors and focused onto a tip of a graphite rod. This rod is mounted inside a Pyrex tube. To minimize conductive heat loss and to provide suitable conditions for the annealing process of the carbon clusters, the graphite rod was enclosed by a helical tungsten preheater. After degassing the system with the preheater, it is filled with about 50 Torr of argon and sealed off. To run the reaction the apparatus is adjusted so that the sunlight is focused directly onto the tip of the graphite target. The argon gas heated by the tungsten preheater is efficiently carried up over the solar-irradiated carbon tip by convection (solar flux: $800\text{--}900\text{ W m}^{-2}$). The condensing carbon vapor quickly moves from the intensive sunlight, cools in the upper regions of the Pyrex tube and subsequently deposits on the upper walls. Although fullerenes can be obtained this way, the efficiency of the prototype “Solar-1” generator is not very high.

1.3.1.4 Inductive Heating of Graphite and Other Carbon Sources

Fullerenes can also be produced by direct inductive heating of a carbon sample held in a boron nitride support [43]. Evaporation at $2700\text{ }^{\circ}\text{C}$ in a helium atmosphere affords fullerene-containing soot that is collected on the cold Pyrex glass of the reaction tube. This method allows a continuous operation by keeping the graphite

sample in the heating zone. Upon evaporating 1 g of graphite, 80 to 120 mg of fullerene extract can be obtained in 10 min.

Continuous production of fullerenes was possible by pyrolysis of acetylene vapor in a radio-frequency induction heated cylinder of glassy polymeric carbon having multiple holes through which the gas mixture passes [44]. Fullerene production is seen at temperatures not exceeding 1500 K. The yield of fullerenes, however, generated by this method is less than 1%. A more efficient synthesis (up to 4.1% yield) was carried out in an inductively coupled radio-frequency thermal plasma reactor [45].

1.3.2

Fullerene Synthesis in Combustion

The existence of fullerenes in sooting flames was first revealed by mass spectrometry studies [46, 47]. Also, the production of fullerenes in optimized sooting flames is possible [48–52]. For this purpose premixed laminar benzene–oxygen–argon flames have been operated under a range of conditions, including different pressures, temperatures and carbon-to-oxygen ratios. Along with fullerenes and soot, polyaromatic hydrocarbons (PAHs) are formed simultaneously. The yield of fullerenes, as well as the $C_{70}:C_{60}$ ratio, strongly depends on the operation mode. The amount of C_{60} and C_{70} , produced under different sooting flame conditions is in the range 0.003–9% of the soot mass. Expressed as percentage of fuel carbon, the yields varies from $2 \cdot 10^{-4}$ to 0.3% for a non-sooting flame, obtained at optimum conditions, at a pressure of 20 Torr, a carbon-to-oxygen ratio of 0.995 with 10% argon and a flame temperature of about 1800 K. The $C_{70}:C_{60}$ ratio varies from 0.26 to 5.7, which is much larger than that observed for graphite vaporization methods (0.02–0.18). This ratio tends to increase with increasing pressure [48].

Further optimization of the formation of fullerenes in combustion lead to the development of efficient pilot plants [53–56]. Currently, 400 kg of fullerenes per year (Mitsubishi's Frontier Carbon Corporation) are obtained by these methods. Ton scale production is expected in the near future. This remarkable development has allowed fullerenes to be sold for less than $\$300 \text{ kg}^{-1}$, a sharp improvement on the $\$40\,000 \text{ kg}^{-1}$ rate that prevailed not long ago [57].

1.3.3

Formation of Fullerenes by Pyrolysis of Hydrocarbons

Fullerenes can also be obtained by pyrolysis of hydrocarbons, preferably aromatics. The first example was the pyrolysis of naphthalene at 1000 °C in an argon stream [58, 59]. The naphthalene skeleton is a monomer of the C_{60} structure. Fullerenes are formed by dehydrogenative coupling reactions. Primary reaction products are polynaphthyls with up to seven naphthalene moieties joined together. Full dehydrogenation leads to both C_{60} as well as C_{70} in yields less than 0.5%. As side products, hydrofullerenes, for example $C_{60}H_{36}$, have also been observed by mass spectrometry. Next to naphthalene, the bowl-shaped corannulene and benzo[*k*]fluoranthene were

also used as precursors to C_{60} [60]. Fullerene synthesis by laser pyrolysis is possible using benzene and acetylene as carbon sources [61]. Soot-free C_{60} has been produced in the liquid phase of an aerosol precursor of soot at 700 °C [62]. The precursor soot aerosol, a high temperature stable form of hydrocarbon, was produced by pyrolysis of acetylene at atmospheric pressure in a flow tube reactor. Further pyrolysis-based methods for the generation of fullerenes include CO_2 -laser pyrolysis of small hydrocarbons such as butadiene and thermal plasma dissociation of hydrocarbons [63].

1.3.4

Generation of Endohedral Fullerenes

Since fullerenes are hollow molecules it should be possible to trap atoms inside the cage. Indeed, one week after the initial discovery of C_{60} , evidence for an endohedral lanthanum complex of C_{60} was obtained [64]. Laser vaporization of a graphite disk soaked in $LaCl_3$ solution produced an additional peak in the time-of-flight (TOF) mass spectrum due to La encapsulated by C_{60} . Evidence that endohedral complexes are so-formed came from “shrink-wrap” experiments showing that these complexes can lose, successively, C_2 fragments without bursting the cluster or losing the incorporated metal (Scheme 1.3) [65]. This is valid up to a certain limit, dictated by the ionic radius of the internal atom. For example, it was difficult to fragment past LaC_{44}^+ and impossible to go past LaC_{36}^+ without bursting the cluster [66].



Scheme 1.3

To facilitate discussion of these somewhat more complicated fullerenes with one or more atoms inside the cage, a special symbolism and nomenclature was introduced [66]. Thereby the symbol @ is used to indicate the atoms in the interior of the fullerene. All atoms listed to the left of the @ symbol are located inside the cage and all atoms to the right are a part of the cage structure, which includes heterofullerenes, e.g. $C_{59}B$. A C_{60} -caged metal species is then written as $M@C_{60}$, expanded as “metal at C_{60} ”. The corresponding IUPAC nomenclature is different from the conventional $M@C_n$ representation. IUPAC recommend that $M@C_n$ be called *[n]fullerene-incar-lanthanum* and should be written *iMC_n* [4].

The production of endohedral fullerene complexes in visible amounts was first accomplished by a pulsed laser vaporization of a lanthanum oxide–graphite composite rod in a flow of argon gas at 1200 °C [66]. In this procedure, the newly formed endohedrals, together with empty fullerenes, sublime readily and are carried away in the flowing gas, depositing on the cool surfaces of the apparatus. This sublimate contains the complexes $La@C_{60}$, $La@C_{74}$ and $La@C_{82}$ (Figure 1.9). Among these, the endohedral molecule $La@C_{82}$ exhibits an extra stability. It can

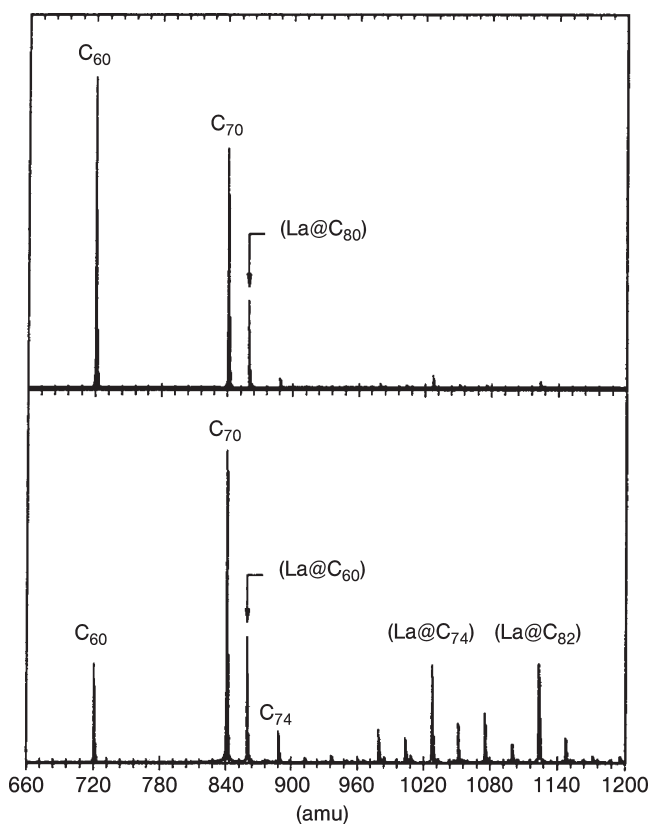


Figure 1.9 FT-ICR mass spectrum of hot toluene extract produced by laser vaporization of a lanthanum oxide-graphite composite rod [66].

be dissolved in toluene or carbon disulfide and exposed to air. The smaller lanthanum fullerenes are less stable and do not survive a hot extraction with toluene on air. The laser vaporization technique was also successful for the production of yttrium fullerenes such as $Y@C_{60}$, $Y@C_{70}$ and $Y_2@C_{82}$ in addition to $Y@C_{82}$ [67].

Along with laser vaporization methods, endohedral fullerene complexes can also be produced by arc vaporization of graphite impregnated with various metal oxides [66, 68–73] or rare earth metal carbides [74]. The yield of the lanthanofullerene $La@C_{82}$, for example, increases by a factor of 10 when, instead of metal-oxide-, metal-carbide-enriched composite graphite rods are used to generate soot [74]. More recent developments in the generation and characterization of endohedral metallofullerenes have been extensively reviewed by Shinohara [75, 76] and Nagase et al. [77]. In general, the endohedral complexes $M_n@C_{82}$ ($n = 1–3$) are the most abundant in the toluene or carbon disulfide extracts. However, metals, encapsulated in C_{60} , C_{74} , C_{76} , C_{80} , C_{84} and even in heterofullerenes such as $C_{79}N$ [78] have also been generated [75–77]. Endohedral complexes of inter alia La, Y, Sc, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and also of Ca, Sr, Ba and Ti, can be prepared

[75–77]. The interior of C_{82} , approximately 8 Å in diameter, can readily accommodate three rare earth trivalent ions, which have average diameters of 2.06 to 2.34 Å [69]. The yield of dimetallo- or trimetallofullerenes depends on the metal-to-carbon ratio, whereas higher yields of multiple metal species are obtained by a higher metal content in the composite. Significantly, metallofullerenes encaged by C_{60} generally exhibit a very low abundance within most solvent-extracts, although empty C_{60} is the most abundant fullerene generated by the usual production methods. Possible reasons for this phenomenon are [72]: (1) $M@C_{60}$ fullerenes are unstable and destroyed upon exposure to air or moisture; (2) $M@C_{60}$ fullerenes are insoluble in organic solvents; and (3) the $M@C_{60}$ fullerenes are not preferably formed by this production method.

Interestingly, $M_n@C_{82}$ fullerenes are the most abundant, although empty C_{82} is not a dominant species formed under normal conditions. The fact that C_{80} , which in the empty case is an open shell system and therefore very unstable, also efficiently encapsulates rare earth metals, to form stable endohedrals $M_2@C_{80}$, suggests, that the electronic structure of the fullerene shell is dramatically influenced by the central metals. This, conversely, may be one reason for the possible instability of $M@C_{60}$. ESR studies on $M@C_{82}$ ($M = Sc, Y, La$) demonstrate that the metals are in the +3 oxidation state, [68, 73, 79] which leaves the fullerene in the trianionic state. This finding is corroborated by cyclic voltammetry studies on HPLC purified $La@C_{82}$ [80]. The cyclic voltammogram of dark green dichlorobenzene solutions of $La@C_{82}$ shows one reversible oxidation peak, the oxidation potential of which is approximately equal to that of ferrocene, implying that the complex is a moderate electron donor and therefore an oxygen-stable molecule. In addition, five reversible reductions are observed, showing that $La@C_{82}$ is a stronger electron acceptor than empty fullerenes, with the first reduction potential being especially low lying. These findings can be interpreted with the proposed molecular orbital diagram (Figure 1.10).

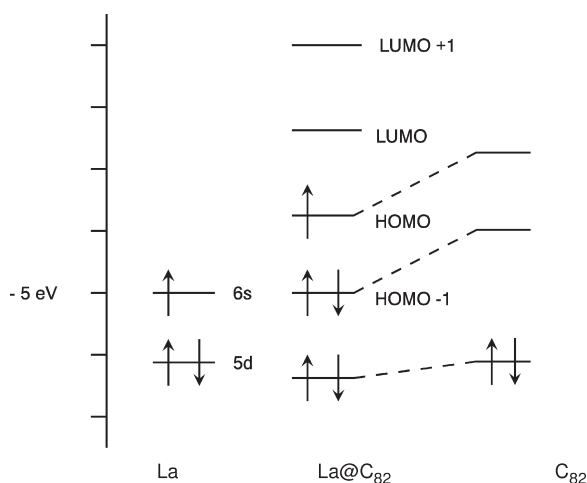


Figure 1.10 Schematic molecular orbital diagram of $La@C_{82}$ [80].

The removal of the radical electron corresponds to the first oxidation process. The resulting cation should be diamagnetic. The first reduction is relatively easy, because filling of the HOMO leads to the closed shell species La@C_{82}^- . Theoretical calculations predicted that the location of the lanthanum within the cage is off-center, which allows a stronger interaction with carbon atoms of the fullerene sphere [81–83].

Dynamic circular motion of the metal atoms within $\text{La}_2\text{@C}_{80}$ the cage has been investigated by NMR spectroscopy [77, 84, 85]. Synchrotron X-ray diffraction, ^{13}C NMR and ultra-high vacuum scanning tunneling microscopy (UHV-STM) studies also demonstrate the encapsulation of the metal atoms by the carbon cage [75, 76]. The metal atoms are not in the center of the fullerene cage but very close to the carbon cage, indicating a strong metal–cage interaction. Further electronic properties of endohedral metallofullerenes, such as redox behavior, have been investigated by cyclic voltammetry [75, 76, 86]. Various exohedral chemical functionalizations of endohedral metallofullerenes such as La@C_{82} , Pr@C_{82} and Gd@C_{82} have been carried out [87, 88]. The endohedral metallofullerene Gd@C_{82} is considered to be a promising agent for magnetic resonance imaging (MRI) due to the high spin state of the encapsulated ion [89].

Major drawbacks of the above synthesis methods are their low yields, typically $< 0.5\%$, and the formation of multiple endohedral fullerene isomers. This makes it difficult to perform detailed studies of their properties and to use them for practical applications. In the regard the preparation of endohedral fullerenes such as $\text{Sc}_3\text{N@C}_{80}$ stands out [90]. The presence of small quantities of N_2 in a fullerene reactor allowed the synthesis of new endohedral fullerenes, such as the trigonal-planar Sc_3N unit encased in the high-symmetry, icosahedral C_{80} . The exact structure of $\text{Sc}_3\text{N@C}_{80}$ was determined by X-ray crystal structure analysis. ^{13}C NMR spectroscopic investigations revealed that, at room temperature, the Sc_3N unit is free to move in the C_{80} cage and so only two signals for the C-atoms in C_{80} are observed. This C_{80} isomer (Figure 1.11) is a third icosahedral fullerene, alongside C_{20} and C_{60} , and has an unstable and antiaromatic ground-state open-shell structure as an

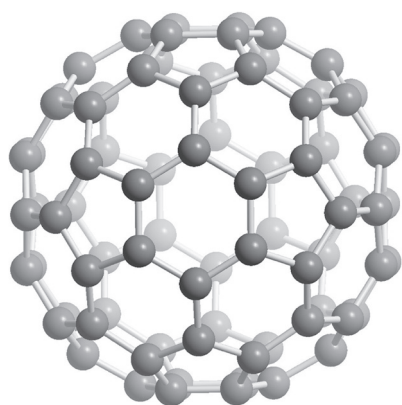


Figure 1.11 Icosahedral C_{80} cage of $\text{Sc}_3\text{N@C}_{80}$.

empty cage and has not yet been isolated. For $\text{Sc}_3\text{N@C}_{80}$, the cage is stabilized by six negative charges, which results in aromaticity [91]. Next to $\text{Sc}_3\text{N@C}_{80}$ a whole new family of stable endohedral fullerenes encapsulating trimetallic nitride clusters, $\text{Er}_x\text{Sc}_{3-x}\text{N@C}_{80}$ ($x = 0-3$), has been generated [90, 92]. This ‘trimetallic nitride template’ process generates significant quantities of product, containing 3–5% $\text{Sc}_3\text{N@C}_{80}$. Also, the endohedral fullerene $\text{Sc}_3\text{N@C}_{78}$ was prepared and completely characterized [93]. Exohedral modification of $\text{Sc}_3\text{N@C}_{80}$ using Diels–Alder chemistry has been carried out [94]. Encapsulation has even been achieved of Sc_3N by the fullerene C_{68} , which does not obey the isolated pentagon rule [95], and by a C_{80} with D_{5h} symmetry [96].

Although electropositive metals afford endohedral complexes with fullerenes during their formation in macroscopic quantities, this is not the case with helium, the buffer gas used for the fullerene synthesis. Of 880 000 fullerene molecules generated by the arc-vaporization method only one was shown to contain a helium atom [97]. Conversely, mass spectrometry studies showed that an intact empty fullerene can be penetrated by the noble gas atoms He and Ne [98–104]. For this purpose singly and multiply charged C_x^{n+} fullerene molecules ($x = 60, 70$; $n = 1-3$) are shot through a stationary noble gas atmosphere in a molecular beam experiment. The resulting M@C_{60}^+ species show the “shrink-wrap” behavior with retention of M and successive elimination of C_2 (Scheme 1.3) that is typical for endohedral complexes. Upon reduction of He@C_{60}^+ the neutral complex He@C_{60} can be obtained, which has a finite lifetime of $> 90 \mu\text{s}$ [101]. This is further evidence that the noble gas is physically trapped inside the fullerene cage. The endohedral complex He@C_{60} is the first noble gas–carbon compound.

To investigate the properties of endohedral noble gas fullerene compounds it is necessary to increase the fraction of the molecules occupied. This has been achieved by heating C_{60} or C_{70} in a noble gas atmosphere at high pressures (e.g. 2700 bar) and temperatures (e.g. 600 °C) [105, 106]. Next to helium, neon, argon, krypton and xenon have also been incorporated into fullerenes by this method. Mole fractions of X@C_{60} and X@C_{70} ($\text{X} = \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$) in the range 0.04–0.3% have been estimated by mass spectrometry [106, 107]. In addition, beam implantation methods have been used for the generation of endohedral noble gas fullerenes [108]. Since the abundance of C_{60} and C_{70} with four ^{13}C atoms is high enough to interfere with the peaks of He@C_{60}^+ and He@C_{70}^+ it is difficult to measure the extent of helium incorporation by mass spectrometric methods. The use of ^3He , however, allows one to record ^3He NMR spectra since ^3He has spin = $\frac{1}{2}$. The ^3He NMR spectra of $^3\text{He@C}_{60}$ and $^3\text{He@C}_{70}$ show that the incorporation fraction is about 0.1% [105, 106]. ^3He NMR spectroscopy can also be used to measure the shielding environment inside the fullerene cavity. The ^3He nuclei encapsulated in C_{60} and C_{70} are shielded by 6.3 and 28.8 ppm respectively relative to free ^3He [105, 106]. These shieldings indicate significant diamagnetic ring currents in C_{60} and very large ones in C_{70} . ^3He NMR spectroscopy of endohedral He complexes of a whole series of fullerenes [109–111], including exohedral fullerenes adducts [112–119], charged fullerenes [120, 121] heterofullerenes [122] and other cluster modified fullerenes [123], is a very powerful method for investigating the magnetic properties of carbon cages

[124]. It can be also very important for determining the number of isomers of higher fullerenes of regioisomers of exohedral fullerene adducts and for carrying out mechanistic investigations on the escape of the endohedral guest and reversible addition reactions [125]. The ^{129}Xe NMR spectrum of $\text{Xe}@C_{60}$ has also been reported [126].

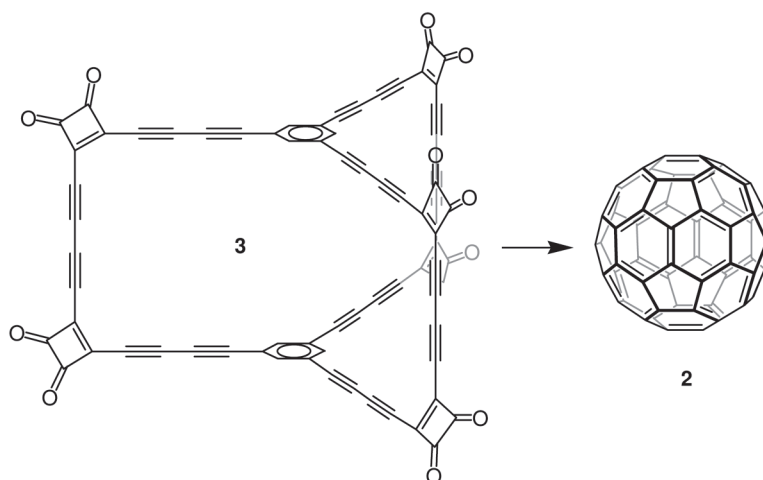
Since the penetration of a noble gas atom through a six-membered ring would afford a very high activation energy, the formation of $\text{X}@C_{60}$ or $\text{X}@C_{70}$ (X = noble gas) must be accompanied by the breaking of at least one bond of the fullerene core. A window mechanism has been proposed to explain the penetration of noble gases into the fullerene cages [127]. The energetics of opening both the [6,6]-bond and the [5,6]-bond have been calculated [127]. A comparison of the reaction coordinates for the processes of breaking a [6,6]-bond in the C_{60} singlet ground state and a [5,6]-bond in the triplet state reveals an energetic preference for the latter process. The opening of one [5,6]-bond leads to the formation of a nine-membered ring, which is expected to be large enough for atoms to pass in or out. After the thermal breaking of a bond the fullerene, either filled with a noble gas atom or empty, can reform by closing the opened bond or it can react further, via another irreversible pathway, to form degraded fullerenes. Degradation products have indeed been found by the synthesis of $\text{X}@C_{60}$ or $\text{X}@C_{70}$ [105, 106].

Another striking development with endohedral fullerenes was the synthesis of $\text{N}@C_{60}$, the first example of encapsulation of a reactive nonmetal atom [128–132]. It is particularly surprising that the enclosed nitrogen exists as a single atom and no bonding to the fullerene framework is apparent. The fullerene therefore represents a trap for extremely reactive atomic nitrogen. This occurs because curvature results in the inner surface of the fullerene cage being inert, whilst the outer surface is distinguished by high reactivity [133]. The formation of a covalent bond with the enclosed N-atom, which has a half-filled p-shell (three unpaired electrons) and so displays minimal electron affinity, would lead to a distinct rise in the strain energy of the total system. Thanks to the absence of relaxation mechanisms, the lowest ESR linewidths observed occur in the spectra of $\text{N}@C_{60}$ [134]. The wavefunction of the enclosed N atom is influenced by subsequent exohedral adduct formation with one or more addends [134]. This is caused by the altered cage structure of the adducts. The analogous complexes $\text{N}@C_{70}$ and $\text{P}@C_{60}$ are made similarly to $\text{N}@C_{60}$, by bombarding a thin layer of fullerene on a cathode with energy-rich N- or P-ions, respectively [135, 136].

1.3.5

Total Synthesis Approaches

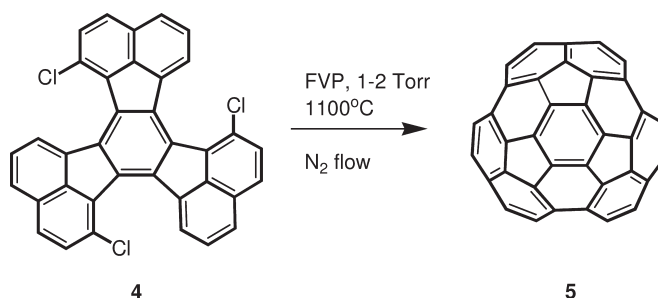
Fullerene generation by vaporization of graphite or by combustion of hydrocarbons is very effective and certainly unbeatable what facile production in large quantities is concerned. However, total synthesis approaches are attractive because (a) specific fullerenes could be made selectively and exclusively, (b) new endohedral fullerenes could be formed, (c) heterofullerenes and (d) other cluster modified fullerenes could be generated using related synthesis protocols.



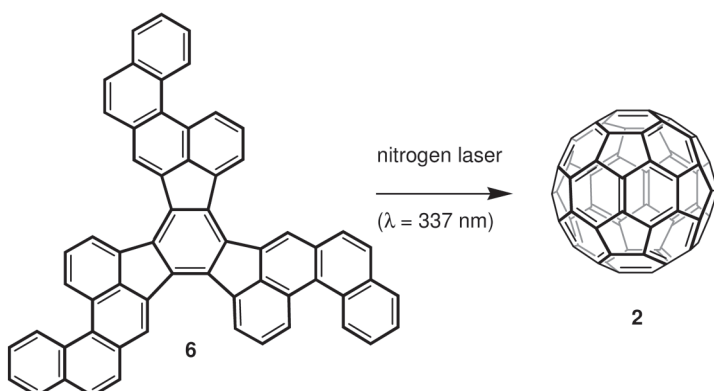
Scheme 1.4 Conversion of cyclophane **3** into C_{60} in the gas phase in laser desorption mass spectrometry.

Three approaches for rational syntheses of fullerenes have been developed. The first approach is the zipping up of fullerene precursors [137–144]. Carbon-rich acetylenic spherical macrocycles such as **3** (Scheme 1.4) may function as precursors of C_{60} and even its endohedral metal complexes in a process analogous to the coalescence annealing of mono- and polycycles with sp -hybridized C-atoms [139] during gas-phase formation of fullerenes from evaporated graphite [137]. Indeed **3** is effectively converted into $C_{60}H_6$ and C_{60} ions in the gas phase in laser desorption mass spectrometry experiments [138]. Related cyclophanes involving pyridine – instead of benzene moieties – are precursors for the conversion into the heterofullerene $C_{58}N_2$ in a mass spectrometer [143].

The second approach is based on the idea of synthesizing bowl-shaped hydrocarbons in which curved networks of trigonal C-atoms map out the same patterns of five- and six-membered rings as those found on the surfaces of C_{60} and/or the higher fullerenes [145–152]. An example for such an “open geodesic polyarene” is circumtrindene (**5**), generated by flash-vacuum pyrolysis (FVP) of trichlorodecacyclene **4** (Scheme 1.5) [152]. Circumtrindene represents 60% of the framework of C_{60} .



Scheme 1.5 Synthesis of circumtrindene (**5**), representing 60% of C_{60} .



Scheme 1.6 Generation of C₆₀ by cyclodehydrogenation of polyarene **6**.

All 60 C-atoms of C₆₀ are incorporated in the C₆₀H₃₀ polycyclic aromatic hydrocarbon (PAH) **6**, for which an efficient synthesis was developed [153]. Laser irradiation of **6** at 337 nm induces hydrogen loss and the formation of C₆₀, as detected by mass spectrometry (Scheme 1.6). Control experiments with ¹³C-labeled material and with the C₄₈H₂₄ homologue of **6** verified that the C₆₀ is formed by a molecular transformation directly from the C₆₀H₃₀ PAH and not by fragmentation and recombination in the gas phase.

In a third approach substituents were removed from a preformed dodecahedrane cage. In this way the synthesis of [20-*I_h*]fullerene was possible in the gas phase [154]. However, extensions of this approach to syntheses of fullerenes consisting of 60 or more C-atoms are conceptually very difficult.

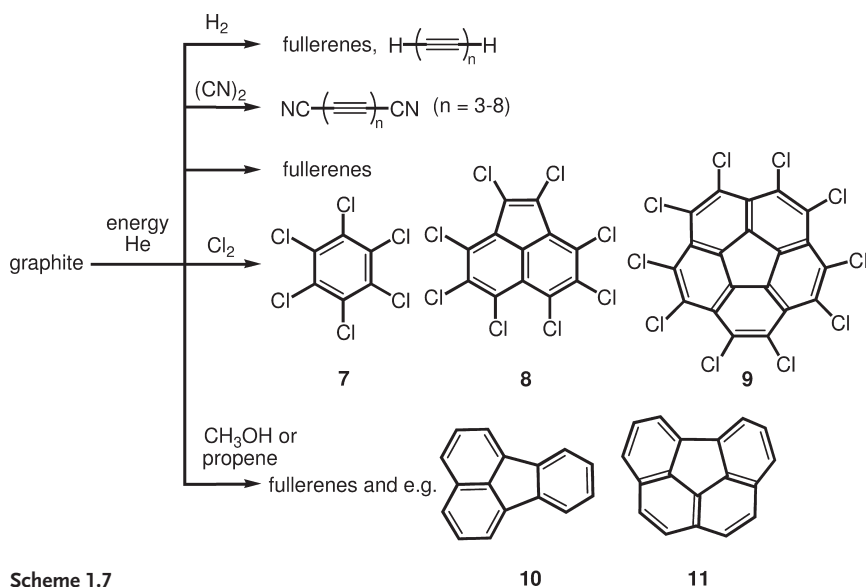
1.3.6

Formation Process

Even though fullerenes are significantly destabilized with respect to graphite [155], they are readily formed out of a chaotic carbon plasma at about 3000 K. A thermodynamically controlled pathway leading to highly symmetric fullerenes can be ruled out. If the fullerene formation would be thermodynamically controlled, then, for example, the yield of C₇₀, which is more stable than C₆₀, [156, 157] should be much higher than found in extracts from graphitic soot. The toluene extract of soot, obtained by carbon vaporization, contains predominantly C₆₀ followed by C₇₀. The ratio C₆₀:C₇₀ is about 85 : 15 [25]. Therefore kinetic factors must govern the fullerene generation. [60-*I_h*]Fullerene is the most stable C₆₀ isomer. Furthermore, the energy per carbon of [60-*I_h*]fullerene is much lower than any isomer of C₅₈ and C₆₂. Locally, [60-*I_h*]fullerene is in a deep potential well and, if once formed from clustering carbon, it is chemically inert. This explains the much lower abundance of the higher fullerenes. One reason for the stability of C₆₀ is that it obeys the "isolated pentagon rule" (IPR), which allows only fullerenes in which all pentagons are completely separated from each other by hexagons [158, 159]. [60-*I_h*]Fullerene is at the same

time the smallest possible fullerene that obeys the IPR. The next most stable isomer of C_{60} has two pairs of adjacent pentagons and has been calculated to be 2 eV higher in energy [160]. These stability considerations already imply that if clusters smaller than C_{60} are formed they will undergo further reactions in the plasma and if those being a little bit larger than C_{60} are formed, for example C_{62} , they can be stabilized by loss of small fragments (C_2) and rearrangements, leading to the survivor $[60-I_h]$ fullerene. Analogous processes should be valid for the higher fullerenes.

A mechanism for fullerene generation [38, 88, 161–167] by vaporization of graphite has to consider three major stages: (1) the vaporization itself and the nature of the initially formed intermediates; (2) the structure of the growing clusters and (3) the annealing to the fullerenes. The first step in the fullerene generation by evaporation of graphite is the formation of carbon atoms, as shown experimentally by $^{12}C/^{13}C$ isotope scrambling measurements [168–170]. The distribution of ^{13}C among the C_{60} molecules follows exactly Poisson statistics. The next step is the clustering of the carbon atoms. The smaller clusters are linear carbon chains or carbon rings. This was concluded by mass spectrometry studies of carbon clusters generated by laser desorption [171–174] and is supported by calculations [175, 176]. If reactive components are added to the buffer gas during the graphite vaporization such early intermediates can be quenched and the fullerene formation is suppressed (Scheme 1.7) [19, 177–179]. Laser desorption of graphite in the presence of H_2 allowed the mass spectrometric observation of polyynes [19]. Similar rod-shaped molecules, the dicyanopolyynes $NC-(C\equiv C)_n-CN$ ($n = 3-7$), are obtained in high yields upon vaporization of graphite in an $He/(CN)_2$ atmosphere (Scheme 1.7) [178]. Obviously, in both cases irreversible additions of H atoms and CN-radicals to the ends of linear carbon chain intermediates are occurring. If Cl_2 is added to the



Scheme 1.7

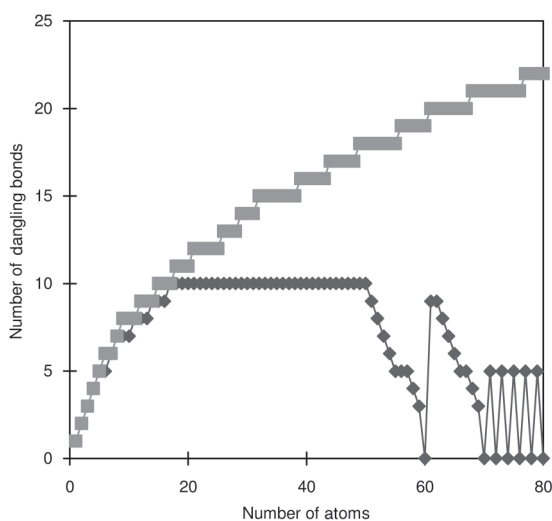
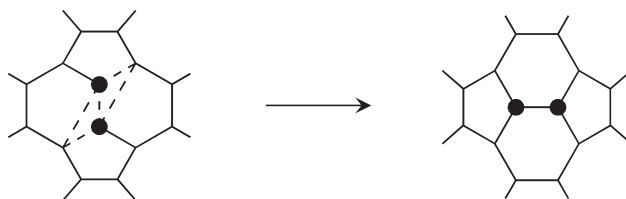


Figure 1.12 Number of dangling bonds in the best possible structure for a graphitic sheet with (*top*) all hexagons, compared to (*bottom*) those which obey the IPR, as a function of the number of atoms in the sheet [181].

buffer gas, instead of linear chains, perchlorinated cyclic compounds are found in the toluene extract of the soot (Scheme 1.7). The amount of fullerenes in the extract is < 5%. Each carbon framework of the cyclic compounds 7–9 represents a part of the C_{60} -structure. Thereby, it is remarkable that, already, structures containing pentagons, for example, the decachlorocorannulene 9 are formed. Polyaromatic hydrocarbons (PAHs) such as 10 and 11 can be isolated, if the vaporization of graphite is carried out in an atmosphere of He/propene or He/methanol (Scheme 1.7). Systems with a similar carbon framework are suggested to be present as intermediates during the formation of fullerenes in benzene flames [51]. However, it can not be concluded from the quenching experiments alone whether clusters with structures like 7–11 are indeed predominant intermediates in the fullerene formation, since the presence of reactive species influences the growth process. The mechanisms of fullerene formation by graphite evaporation and by combustion or pyrolysis of naphthalene are thought to be different.

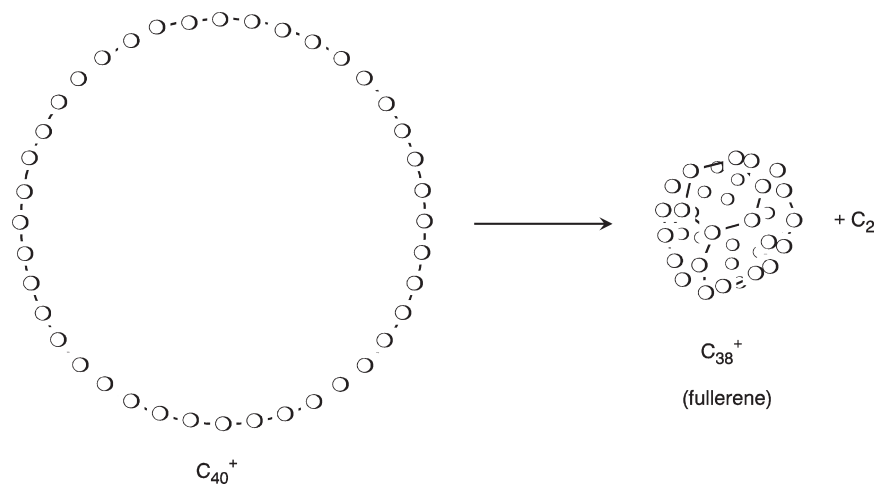
Graphitic sheets as intermediates for cluster sizes of 30 or more C-atoms are proposed in the “pentagon road” model [162, 180, 181]. Thereby it is emphasized that the growth process of the graphitic sheet follows a low energy path by minimizing the number of dangling bonds. This can be achieved by the introduction of pentagons accompanied by a curling process (Figure 1.12). A complete closure to a fullerene reduces the number of dangling bonds to zero. This model also takes into account that high energy adjacent pentagon structures are avoided and also explains (1) the need for an elevated temperature for effective fullerene formation, because prior to a further growth an annealing process leads to an isolated pentagon network and (2) the role of the buffer gas as well as the pressure dependence on the

fullerene yield, because the helium concentration controls the diffusion of the C_n species from the hot into cooler zones of the plasma. Higher buffer gas pressures lead to an increase in concentration of reactive C_n , which causes the annealing process to be not competitive with the cluster growth. During annealing, the formation of a low energy structure obeying the IPR could be accomplished inter alia by the Stone–Wales rearrangement (Scheme 1.8) [182]. This is a concerted process, involving a Hückel four-center transition state.



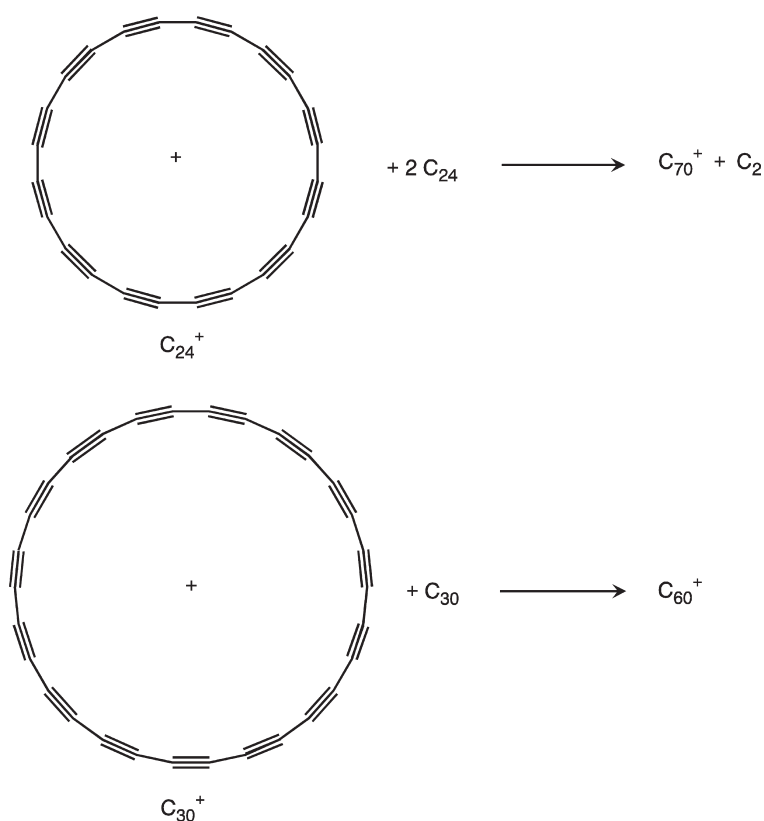
Scheme 1.8

Graphitic sheets, however, are not detectable in the carbon-plasma by ion chromatography (IC) [162, 174, 183–185]. This method provides a means for separating carbon cluster ions with different structures because the reciprocal of the ion mobility is proportional to the collision cross-section. Several species C_n^+ with different structures coexist and their relative amount depends on the cluster size. Small clusters C_n^+ ($n < 7$) are linear. In the range $n = 7$ –10 chains as well as monocycles coexist. The clusters C_{11}^+ – C_{20}^+ are exclusively monocycles and the range between C_{21}^+ and C_{28}^+ is characterized by planar mono- and bicyclic systems. The first three-dimensional structure is detected at C_{29}^+ and the first fullerenes appear at C_{30}^+ and dominate from C_{50}^+ . Therefore, the growth pattern for carbon in the plasma starting from atoms is linear \rightarrow monocyclic rings \rightarrow polycyclic rings and finally \rightarrow fullerenes.

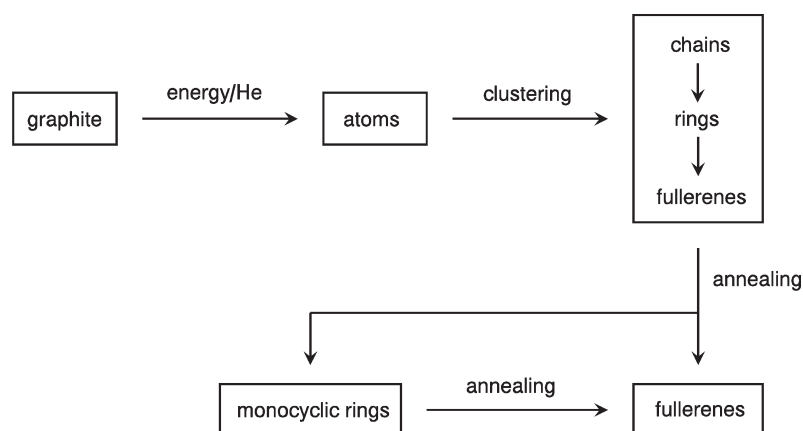
Figure 1.13 Generation of the fullerene C_{38}^+ by collision induced heating of the macrocycle C_{40}^+ .

If such mixtures of ions, generated by laser desorption of graphite, are annealed by collisions, predominantly monocyclic rings are formed upon isomerization of the initial structures. At very high collision energies, isomerization to fullerenes occurs. The fullerenes C_n^+ so-obtained carry enormous internal energy, which can be dissipated by the cleavage of C_1 - or C_3 - (for odd n) or C_2 -fragments (for even n) (Figure 1.13). From drift experiments, the more rings the initial structure contains the smaller the ring barrier is to rearrangement to a fullerene [162]. Tricyclic or tetracyclic isomers rearrange readily to form fullerenes, while bicyclic and monocyclic rings are significantly slower.

Another important series of experiments has shown, by ion-cyclotron-resonance (ICR) studies, that monocyclic carbon rings can coalesce very efficiently to fullerenes (Scheme 1.9) [139]. The carbon rings are obtained by laser desorption of carbon oxide $C_n(CO)_{n/3}$ precursors, out of which, upon loss of CO, the cyclo[n]carbons C_{18} , C_{24} and C_{30} are generated. Fullerene formation proceeds via collisions of positively charged cluster ions C_n^+ with the corresponding neutrals. In the positive ion mode, reactions between cations and neutral molecules of the cyclo[n]carbons lead to fullerene ions. Remarkably, the cyclocarbons C_{18} and C_{24} predominantly lead, via



Scheme 1.9



Scheme 1.10

C_{72}^+ , to C_{70}^+ and no signal for C_{60}^+ is observed. Conversely, C_{30} precursors coalesce almost exclusively to C_{60} . Subsequent losses of C_2 fragments demonstrate the fullerene nature of the products. The distribution of fullerenes can therefore be directly affected by the size of the precursors [163, 186].

These investigations impressively demonstrate that fullerenes can form through excitation or coalescence of relatively large monocyclic precursors. A growth mechanism of smaller fullerenes by subsequent incorporation of C_2 - or C_3 -units is not necessarily required. In the excitation experiments of C_n^+ clusters as well as the coalescence studies of cyclocarbons, a scenario is investigated that comes close to the situation in a carbon plasma generated by Krätschmer–Huffman graphite evaporation. Based on the experimental data available, fullerene generation is schematically summarized in Scheme 1.10. Upon vaporization of graphite carbon atoms are formed, which subsequently cluster to a mixture of chains, monocyclic rings, polycyclic rings and fullerenes. In an annealing process these clusters rearrange, especially efficiently via monocyclic rings, to fullerenes. During this annealing, stable fullerenes can be formed by loss of small fragments (e.g. C_2 , C_3) and by ring rearrangements (e.g. Stone–Wales rearrangement). However, the availability of fullerenes by several methods implies the existence of different mechanisms, which may also operate simultaneously.

1.4

Separation and Purification

The raw product obtained by the evaporation of graphite is soot and slag. Next to soluble fullerenes the soot and slag contain other kinds of closed carbon structures, e.g. giant fullerenes [187] and nanotubes [188, 189]; the rest is amorphous carbon. Fullerenes can be isolated from the soot either by sublimation or by extraction. The first isolation of fullerenes was achieved by a simple sublimation with a Bunsen

burner as heat source [190]. In a more controlled procedure, sublimation from soot was achieved by gradient sublimation [191]. Thereby, the fullerenes are deposited on a quartz rod along a temperature gradient. With this method a partial separation or enrichment of the different fullerenes is possible. In addition, endohedrals can be enriched and C_{74} , not obtainable by extraction, sublimes out of the soot. However, these methods put thermal stress on the fullerenes, leading to partial decomposition. This has been overcome, at least partly, by using microwave-aided sublimation [192].

The most common method for isolating the fullerenes from soot is by extraction with organic solvents [20, 25, 187, 193, 194]. In general, toluene is used since it provides a sufficient solubility and is less toxic than benzene or carbon disulfide. Either a hot extraction of the soot followed by filtration or a Soxhlet extraction is possible. Longer extraction times lead to higher yields of fullerenes [187]. Alternatively, hexane or heptane can also be used as solvents for this method. Fullerene yields of up to 26% from the soot have been reported for Soxhlet extractions [187]. The toluene extract is typically red to red brown. It contains, along with C_{60} and C_{70} , higher fullerenes such as C_{76} , C_{78} , C_{84} , C_{90} and C_{96} ; [60- I_h]fullerene is the most abundant species. Upon further extractions of soot with other solvents, for example pyridine or 1,2,3,5-tetramethylbenzene, additional soluble material is accessible. In such fractions clusters with very high masses (giant fullerenes) up to C_{466} are detectable by mass spectrometry [187]. However, under these more drastic extraction conditions, chemical reactions between fullerenes and the solvent have been observed [187]. The preferred method of isolating fullerenes from the soot is Soxhlet extraction with toluene.

To separate fullerenes predominantly chromatographic methods are used. A clean separation of C_{60} as the first fullerene fraction is obtained by column chromatography with alumina as stationary phase with either pure hexane or hexane–toluene (95 : 5) as eluent [25, 195, 196]. However, since fullerenes are not very soluble in hexane, enormous amounts of alumina and solvents are needed, rendering this method inefficient. Also, a one-step separation of the higher fullerenes is impossible, because of the pronounced tailing effect of the preceding fullerenes. Solvents with a higher solubility, for example toluene, cause the fullerenes to elute together without retention on alumina. The efficiency of the separation of fullerenes on alumina with hexane as mobile phase has been dramatically improved by using Soxhlet-chromatography (Figure 1.14) [197, 198].

This method combines distillation or Soxhlet extraction with chromatography and therefore does not require either large quantities of solvent or constant monitoring. Gram quantities of pure C_{60} can be obtained in reasonable periods of time. After C_{60} is eluted, a new hexane-containing flask is used to collect eluting C_{70} .

With chromatography on graphite, higher amounts of toluene in the hexane–toluene mixture can be used to improve solubility [199, 200]. The major breakthrough, however, allowing the use of pure toluene as mobile phase was achieved by chromatography on mixtures of charcoal and silica gel [201, 202]. This is the most inexpensive and efficient method for a fast separation of C_{60} . A flash

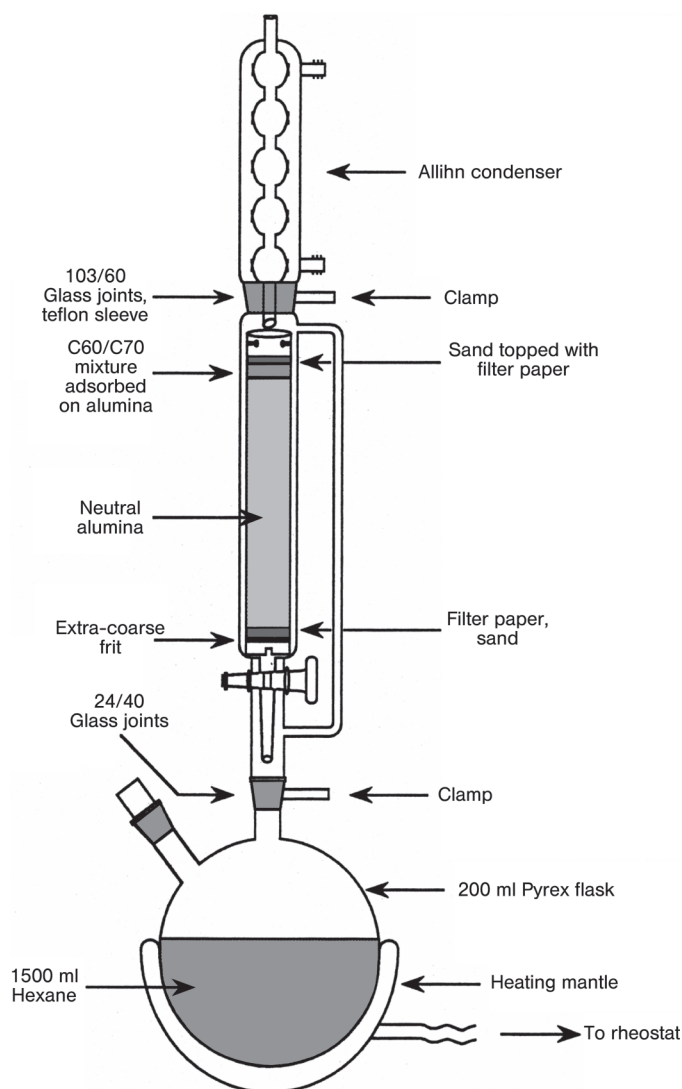


Figure 1.14 Schematic representation of the modified Soxhlet chromatography apparatus [198].

chromatography – or even simpler a plug filtration – setup can be used. For example [202], a fritted funnel (10 cm diameter) is covered with a slurry of 63 g charcoal and 125 g silica gel, which gives a plug of 5.5 cm height. A concentrated toluene solution of fullerene extract is loaded and eluted by the application of a slight vacuum at the filter flask. After a few minutes a dark purple solution of 1.5 g of C_{60} can be obtained from the initial 2.5 g extract.

In a related and even more efficient method the purification was accomplished by filtration of a fullerene extract through a thin layer of activated carbon [203].

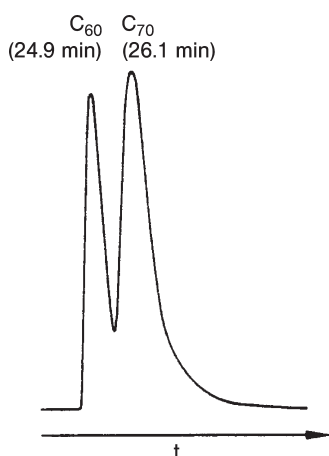


Figure 1.15 Separation of C_{60} and C_{70} on polystyrene gel column with toluene as mobile phase [207].

Under the optimum conditions, chlorobenzene was used as eluent to diminish the volume of the solvent. The carbon layer was only 3–17 mm thick, enough to obtain pure C_{60} and C_{70} in good yields.

Although Soxhlet chromatography on alumina and chromatography on charcoal are very simple and efficient methods, a certain amount of the fullerenes decomposes or irreversibly adsorbs on these stationary phases. Especially, higher fullerenes hardly elute from charcoal columns. Upon chromatography on alumina, light-catalyzed degradation of the fullerenes was observed [204]. Polystyrene gel, however, is completely unreactive towards fullerenes, and a good separation of fullerenes can be obtained on this stationary phase with toluene as mobile phase (Figure 1.15) [205–207].

A completely automated system with reinjection/sample collection and solvent recovery allows the separation of up to 10 g of extract a day. The C_{60} is obtained in very high purity and the recovery is nearly 100%. A simple benchtop method for the enrichment of preparative amounts of C_{60} , C_{70} and higher fullerenes (up to C_{100}) from a crude fullerene mixture is based on a single elution through a column of poly(dibromostyrene)–divinylbenzene using chlorobenzene as mobile phase [208].

Various other packing materials have been used for the separation of fullerenes both by analytical and preparative HPLC, including C_{18} reversed phase [209–211], Pirkle-type phases [212–214], γ -cyclodextrin phases [215], and reversed phases containing polycyclic aromatics [216], cyclopentadiene moieties [217] or multi-legged phenyl groups [218]. The eluent most commonly used is hexane, either pure or in combination with more polar components such as CH_2Cl_2 , Et_2O , THF or toluene. For HPLC on C_{18} -reversed phase silica, toluene/MeCN 75 : 25 or $CHCl_3$ /MeCN 60 : 40, for example, are suitable mobile phases. Although the solubility of parent fullerenes is very low in these combinations of solvents, such HPLC methods are

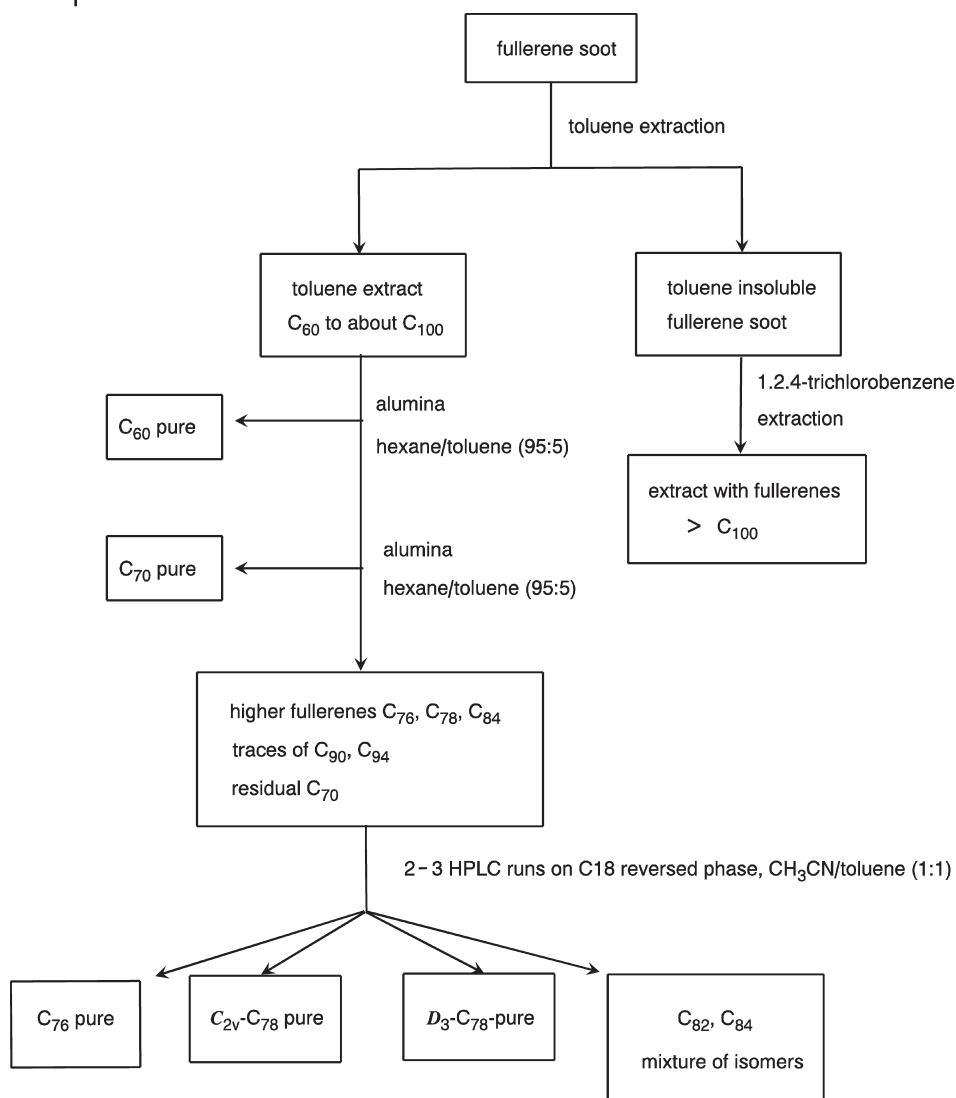


Figure 1.16 Protocol for fullerene separation and isolation [219].

useful for analytical purposes or for the separation of higher fullerenes [210, 211]. The currently most efficient columns for the HPLC separation of parent fullerenes, including endohedral fullerenes and heterofullerenes, are the commercially available COSMOSIL columns (Nacalai Tesque, Japan), which allow the use of toluene as mobile phase. A complete protocol for the isolation of fullerenes from soot and their separation by column chromatography and HPLC elaborated by Diederich is represented in Figure 1.16 [219].

To separate fullerene derivatives containing covalently bound groups, HPLC methods are also very important. Addends on the fullerene core have a dramatic influence on the solubility properties and the retention behavior. Often, more polar eluents in mixtures or in a pure form can be used and efficient separations on silica gel or several reversed phases (medium polarity), even of different regioisomers of addition products, are possible [220–228]. A separation of C_{60} from C_{70} has also been achieved on the basis of the small difference in their chemical reactivity [229]. The treatment of a carbon disulfide solution of a C_{60}/C_{70} mixture with $AlCl_3$ leads to a preferred precipitation of a $C_{70}[AlCl_3]_n$ complex, whereas the purple C_{60} is mostly unaffected and its solutions can be separated by filtration from the precipitate. The parent fullerenes can be recovered from the C_{70} enriched precipitate by treatment with water.

Purification of C_{60} by fractional crystallization in 1,3-diphenylacetone represents another inexpensive method [230]. After three steps, 99.5% pure C_{60} was obtained with a total yield of 69%. The purity of C_{60} can be increased up to 99.99% by adsorption of the residual C_{70} fullerene on charcoal. Preferential precipitation of C_{70} over C_{60} has been obtained by the addition of *p*-trihalohomocalix[3]arenes [231]. In this way C_{70} with up to 92% purity was obtained.

1.5 Properties

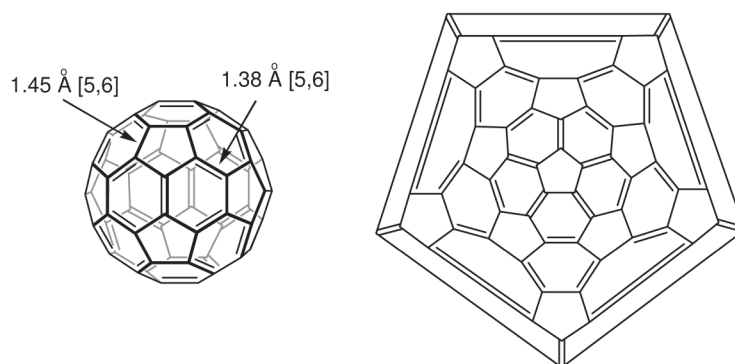
1.5.1 Structures

Each fullerene contains $2(10 + M)$ carbon atoms corresponding to exactly 12 pentagons and M hexagons. This building principle is a simple consequence of Euler's theorem. Hence, the smallest fullerene that can be imagined is C_{20} . Starting at C_{20} any even-membered carbon cluster, except C_{22} , can form at least one fullerene structure. With increasing M the number of possible fullerene isomers rises dramatically, from only 1 for $M = 0$ to over 20 000 for $M = 29$ and so on [232, 233]. The soccer-ball shaped C_{60} isomer $[60-I_h]$ fullerene is the smallest stable fullerene. The structure of $[60-I_h]$ fullerene was determined theoretically [234–238] and experimentally (Table 1.1) [239–242]. These investigations confirm the icosahedral structure of $[60-I_h]$ fullerene. Two features of this C_{60} structure are of special significance: (1) all twelve pentagons are isolated by hexagons and (2) the bonds at the junctions of two hexagons ([6,6] bonds) are shorter than the bonds at the junctions of a hexagon and a pentagon ([5,6] bonds) (Table 1.1 and Figure 1.17).

The pentagons within fullerenes are needed to introduce curvature, since a network consisting of hexagons only is planar. $[60-I_h]$ fullerene is the only C_{60} isomer and at the same time the smallest possible fullerene to obey the “isolated pentagon rule” (IPR) [158, 159]. The IPR predicts fullerene structures with all the pentagons isolated by hexagons to be stabilized against structures with adjacent pentagons. A destabilization caused by adjacent pentagons is due to (1) pentalene-type

Table 1.1 Calculated and measured bond distances in $[60-I_h]$ fullerene in Å.

Method	[5,6]-bonds	[6,6]-bonds	Reference
HF(STO-3G)	1.465	1.376	234
HF(7s3p/4s2p)	1.453	1.369	235
LDF(11s6p)	1.43	1.39	236
HF	1.448	1.37	237
MP2	1.446	1.406	238
NMR	1.448	1.370	239
Neutron diffraction	1.444	1.391	240
Electron diffraction	1.458	1.401	241
X-ray	1.467	1.355	242

**Figure 1.17** Schematic representation of $[60-I_h]$ fullerene with the lengths of the two different bonds in the molecule and Schlegel diagram of the lowest energy Kekulé structure.

8π -electron systems, leading to resonance destabilization and (2) an increase of strain energy, as a consequence of the enforced bond angles. The formation of IPR structures is accompanied with an enhancement of the sphericity of the molecules. A spherical shape distributes the strain as evenly as possible and minimizes the anisotropic contribution to the strain energy [243]. The bond length alternation in $[60-I_h]$ fullerene shows that, in the lowest energy Kekulé structure, the double bonds are located at the junctions of the hexagons ([6,6] double bonds) and there are no double bonds in the pentagonal rings. Each hexagon in $[60-I_h]$ fullerene exhibits cyclohexatriene character and each pentagon [5]radialene character. The diameter of $[60-I_h]$ fullerene has been determined by NMR measurements to be 7.10 ± 0.07 Å [239, 244]. When taking into account of the size of the π -electron cloud associated with the C-atoms, the outer diameter of the C_{60} molecule can be estimated as $7.10 + 3.35 = 10.34$ Å, where 3.35 Å is an estimate of the thickness of the π -electron cloud surrounding the C-atoms on the C_{60} framework [244]. The volume per C_{60} molecule is estimated to be $1.87 \cdot 10^{-22}$ cm³ [244].

The next higher stable and IPR satisfying fullerene is $[70-D_{5h}]$ fullerene [25]. Its structure was calculated [245] and determined by X-ray crystallography (Figure

Table 1.2 Calculated and experimental structure of [70- D_{5h}]fullerene.

Bond type	Bond length (Å)		Bond length (Å) Theory (dzp/SCF) [245]
	Experiment		
	a)	b)	
1	1.462	1.462	1.475
2	1.423	1.414	1.407
3	1.441	1.426	1.415
4	1.432	1.447	1.457
5	1.372	1.378	1.361
6	1.453	1.445	1.446
7	1.381	1.387	1.375
8	1.463	1.543	1.451

a) Data taken from the crystal structure of the complex $(\eta^2\text{-C}_{70})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ [246].

b) Data taken from the crystal structure of $\text{C}_{70} \cdot 6 (\text{S}_8)$ [247].

**Figure 1.18** Bond type definitions for the [70- D_{5h}]fullerene.

1.18, Table 1.2) [246, 247]. The geometry at the poles (highest curvature) of [70- D_{5h}]fullerene is very similar to that of [60- I_h]fullerene. The corannulene subunits (bonds 5,6,7,8) have the same type of bond length alternation. In contrast to [60- I_h]fullerene, this fullerene has an equatorial belt consisting of fused hexagons. The analysis of bond lengths within the equatorial phenylene belt of [70- D_{5h}]fullerene as well as its D_{5h} -symmetry per se makes clear that two equivalent lowest-energy Kekulé structures per equatorial hexagon are required to describe its structure and reactivity properties (see Chapter 14).

The number of possible fullerene isomers without any constraints reduces considerably if only IPR structures are allowed. Taking into account that open-shell structures are avoided [233, 248, 249] and that the number of double bonds in pentagons is minimized [250], which favors a meta over a para relationship of the pentagons (Figure 1.19) [251], the number of allowed isomers is further reduced.

With these constraints, magic numbers n for stable fullerenes C_n can be predicted, which are $n = 60, 70, 72, 76, 78, 84$ [233]. With the exception of C_{72} at least one representative for all of these fullerenes, including C_{74} [252] and C_{80} [253], has now been produced, isolated and characterized. The number of allowed fullerene isomers are, for example, one for C_{60} , one for C_{70} , one for C_{76} (D_2), five for C_{78} [D_{3h} (1), D_{3h} (2), D_3 , C_{2v} (1), C_{2v} (2)], 24 for C_{84} and 46 for C_{90} [233, 254]. The interplay between theoretical predictions and ^{13}C NMR experiments was the key to structure elucidation.

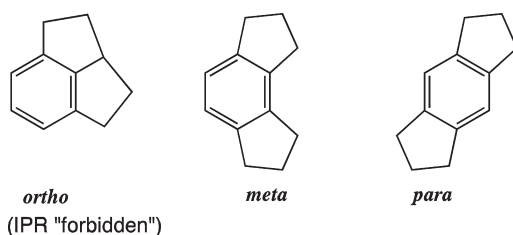


Figure 1.19 Ortho, meta, and para relationships of fused pentagons in a fullerene.

tion of some principle isomers of the higher fullerenes C_{76} , and C_{78} , C_{80} , C_{82} and C_{84} [210, 211, 219, 253, 255–262]. Structure assignments have been accomplished by comparing the ^{13}C NMR spectra (number and intensity of lines) of given isomers, isolated or enriched by HPLC, with the theoretical possible structures suggested by Manolopoulos and Fowler [233]. In addition, the number of lines in different chemical shift regions provide further useful information for the structure determination. In some cases, even structure determination by X-ray crystallography was possible. Certain to confident structure assignment [263] was possible for [74- D_{3h}]-fullerene [264], [76- D_2]fullerene, [210] [78- $C_{2v(1)}$]fullerene [211, 256, 258], [78- $C_{2v(2)}$]fullerene [256, 258], [78- D_3]fullerene [211, 256, 258], [80- D_2]fullerene [253], [82- C_2]fullerene, [84- D_{2d}]fullerene, [260, 261] and [84- D_2]fullerene [256, 258, 261, 262]. A few examples are shown in Figure 1.20. Since only one isomer of each C_{60} , C_{70} and C_{76} is formed, in the following the indication of symmetry will be omitted.

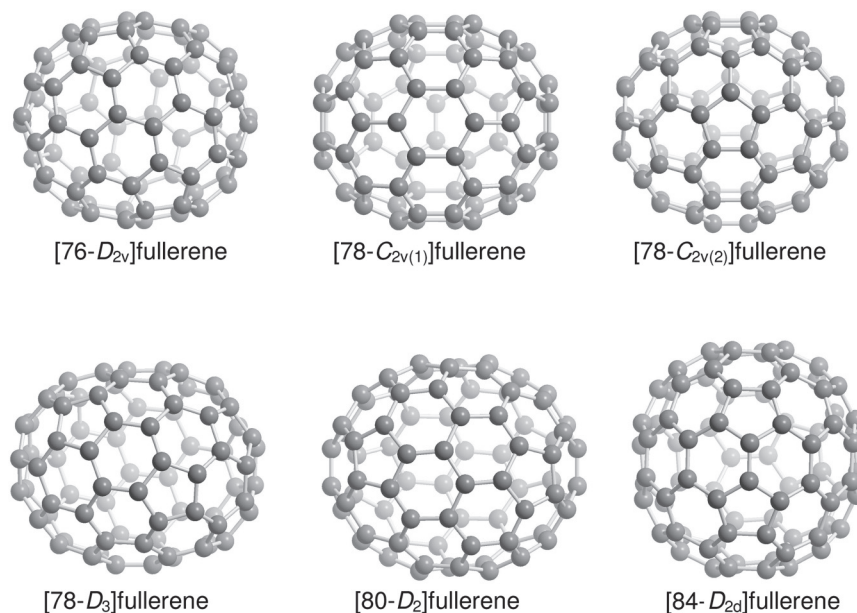


Figure 1.20 A selection of structurally characterized higher fullerenes.

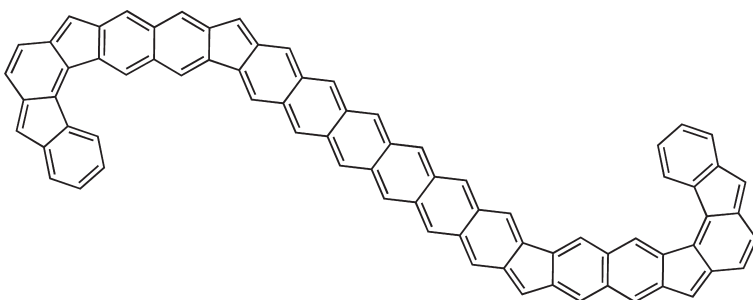


Figure 1.21 Helix motif in double-helical [76- D_2]fullerene.

The fact that for C_{78} the most symmetrical D_{3h} isomer is not favored implies that an important stabilizing factor is the maximization of the sphericity rather than symmetry. Interestingly, some of the higher fullerenes are chiral, for example [76- D_2]fullerene, [80- D_2]fullerene, [82- C_2]fullerene, and [84- D_2]fullerene. The chirality of [76- D_2]fullerene is based on the helical arrangement of the sp^2 -atoms in space (Figure 1.21). To describe the absolute configuration of a chiral fullerene the stereodescriptors ($^{f,s}C$) and ($^{f,s}A$) introduced by Diederich et al. (see also Section 1.1) can be used [265]. Optically pure isomers of [76- D_2]fullerene were obtained by functionalization of (\pm)-[76- D_2]fullerene with an enantiopure chiral addend, separation of the resulting diastereoisomers, and subsequent removal of the functionality [266]. In the same way optical resolution of [84- D_2]fullerene was possible [267]. Comparison of the obtained circular dichroism (CD) spectra with calculated spectra allowed the assignment of the absolute configuration of the enantiomers of [76- D_2]fullerene [263, 268].

1.5.2

Physical and Spectroscopic Properties

Investigations of physical properties in solution as well as in the solid state have been predominantly carried out on C_{60} , and to a minor extent on C_{70} , since these are the most abundant fullerenes. Currently, little material is available for the higher fullerenes or endohedrals, because it takes about 250 h to produce 1 mg of any of these [269].

The heat of formation of C_{60} and C_{70} have been determined theoretically and experimentally by calorimetry to be $10.16 \text{ kcal mol}^{-1}$ per C-atom for C_{60} and $9.65 \text{ kcal mol}^{-1}$ per C-atom for C_{70} [127, 155]. The fullerenes are therefore thermodynamically less stable than graphite and diamond, which exhibit heats of formation of zero and $0.4 \text{ kcal mol}^{-1}$ respectively. It is expected that upon increasing the size of the fullerene the energy content of the spheres asymptotically reaches that of graphite [270, 271]. The binding energy per C-atom of C_{60} was calculated to be about $0.4\text{--}0.7 \text{ eV}$ smaller than that for graphite [244]. The binding energy of C_{70} is about 0.2 eV greater than that of C_{60} [244]. Further physical constants of C_{60} and C_{70} are summarized in Tables 1.3 and 1.4. Measurements of the electron affinity

Table 1.3 Physical constants for C₆₀ molecules [244].

Quantity	Value	Reference
Moment of inertia I	$1.0 \cdot 10^{-43} \text{ kg m}^2$	272
Volume per C ₆₀	$1.87 \cdot 10^{-22} \text{ cm}^{-3}$	–
Number of distinct C sites	1	–
Number of distinct C–C bonds	2	–
Binding energy per atom	7.40 eV	272
Heat of formation (per g C atom)	1.16 kcal	155
Electron affinity	$2.65 \pm 0.05 \text{ eV}$	273
Cohesive energy per C atom	1.4 eV atom^{-1}	274
Spin-orbit splitting of C(2p)	0.00022 eV	275
First ionization potential	7.58 eV	276
Second ionization potential	11.5 eV	272
Optical absorption edge	1.65 eV	272

Table 1.4 Physical constants for C₇₀ molecules [244].

Quantity	Value	Reference
Average C–C distance (Å)	1.43	155, 277
C ₇₀ <i>c</i> -axis diameter (Å)	7.96	277
C ₇₀ <i>a</i> - <i>b</i> -axis diameter (Å)	7.12	277
Moment of inertia I_{\parallel} (kg m ²)	$1.24 \cdot 10^{-43}$	272
Moment of inertia I_{\perp} (kg m ²)	$1.24 \cdot 10^{-43}$	72
Volume per C ₇₀ (cm ⁻³)	$1.56 \cdot 10^{-22}$	–
Number of distinct C sites	5	278
Number of distinct C–C bonds	8	278
Binding energy per C atom (eV)	7.42	278
Heat of formation (kcal g ⁻¹ °C ⁻¹)	9.65	157, 279
Electron affinity (eV)	2.72	280
Ionization potential (1 st) (eV)	7.61	281
Optical absorption edge (eV)	1.7	278, 282–284
Atomic zero point motion (Å)	0.07	285

E_A have been reported also for the higher fullerenes C₇₆ ($2.88 \pm 0.05 \text{ eV}$), C₇₈ ($3.01 \pm 0.07 \text{ eV}$) and C₈₄ ($3.05 \pm 0.08 \text{ eV}$), showing the general increase in E_A with increasing cluster size [244].

To chemically modify fullerenes, in most cases it is necessary that they are in the solution. For extractions or chromatographic separations the solubility also plays a crucial role. The solubility of C₆₀ in various organic solvents has been investigated systematically (Table 1.5) [286–289].

In polar and H-bonding solvents such as acetone, tetrahydrofuran or methanol C₆₀ is essentially insoluble. It is sparingly soluble in alkanes, with the solubility increasing with the number of atoms. In aromatic solvents and in carbon disulfide, in general appreciable solubilities are observed. A significant increase of the solubility takes place on going from benzenes to naphthalenes. Although there are trends for the solution behavior of C₆₀, there is no direct dependence of the solubility on a certain solvent parameter like the index of refraction n . When the solubility is

Table 1.5 Solubility of C₆₀ in various solvents [287].

<i>Solvent</i>	<i>[C₆₀] (mg mL⁻¹)</i>	<i>Mole fraction (· 10⁴)</i>	<i>n</i>
<i>n</i> -Pentane	0.005	0.008	1.36
<i>n</i> -Hexane	0.043	0.073	1.38
Cyclohexane	0.036	0.059	1.43
<i>n</i> -Decane	0.071	0.19	1.41
Decalines	4.6	9.8	1.48
Dichloromethane	0.26	0.27	1.42
Carbon disulfide	7.9	6.6	1.63
Dichloromethane	0.26	0.27	1.42
Chloroform	0.16	0.22	1.45
Tetrachloromethane	0.32	0.40	1.46
Tetrahydrofuran	0.000	0.000	1.41
Benzene	1.7	2.1	1.50
Toluene	2.8	4.0	1.50
Tetraline	16	31	1.54
Benzonitrile	0.41	0.71	1.53
Anisole	5.6	8.4	1.52
Chlorobenzene	7.0	9.9	1.52
1,2-Dichlorobenzene	27	53	1.55
1-Methylnaphthalene	33	68	1.62
1-Chloronaphthalene	51	97	1.63
Acetone	0.001	0.001	1.36
Methanol	0.000	0.000	1.33

expressed in mole fraction units it is evident that C₆₀ is not very soluble even in the best solvents listed in Table 1.5. The solubility of C₇₀ follows qualitatively similar trends.

The electronic absorption spectra [25] of C₆₀ and C₇₀ are characterized by several stronger absorptions between 190 and 410 nm as well as by some forbidden transitions in the visible part of the spectrum (Figures 1.22 and 1.23). For C₆₀, the assignment of the transitions has been carried out using the results of theoretical calculations [290, 291]. The absorptions between 190 and 410 nm are due to allowed ¹T_{1u}–¹A_g-transitions, whereas those between 410 and 620 nm are due to orbital forbidden singlet–singlet transitions. These latter absorptions in the visible are responsible for the purple color of C₆₀ and the red color of C₇₀.

The fullerenes, in particular C₆₀, exhibit a variety of remarkable photophysical properties, making them very attractive building blocks for the construction of photosynthetic antenna and reaction center models (Table 1.6) [292–295].

The singlet excited state of C₆₀ decays very efficiently via intersystem crossing to the energetically lower-lying triplet excited state (Scheme 1.11). The triplet quantum yields are very high (Table 1.6). The triplet excited states are susceptible to various deactivation processes, including ground state quenching, triplet–triplet annihilation, quenching by molecular oxygen leading to ¹O₂ and electron transfer to donor molecules [295]. The reorganization energy of the rigid fullerene core in electron transfer reaction is exceptionally low. The covalent binding of fullerene to electroactive donor molecules such as porphyrins allows for the development of molecular

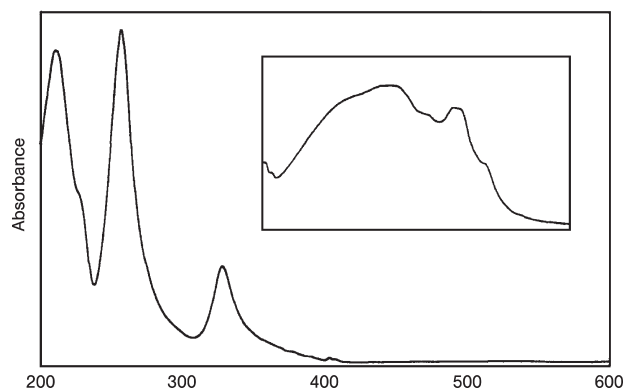


Figure 1.22 Electronic absorption spectrum of C_{60} in hexane. Inset: 420–470 nm region.

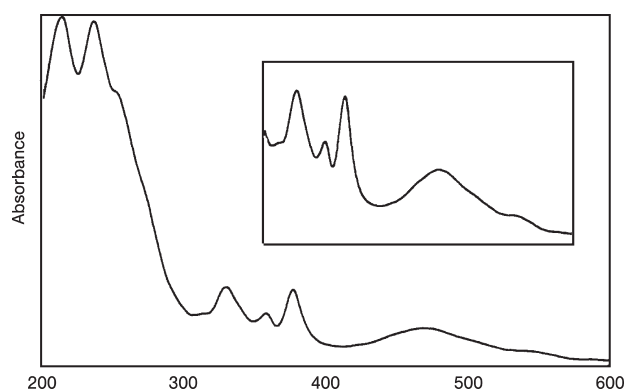
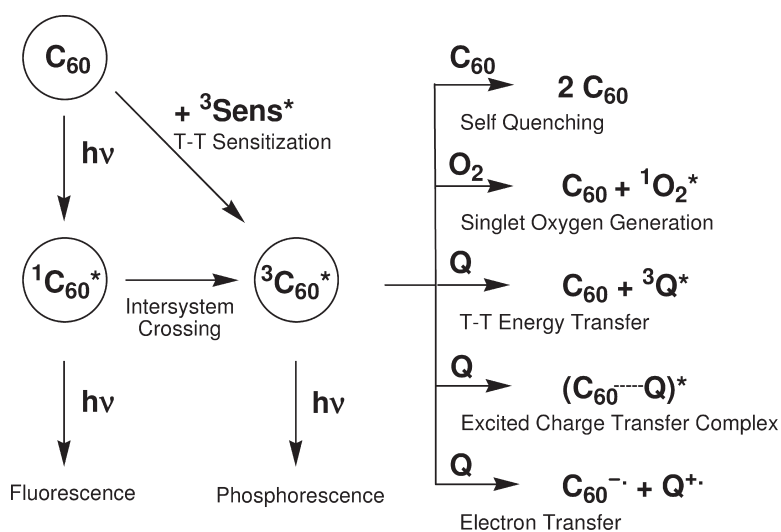


Figure 1.23 Electronic absorption spectrum of C_{70} in hexane. Inset: 300–600 nm region.

Table 1.6 Photophysical properties of C_{60} and C_{70} [295].

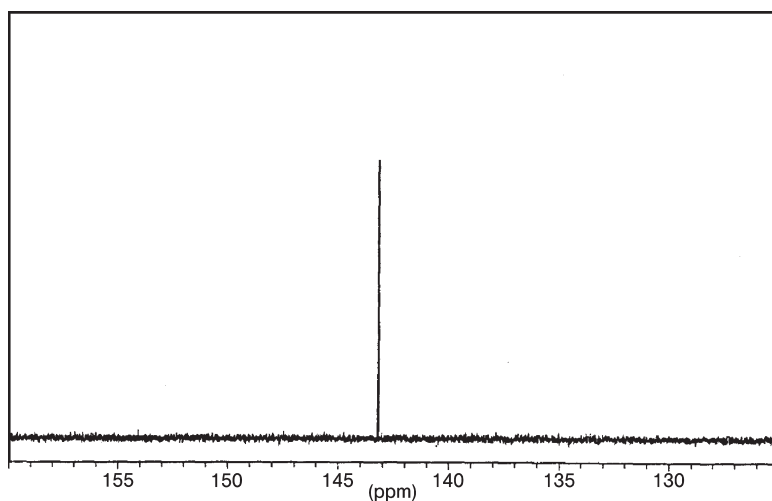
Property	C_{60}	C_{70}
E (singlet)	1.99 eV	1.90 eV
E (triplet)	1.57 eV	1.60 eV
λ_{\max} (singlet)	920 nm	660 nm
λ_{\max} (triplet)	747 nm	400 nm
ϵ (triplet)	$20\,000\text{ M}^{-1}\text{ cm}^{-1}$	$14\,000\text{ M}^{-1}\text{ cm}^{-1}$
τ (singlet)	1.3 ns	0.7 ns
τ (triplet)	135 μs	11.8 ms
$E_{1/2}$ ($^1C_{60}/C_{60}^{\bullet+}$)	1.44 V vs SCE	1.39 vs SCE
$E_{1/2}$ ($^3C_{60}/C_{60}^{\bullet+}$)	1.01 vs SCE	1.09 vs SCE
Φ (fluorescence)	$1.0 \cdot 10^{-4}$	$3.7 \cdot 10^{-4}$
Φ (triplet)	0.96	0.9
k_{q} (oxygen)	$1.6 \cdot 10^9\text{ M}^{-1}\text{ s}^{-1}$	$1.9 \cdot 10^9\text{ M}^{-1}\text{ s}^{-1}$
k_{q} (DABCO)	$2.5 \cdot 10^9\text{ M}^{-1}\text{ s}^{-1}$	
k_{ET} (biphenyl)	$1.7 \cdot 10^{10}\text{ M}^{-1}\text{ s}^{-1}$	$2.0 \cdot 10^{10}\text{ M}^{-1}\text{ s}^{-1}$



Scheme 1.11

dyads in which photoinduced energy- and/or electron transfer takes place. In many of such architectures C_{60} accelerates photoinduced charge separation and retards charge recombination in the dark [292–295]. As a consequence, long-lived charge separated states can be generated, which can be used for subsequent energy conversion processes.

As expected for the icosahedral symmetry, the ^{13}C NMR spectrum of C_{60} (Figure 1.24) shows one signal, at $\delta = 143.2$ [25]. Since the amount of fullerene in the NMR samples due to low solubility is small and the spin–lattice relaxation

Figure 1.24 ^{13}C NMR spectrum of C_{60} .

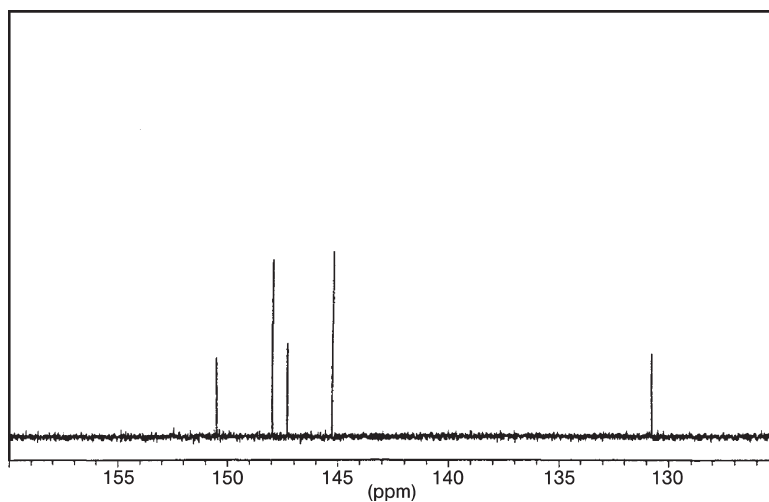


Figure 1.25 ^{13}C NMR spectrum of C_{70} .

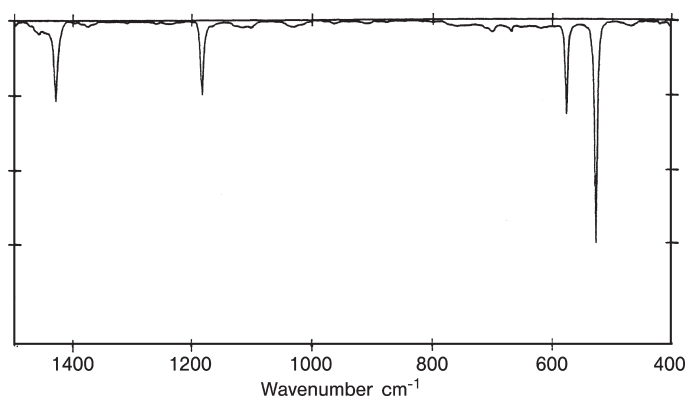


Figure 1.26 IR spectrum (KBr) of C_{60} .

times are quite long (≥ 20 s for C_{60}) [25] a comparatively large number of accumulations is necessary. The ^{13}C NMR spectrum of C_{70} (Figure 1.25) shows five peaks [25] in the intensity ratio of 1 : 2 : 1 : 2 : 1, which have been attributed to the five different sets of C-atoms by 2D NMR analysis [296]. The center of gravity of the ^{13}C resonances shifts continuously towards higher field on going from C_{70} to the higher fullerenes C_{76} , C_{78} , C_{82} and C_{84} [219]. This can be interpreted in terms of an increase of the more benzoid pyrene-type carbons with increasing size of the carbon spheres.

Out of the 174 vibrational modes [23] for C_{60} giving rise to 42 fundamentals of various symmetries, four have t_{1u} symmetry and are IR active (Figure 1.26). This fact has historical significance in the first detection of C_{60} [20].

Solid C_{60} forms a face-centered-cubic (FCC) structure at room temperature [244, 297, 298]. The density in the solid state d_{fcc} is 1.72 g cm^{-3} [299]. Four equivalent molecules are contained in a unit cube with edge length $a = 14.17 \text{ \AA}$, at the origin

and face centers. Due to weak intermolecular interactions the spherical molecules in this “plastic crystal” almost freely rotate at room temperature. As determined by solid-state NMR measurements [239, 300–302] the C_{60} molecules reorient with a rotational diffusion constant of $10 \cdot 10^{10} \text{ s}^{-1}$. Below 255 K, a first-order phase transition to a simple-cubic (SC) structure takes place [303–305]. Also, C_{70} is rotationally disordered at room temperature and undergoes a phase transition to a low-temperature phase [306]. For a comprehensive collection of solid state data of C_{60} and C_{70} see [244].

A slow crystallization from benzene gives a solvate $C_{60}(C_6H_6)_4$ in which the rotation is slowed considerably. This allowed the determination of the crystal structure by X-ray crystallography [307, 308]. Co-crystallates with other molecules have also been characterized, for example, cyclohexane [309], ferrocene [310], [bis(ethylenedithio)tetrathiafulvalene] [311, 312] $[Fe_4(CO)_4(\eta^5-C_5H_5)_4]$ [313], decamethylcobaltocene [314], various porphyrins [315–319], 1,1,2-trichloroethane [320] and iodine [321]. In addition, C_{60} forms host–guest complexes with 1,4-hydroquinone [322], sulfur (S_8) [247, 323] and γ -cyclodextrin [324] to give the water-soluble complex $C_{60}(\gamma\text{-cyclodextrin})_2$ and calixarenes [325, 326].

References

- 1 H. W. KROTO, A. W. ALLAF, S. P. BALM, *Chem. Rev.* **1991**, 91, 1213.
- 2 W. H. POWELL, F. COZZI, G. P. MOSS, C. THILGEN, R. J. R. HWU, A. YERIN, *Pure Appl. Chem.* **2002**, 74, 629.
- 3 F. COZZI, C. THILGEN, W. H. POWELL, personal communication **2004**.
- 4 E. W. GODLY, R. TAYLOR, *Pure Appl. Chem.* **1997**, 69, 1411.
- 5 D. E. JONES, *New Scientist* **1966**, 35, 245.
- 6 D. E. H. JONES, *Freeman: Oxford* **1982**, 118.
- 7 W. E. BARTH, R. G. LAWTON, *J. Am. Chem. Soc.* **1966**, 88, 380.
- 8 E. OSAWA, *Kagaku (Kyoto)* **1970**, 25, 854.
- 9 Z. YOSHIDA, Z. OSAWA, *Kagakudojin: Kyoto* **1971**, 174 pp.
- 10 D. A. BOCHVAR, E. G. GAL'PERN, *Dokl. Akad. Nauk SSSR* **1973**, 209, 610.
- 11 I. V. STANKEVICH, M. V. NIKEROV, D. A. BOCHVAR, *Uspekhi Khimii* **1984**, 53, 1101.
- 12 R. A. DAVIDSON, *Theor. Chim. Acta* **1981**, 58, 193.
- 13 A. D. J. HAYMET, *Chem. Phys. Lett.* **1985**, 122, 421.
- 14 E. A. ROHLFING, D. M. COX, A. KALDOR, *J. Chem. Phys.* **1984**, 81, 3322.
- 15 H. W. KROTO, J. R. HEATH, S. C. O'BRIEN, R. F. CURL, R. E. SMALLEY, *Nature* **1985**, 318, 162.
- 16 T. G. DIETZ, M. A. DUNCAN, D. E. POWERS, R. E. SMALLEY, *J. Chem. Phys.* **1981**, 74, 6511.
- 17 L. W. AVERY, N. W. BROTEN, J. M. MACLEOD, T. OKA, H. W. KROTO, *Astrophys. J.* **1976**, 205, L173.
- 18 H. W. KROTO, C. KIRBY, D. R. M. WALTON, L. W. AVERY, N. W. BROTEN, J. M. MACLEOD, T. OKA, *Astrophys. J.* **1978**, 219, L133.
- 19 J. R. HEATH, Q. ZHANG, S. C. O'BRIEN, R. F. CURL, H. W. KROTO, R. E. SMALLEY, *J. Am. Chem. Soc.* **1987**, 109, 359.
- 20 W. KRÄTSCHMER, L. D. LAMB, K. FOSTIROPOULOS, D. R. HUFFMAN, *Nature* **1990**, 347, 354.
- 21 D. R. HUFFMAN, *Adv. Phys.* **1977**, 26, 129.
- 22 W. KRÄTSCHMER, K. FOSTIROPOULOS, D. R. HUFFMAN, *Chem. Phys. Lett.* **1990**, 170, 167.
- 23 S. J. CYVIN, E. BRENDSDAL, B. N. CYVIN, J. BRUNVOLL, *Chem. Phys. Lett.* **1988**, 143, 377.
- 24 D. E. BRADLEY, *Brit. J. Appl. Phys.* **1954**, 5, 96.

- 25 H. AJIE, M. M. ALVAREZ, S. J. ANZ, R. D. BECK, F. DIEDERICH, K. FOSTIROPOULOS, D. R. HUFFMAN, W. KRÄTSCHMER, Y. RUBIN, K. E. SHRIVER, D. SENSHARMA, R. L. WHETTEN, *J. Phys. Chem.* **1990**, *94*, 8630.
- 26 R. L. WHETTEN, M. M. ALVAREZ, S. J. ANZ, K. E. SCHRIVER, R. D. BECK, F. N. DIEDERICH, Y. RUBIN, R. ETTL, C. S. FOOTE, *Mater. Res. Soc. Symp. Proc.* **1991**, *206*, 639.
- 27 A. S. KOCH, K. C. KHEMANI, F. WUDL, *J. Org. Chem.* **1991**, *56*, 4543.
- 28 T. GRÖSSER, Dissertation, University of Tübingen **1992**.
- 29 R. E. HAUFLE, Y. CHAI, L. P. F. CHIBANTE, J. CONCEICAO, C. JIN, L. S. WANG, S. MARUYAMA, R. E. SMALLEY, *Mater. Res. Soc. Symp. Proc.* **1991**, *206*, 627.
- 30 L. P. F. CHIBANTE, A. TRESS, J. M. ALFORD, M. D. DIENER, R. E. SMALLEY, *J. Phys. Chem.* **1993**, *97*, 8696.
- 31 R. E. HAUFLE, J. CONCEICAO, L. P. F. CHIBANTE, Y. CHAI, N. E. BYRNE, S. FLANAGAN, M. M. HALEY, S. C. O'BRIEN, C. PAN, Z. XIAO, W. E. BILLUPS, M. A. CIUFOLINI, R. H. HAUGE, I. L. MARGRAVE, L. J. WILSON, R. F. CURL, R. E. SMALLEY, *J. Phys. Chem.* **1990**, *94*, 8634.
- 32 W. A. SCRIVENS, J. M. TOUR, *J. Org. Chem.* **1992**, *57*, 6932.
- 33 K. KIKUCHI, N. NAKAHARA, M. HONDA, S. SUZUKI, K. SAITO, H. SHIROMARU, K. YAMAUCHI, I. IKEMOTO, T. KURAMOCHI, *Chem. Lett.* **1991**, 1607.
- 34 R. E. HAUFLE, *Proc. – Electrochem. Soc.* **1994**, *94-24*, 50.
- 35 P. E. ANDERSON, T. T. ANDERSON, P. L. DYER, J. W. DYKES, S. H. IRONS, C. A. SMITH, R. D. KYLIN, P. KLAVINS, J. Z. LIU, et al., *Proc. – Electrochem. Soc.* **1994**, *94-24*, 40.
- 36 Z. M. MARKOVIC, T. L. JOKIC, B. M. TODOROVIC-MARKOVIC, J. L. BLANUSA, T. M. NENADOVIC, *Fullerene Sci. Technol.* **1997**, *5*, 903.
- 37 R. E. HAUFLE, L. S. WANG, L. P. F. CHIBANTE, C. JIN, J. CONCEICAO, Y. CHAI, R. E. SMALLEY, *Chem. Phys. Lett.* **1991**, *179*, 449.
- 38 A. V. KRESTININ, A. P. MORAVSKY, *Chem. Phys. Lett.* **1998**, *286*, 479.
- 39 K. TOHJI, A. PAUL, L. MORO, R. MALHOTRA, D. C. LORENTS, R. S. RUOFF, *J. Phys. Chem.* **1995**, *99*, 17785.
- 40 K. TOHJI, A. PAUL, L. MORO, R. MALHOTRA, D. C. LORENTS, R. S. RUOFF, *Proc. – Electrochem. Soc.* **1995**, *95-10*, 51.
- 41 A. WESTON, M. MURTHY, S. LAIVANI, *Fuel Process. Technol.* **1995**, *45*, 203.
- 42 C. L. FIELDS, J. R. PITTS, M. J. HALE, C. BINGHAM, A. LEWANDOWSKI, D. E. KING, *J. Phys. Chem.* **1993**, *97*, 8701.
- 43 G. PETERS, M. JANSEN, *Angew. Chem.* **1992**, *104*, 240; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 223.
- 44 G. M. JENKINS, L. R. HOLLAND, H. MALEKI, J. FISHER, *Carbon* **1998**, *36*, 1725.
- 45 B. TODOROVIC-MARKOVIC, Z. MARKOVIC, I. MOHAI, Z. KAROLY, L. GAL, K. FOGLEIN, P. T. SZABO, J. SZEPEVOLGYI, *Chem. Phys. Lett.* **2003**, *378*, 434.
- 46 P. GERHARDT, S. LÖFFLER, K. H. HOMANN, *Chem. Phys. Lett.* **1987**, *137*, 306.
- 47 P. GERHARDT, K. H. HOMANN, *J. Phys. Chem.* **1990**, *94*, 5381.
- 48 J. B. HOWARD, J. T. MCKINNON, Y. MAKAROVSKY, A. L. LAFLEUR, M. E. JOHNSON, *Nature* **1991**, *352*, 139.
- 49 J. B. HOWARD, J. T. MCKINNON, M. E. JOHNSON, Y. MAKAROVSKY, A. L. LAFLEUR, *J. Phys. Chem.* **1992**, *96*, 6657.
- 50 J. B. HOWARD, A. L. LAFLEUR, Y. MAKAROVSKY, S. MITRA, C. J. POPE, T. K. YADAV, *Carbon* **1992**, *30*, 1183.
- 51 C. J. POPE, J. A. MARR, J. B. HOWARD, *J. Phys. Chem.* **1993**, *97*, 11001.
- 52 K.-H. HOMANN, *Angew. Chem.* **1998**, *110*, 2572; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2435.
- 53 J. M. ALFORD, J. D. WRIGHT, *Book of Abstracts, 212th ACS National Meeting, Orlando, FL, August 25–29 1996*, MTLs.
- 54 J. M. ALFORD, M. D. DIENER, J. D. WRIGHT, *Book of Abstracts, 215th ACS National Meeting, Dallas, March 29 – April 2 1998*, PHYS.
- 55 J. M. ALFORD, M. D. DIENER, in *PCT Int. Appl.*, (Tda Research, Inc., USA). Wo, **2003**, p. 27 pp.
- 56 J. M. ALFORD, M. D. DIENER, J. NABITY, M. KARPUK, in *U.S. Pat. Appl. Publ.*, (USA). US, **2003**, p. 14 pp.
- 57 J.-F. TREMBLAY, *Chem. Eng. News* **2003**, *13*.
- 58 R. TAYLOR, G. J. LANGLEY, H. W. KROTO, D. R. M. WALTON, *Nature* **1993**, *366*, 728.

- 59 R. TAYLOR, G. J. LANGLEY, *Proc. – Electrochem. Soc.* **1994**, 94-24, 68.
- 60 C. CROWLEY, R. TAYLOR, H. W. KROTO, D. R. M. WALTON, P.-C. CHENG, L. T. SCOTT, *Synth. Met.* **1996**, 77, 17.
- 61 X. ARMAND, N. HERLIN, I. VOICU, M. CAUCHETIER, *J. Phys. Chem. Solids* **1997**, 58, 1853.
- 62 R. P. RODGERS, P. T. A. REILLY, W. B. WHITTEN, J. M. RAMSEY, *Carbon* **2003**, 41, 1469.
- 63 F. TENEGAL, I. VOICU, X. ARMAND, N. HERLIN-BOIME, C. REYNAUD, *Chem. Phys. Lett.* **2003**, 379, 40.
- 64 J. R. HEATH, S. C. O'BRIEN, Q. ZHANG, Y. LIU, R. F. CURL, F. K. TITTEL, R. E. SMALLEY, *J. Am. Chem. Soc.* **1985**, 107, 7779.
- 65 F. D. WEISS, J. L. ELKIND, S. C. O'BRIEN, R. F. CURL, R. E. SMALLEY, *J. Am. Chem. Soc.* **1988**, 110, 4464.
- 66 Y. CHAI, T. GUO, C. JIN, R. E. HAUFLE, L. P. F. CHIBANTE, J. FURE, L. WANG, J. M. ALFORD, R. E. SMALLEY, *J. Phys. Chem.* **1991**, 95, 7564.
- 67 J. H. WEAVER, Y. CHAI, G. H. KROLL, C. JIN, T. R. OHNO, R. E. HAUFLE, T. GUO, J. M. ALFORD, J. CONCEICAO, L. P. F. CHIBANTE, A. JAIN, G. PALMER, R. E. SMALLEY, *Chem. Phys. Lett.* **1992**, 190, 460.
- 68 H. SHINOHARA, H. SATO, Y. SAITO, M. OHKOHCHI, Y. ANDO, *J. Phys. Chem.* **1992**, 96, 3571.
- 69 E. G. GILLAN, C. YERETZIAN, K. S. MIN, M. M. ALVAREZ, R. L. WHETTEN, R. B. KANER, *J. Phys. Chem.* **1992**, 96, 6869.
- 70 M. M. ALVAREZ, E. G. GILLAN, K. HOLCZER, R. B. KANER, K. S. MIN, R. L. WHETTEN, *J. Phys. Chem.* **1991**, 95, 10561.
- 71 S. SUZUKI, S. KAWATA, H. SHIROMARU, K. YAMAUCHI, K. KIKUCHI, T. KATO, Y. ACHIBA, *J. Phys. Chem.* **1992**, 96, 7159.
- 72 S. BANDOW, H. KITAGAWA, T. MITANI, H. INOKUCHI, Y. SAITO, H. YAMAGUCHI, N. HAYASHI, H. SATO, H. SHINOHARA, *J. Phys. Chem.* **1992**, 96, 9609.
- 73 H. SHINOHARA, H. SATO, M. OHKOHCHI, Y. ANDO, T. KODAMA, T. SHIDA, T. KATO, Y. SAITO, *Nature* **1992**, 357, 52.
- 74 S. BANDOW, H. SHINOHARA, Y. SAITO, M. OHKOHCHI, Y. ANDO, *J. Phys. Chem.* **1993**, 97, 6101.
- 75 H. SHINOHARA, *Fullerene: Chem. Phys. Technol.* **2000**, 357.
- 76 H. SHINOHARA, *Rep. Progr. Phys.* **2000**, 63, 843.
- 77 S. NAGASE, K. KOBAYASHI, T. AKASAKA, T. WAKAHARA, *Fullerene: Chem. Phys. Technol.* **2000**, 395.
- 78 T. AKASAKA, S. OKUBO, T. WAKAHARA, K. YAMAMOTO, K. KOBAYASHI, S. NAGASE, T. KATO, M. KAKO, Y. NAKADAIRA, Y. KITAYAMA, K. MATSUURA, *Chem. Lett.* **1999**, 945.
- 79 R. D. JOHNSON, M. S. DE VRIES, J. SALEM, D. S. BETHUNE, C. S. YANNONI, *Nature* **1992**, 355, 239.
- 80 T. SUZUKI, Y. MARUYAMA, T. KATO, K. KIKUCHI, Y. ACHIBA, *J. Am. Chem. Soc.* **1993**, 115, 11006.
- 81 K. LAASONEN, W. ANDREONI, M. PARRINELLO, *Science* **1992**, 258, 1916.
- 82 S. NAGASE, K. KOBAYASHI, T. KATO, Y. ACHIBA, *Chem. Phys. Lett.* **1993**, 201, 475.
- 83 S. SAITO, S. SAWADA, *Chem. Phys. Lett.* **1992**, 198, 466.
- 84 T. AKASAKA, S. NAGASE, K. KOBAYASHI, T. SUZUKI, T. KATO, K. KIKUCHI, Y. ACHIBA, K. YAMAMOTO, H. FUNASAKA, T. TAKAHASHI, *Angew. Chem.* **1995**, 107, 2303; *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 2139.
- 85 T. AKASAKA, S. NAGASE, K. KOBAYASHI, M. WALCHLI, K. YAMAMOTO, H. FUNASAKA, M. KAKO, T. HOSHINO, T. ERATA, *Angew. Chem.* **1997**, 109, 1716; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 1643.
- 86 T. SUZUKI, K. KIKUCHI, F. OGURI, Y. NAKAO, S. SUZUKI, Y. ACHIBA, K. YAMAMOTO, H. FUNASAKA, T. TAKAHASHI, *Tetrahedron* **1996**, 52, 4973.
- 87 T. AKASAKA, T. KATO, K. KOBAYASHI, S. NAGASE, K. YAMAMOTO, H. FUNASAKA, T. TAKAHASHI, *Nature* **1995**, 374, 600.
- 88 A. L. ALEXANDROV, V. A. SCHWEIGERT, *Chem. Phys. Lett.* **1996**, 263, 551.
- 89 S. R. WILSON, *Fullerene: Chem. Phys. Technol.* **2000**, 437.
- 90 S. STEVENSON, G. RICE, T. GLASS, K. HARLICH, F. CROMER, M. R. JORDAN, J. CRAFT, E. HADJU, R. BIBLE, M. M. OLMSTEAD, K. MALTRA, A. J. FISHER, A. L. BALCH, H. C. DORN, *Nature* **1999**, 401, 55.
- 91 A. HIRSCH, Z. CHEN, H. JIAO, *Angew. Chem.* **2000**, 112, 4079; *Angew. Chem. Int. Ed. Engl.* **2000**, 39, 3915.

- 92 M. M. OLMSTEAD, A. DE BETTENCOURT-DIAS, J. C. DUCHAMP, S. STEVENSON, H. C. DORN, A. L. BALCH, *J. Am. Chem. Soc.* **2000**, *122*, 12220.
- 93 M. M. OLMSTEAD, A. DE BETTENCOURT-DIAS, J. C. DUCHAMP, S. STEVENSON, D. MARCIU, H. C. DORN, A. L. BALCH, *Angew. Chem.* **2001**, *113*, 1263; *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 1223.
- 94 H. M. LEE, M. M. OLMSTEAD, E. IEZZI, J. C. DUCHAMP, H. C. DORN, A. L. BALCH, *J. Am. Chem. Soc.* **2002**, *124*, 3494.
- 95 M. M. OLMSTEAD, H. M. LEE, J. C. DUCHAMP, S. STEVENSON, D. MARCIU, H. C. DORN, A. L. BALCH, *Angew. Chem.* **2003**, *115*, 928; *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 900.
- 96 J. C. DUCHAMP, A. DEMORTIER, K. R. FLETCHER, D. DORN, E. B. IEZZI, T. GLASS, H. C. DORN, *Chem. Phys. Lett.* **2003**, *375*, 655.
- 97 M. SAUNDERS, H. A. JIMENEZ-VAZQUEZ, R. J. CROSS, R. J. POREDA, *Science* **1993**, *259*, 1428.
- 98 V. T. WEISKE, D. K. BOEHME, J. HRUSAK, W. KRAETSCHMER, H. SCHWARZ, *Angew. Chem.* **1991**, *103*, 898; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 884.
- 99 T. WEISKE, J. HRUSAK, D. K. BOEHME, H. SCHWARZ, *Chem. Phys. Lett.* **1991**, *186*, 459.
- 100 T. WEISKE, D. K. BOEHME, H. SCHWARZ, *J. Phys. Chem.* **1991**, *95*, 8451.
- 101 T. WEISKE, T. WONG, W. KRÄTSCHMER, J. K. TERLOUW, H. SCHWARZ, *Angew. Chem.* **1992**, *104*, 242; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 183.
- 102 T. WEISKE, H. SCHWARZ, A. HIRSCH, T. GRÖSSER, *Chem. Phys. Lett.* **1992**, *199*, 640.
- 103 M. M. ROSS, J. H. CALLAHAN, *J. Phys. Chem.* **1991**, *95*, 5720.
- 104 K. A. CALDWELL, D. E. GIBLIN, C. S. HSU, D. COX, M. L. GROSS, *J. Am. Chem. Soc.* **1991**, *113*, 8519.
- 105 M. SAUNDERS, H. A. JIMENEZ-VAZQUEZ, R. J. CROSS, S. MROCKOWSKI, D. I. FREEDBERG, F. A. L. ANET, *Nature* **1994**, *367*, 256.
- 106 M. SAUNDERS, H. A. JIMENEZ-VAZQUEZ, R. J. CROSS, S. MROCKOWSKI, M. L. GROSS, D. E. GIBLIN, R. J. POREDA, *J. Am. Chem. Soc.* **1994**, *116*, 2193.
- 107 M. SAUNDERS, R. J. CROSS, H. A. JIMENEZ-VAZQUEZ, R. SHIMSHI, A. KHONG, *Science* **1996**, *271*, 1693.
- 108 R. SHIMSHI, R. J. CROSS, M. SAUNDERS, *J. Am. Chem. Soc.* **1997**, *119*, 1163.
- 109 M. SAUNDERS, H. A. JIMENEZ-VAZQUEZ, R. J. CROSS, W. E. BILLUPS, C. GESENBURG, A. GONZALEZ, W. LUO, R. C. HADDON, F. DIEDERICH, A. HERRMANN, *J. Am. Chem. Soc.* **1995**, *117*, 9305.
- 110 K. KOMATSU, G.-W. WANG, Y. MURATA, T. TANAKA, K. FUJIWARA, K. YAMAMOTO, M. SAUNDERS, *J. Org. Chem.* **1998**, *63*, 9358.
- 111 G.-W. WANG, M. SAUNDERS, A. KHONG, R. J. CROSS, *J. Am. Chem. Soc.* **2000**, *122*, 3216.
- 112 R. J. CROSS, H. A. JIMENEZ-VAZQUEZ, Q. LU, M. SAUNDERS, D. I. SCHUSTER, S. R. WILSON, H. ZHAO, *J. Am. Chem. Soc.* **1996**, *118*, 11454.
- 113 A. W. JENSEN, A. KHONG, M. SAUNDERS, S. R. WILSON, D. I. SCHUSTER, *J. Am. Chem. Soc.* **1997**, *119*, 7303.
- 114 M. RÜTTIMANN, R. F. HALDIMANN, L. ISAACS, F. DIEDERICH, A. KHONG, H. JIMENEZ-VAZQUEZ, R. J. CROSS, M. SAUNDERS, *Chem. Eur. J.* **1997**, *3*, 1071.
- 115 P. R. BIRKETT, M. BUHL, A. KHONG, M. SAUNDERS, R. TAYLOR, *J. Chem. Soc., Perkin Trans. 2: Phys. Org. Chem.* **1999**, 2037.
- 116 O. V. BOLTALINA, M. BÜHL, A. KHONG, M. SAUNDERS, J. M. STREET, R. TAYLOR, *J. Chem. Soc., Perkin Trans. 2: Phys. Org. Chem.* **1999**, 1475.
- 117 S. R. WILSON, M. E. YURCHENKO, D. I. SCHUSTER, A. KHONG, M. SAUNDERS, *J. Org. Chem.* **2000**, *65*, 2619.
- 118 K. FUJIWARA, K. KOMATSU, G.-W. WANG, T. TANAKA, K. HIRATA, K. YAMAMOTO, M. SAUNDERS, *J. Am. Chem. Soc.* **2001**, *123*, 10715.
- 119 T. STERNFELD, M. SAUNDERS, R. J. CROSS, M. RABINOVITZ, *Angew. Chem.* **2003**, *115*, 3244; *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 3136.
- 120 E. SHABTAI, A. WEITZ, R. C. HADDON, R. E. HOFFMAN, M. RABINOVITZ, A. KHONG, R. J. CROSS, M. SAUNDERS, P.-C. CHENG, L. T. SCOTT, *J. Am. Chem. Soc.* **1998**, *120*, 6389.
- 121 T. STERNFELD, R. E. HOFFMAN, M. SAUNDERS, R. J. CROSS, M. S. SYAMALA, M. RABINOVITZ, *J. Am. Chem. Soc.* **2002**, *124*, 8786.

- 122 A. WEITZ, K. HOLCZER, C. BELLAVIA-LUND, F. WUDL, M. SAUNDERS, *Proc. – Electrochem. Soc.* **1998**, 98-8, 1039.
- 123 Y. RUBIN, T. JARROSSON, G.-W. WANG, M. D. BARTBERGER, K. N. HOUK, G. SCHICK, M. SAUNDERS, R. J. CROSS, *Angew. Chem.* **2001**, 113, 1591; *Angew. Chem. Int. Ed. Engl.* **2001**, 40, 1543.
- 124 M. BÜHL, A. HIRSCH, *Chem. Rev.* **2001**, 101, 1153.
- 125 G. W. WANG, M. SAUNDERS, R. J. CROSS, *J. Am. Chem. Soc.* **2001**, 123, 256.
- 126 M. S. SYAMALA, R. J. CROSS, M. SAUNDERS, *J. Am. Chem. Soc.* **2002**, 124, 6216.
- 127 R. L. MURRY, G. E. SCUSERIA, *Science* **1994**, 263, 791.
- 128 T. A. MURPHY, T. PAWLIK, A. WEIDINGER, M. HÖHNE, R. ALCAIA, J. M. SPÄTH, *Phys. Rev. Lett.* **1996**, 77, 1075.
- 129 B. PIETZAK, M. WAIBLINGER, T. ALMEIDA MURPHY, A. WEIDINGER, M. HÖHNE, E. DIETEL, A. HIRSCH, *Chem. Phys. Lett.* **1997**, 279, 259.
- 130 B. PIETZAK, M. WAIBLINGER, T. A. MURPHY, A. WEIDINGER, M. HÖHNE, E. DIETEL, A. HIRSCH, *Carbon* **1998**, 36, 613.
- 131 T. SUETSUNA, N. DRAGOE, W. HARNEIT, A. WEIDINGER, H. SHIMOTANI, S. ITO, H. TAKAGI, K. KITAZAWA, *Chem. Eur. J.* **2002**, 8, 5079.
- 132 A. HIRSCH, *Angew. Chem.* **2001**, 113, 1235; *Angew. Chem. Int. Ed. Engl.* **2001**, 40, 1195.
- 133 H. MAUSER, N. J. R. VAN EIKEMA HOMMES, T. CLARK, A. HIRSCH, B. PIETZAK, A. WEIDINGER, L. DUNSCH, *Angew. Chem.* **1997**, 109, 2858; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2835.
- 134 E. DIETEL, A. HIRSCH, B. PIETZAK, M. WAIBLINGER, K. LIPS, A. WEIDINGER, A. GRUSS, K.-P. DINSE, *J. Am. Chem. Soc.* **1999**, 121, 2432.
- 135 B. PIETZAK, K. LIPS, M. WAIBLINGER, A. WEIDINGER, E. DIETEL, A. HIRSCH, *Proc. – Electrochem. Soc.* **2000**, 2000-12, 353.
- 136 M. WAIBLINGER, K. LIPS, W. HARNEIT, A. WEIDINGER, E. DIETEL, A. HIRSCH, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2001**, 63, 045421/1.
- 137 Y. RUBIN, *Chem. Eur. J.* **1997**, 3, 1009.
- 138 Y. RUBIN, T. C. PARKER, S. J. PASTOR, S. JALISATGI, C. BOULLE, C. L. WILKINS, *Angew. Chem.* **1998**, 110, 1353; *Angew. Chem. Int. Ed. Engl.* **1998**, 37, 1226.
- 139 S. W. McELVANY, M. M. ROSS, N. S. GOROFF, F. DIEDERICH, *Science* **1993**, 259, 1594.
- 140 Y. TOBE, N. NAKAGAWA, K. NAEMURA, T. WAKABAYASHI, T. SHIDA, Y. ACHIBA, *J. Am. Chem. Soc.* **1998**, 120, 4544.
- 141 Y. TOBE, N. NAKAGAWA, J. Y. KISHI, M. SONODA, K. NAEMURA, T. WAKABAYASHI, T. SHIDA, Y. ACHIBA, *Tetrahedron* **2001**, 57, 3629.
- 142 Y. TOBE, H. NAKANISHI, N. NAKAGAWA, R. FURUKAWA, *Proc. – Electrochem. Soc.* **1999**, 99-12, 146.
- 143 Y. TOBE, H. NAKANISHI, M. SONODA, T. WAKABAYASHI, Y. ACHIBA, *Chem. Commun.* **1999**, 1625.
- 144 U. H. F. BUNZ, Y. RUBIN, Y. TOBE, *Chem. Soc. Rev.* **1999**, 28, 107.
- 145 L. T. SCOTT, M. M. HASHEMI, D. T. MEYER, H. B. WARREN, *J. Am. Chem. Soc.* **1991**, 113, 7082.
- 146 L. T. SCOTT, M. M. HASHEMI, M. S. BRATCHER, *J. Am. Chem. Soc.* **1992**, 114, 1920.
- 147 L. T. SCOTT, *Pure Appl. Chem.* **1996**, 68, 291.
- 148 P. W. RABIDEAU, A. SYGULA, *Acc. Chem. Res.* **1996**, 29, 235.
- 149 A. BORCHARDT, A. FUCHICELLO, K. V. KILWAY, K. K. BALDRIDGE, J. S. SIEGEL, *J. Am. Chem. Soc.* **1992**, 114, 1921.
- 150 S. HAGEN, M. S. BRATCHER, M. S. ERICKSON, G. ZIMMERMANN, L. T. SCOTT, *Angew. Chem.* **1997**, 109, 407; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 406.
- 151 L. T. SCOTT, H. E. BRONSTEIN, D. V. PREDA, R. B. M. ANSEMS, M. S. BRATCHER, S. HAGEN, *Pure Appl. Chem.* **1999**, 71, 209.
- 152 R. B. M. ANSEMS, L. T. SCOTT, *J. Am. Chem. Soc.* **2000**, 122, 2719.
- 153 M. M. BOORUM, Y. V. VASIL'EV, T. DREWELLO, L. T. SCOTT, *Science* **2001**, 294, 828.
- 154 H. PRINZBACH, A. WELLER, P. LANDENBERGER, F. WAHL, J. WORTH, L. T. SCOTT, M. GELMONT, D. OLEVANO, B. v. ISSENDORFF, *Nature* **2000**, 407, 60.
- 155 H. D. BECKHAUS, C. RÜCHARDT, M. KAO, F. DIEDERICH, C. S. FOOTE, *Angew. Chem.* **1992**, 104, 69; *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 63.
- 156 R. F. CURL, *Phil. Trans. Royal Soc. London, Ser. A: Math., Phys. Eng. Sci.* **1993**, 343, 19.

- 157 H. D. BECKHAUS, S. VEREVKIN, C. RÜCHARDT, F. DIEDERICH, C. THILGEN, H. U. TER MEER, H. MOHN, W. MÜLLER, *Angew. Chem.* **1994**, *106*, 1033; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 996.
- 158 T. G. SCHMALZ, W. A. SEITZ, D. J. KLEIN, G. E. HITE, *Chem. Phys. Lett.* **1986**, *130*, 203.
- 159 H. W. KROTO, *Nature* **1987**, 329, 529.
- 160 K. RAGHAVACHARI, C. M. ROHLFING, *J. Phys. Chem.* **1992**, *96*, 2463.
- 161 H. SCHWARZ, *Angew. Chem.* **1993**, *105*, 1475; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1412.
- 162 N. S. GOROFF, *Acc. Chem. Res.* **1996**, *29*, 77.
- 163 J. L. MARTINS, F. A. REUSE, *Condensed Matter Theor.* **1998**, *13*, 355.
- 164 G. N. CHURILOV, P. V. NOVIKOV, V. E. TARABANKO, V. A. LOPATIN, N. G. VNUKOVA, N. V. BULINA, *Carbon* **2002**, *40*, 891.
- 165 V. A. SCHWEIGERT, A. L. ALEXANDROV, Y. N. MOROKOV, V. M. BEDANOV, *Chem. Phys. Lett.* **1995**, *235*, 221.
- 166 T. BELZ, H. WERNER, F. ZEMLIN, U. KLEGLER, M. WESEMANN, B. TESCHE, E. ZEITLER, A. RELLER, R. SCHLOEGL, *Angew. Chem.* **1994**, *106*, 1919; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1866.
- 167 P. T. A. REILLY, R. A. GIERAY, W. B. WHITTEN, J. M. RAMSEY, *J. Am. Chem. Soc.* **2000**, *122*, 11596.
- 168 G. MEIJER, D. S. BETHUNE, *J. Chem. Phys.* **1990**, *93*, 7800.
- 169 J. M. HAWKINS, A. MEYER, S. LOREN, R. NUNLIST, *J. Am. Chem. Soc.* **1991**, *113*, 9394.
- 170 T. W. EBBESEN, J. TABUCHI, K. TANIGAKI, *Chem. Phys. Lett.* **1992**, *191*, 336.
- 171 D. C. PARENT, S. W. McELVANY, *J. Am. Chem. Soc.* **1989**, *111*, 2393.
- 172 S. W. McELVANY, B. I. DUNLAP, A. O'KEEFE, *J. Chem. Phys.* **1987**, *86*, 715.
- 173 G. VON HELDEN, M. T. HSU, N. G. GOTTS, P. R. KEMPER, M. T. BOWERS, *Chem. Phys. Lett.* **1993**, *204*, 15.
- 174 G. VON HELDEN, M. T. HSU, N. GOTTS, M. T. BOWERS, *J. Phys. Chem.* **1993**, *97*, 8182.
- 175 V. PARASUK, J. ALMLOF, *Chem. Phys. Lett.* **1991**, *184*, 187.
- 176 M. FEYEREISEN, M. GUTOWSKI, J. SIMONS, J. ALMLOF, *J. Chem. Phys.* **1992**, *96*, 2926.
- 177 M. BROYER, A. GOERES, M. PELLARIN, E. SEDLMAYR, J. L. VIALLE, L. WOESTE, *Chem. Phys. Lett.* **1992**, *198*, 128.
- 178 T. GRÖSSER, A. HIRSCH, *Angew. Chem.* **1993**, *105*, 1390; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1340.
- 179 T. M. CHANG, A. NAIM, S. N. AHMED, G. GOODLOE, P. B. SHEVLIN, *J. Am. Chem. Soc.* **1992**, *114*, 7603.
- 180 G. A. HEATH, S. C. O'BRIEN, R. F. CURL, H. W. KROTO, R. E. SMALLEY, *Comm. Cond. Mater. Phys.* **1987**, *13*, 119.
- 181 R. E. SMALLEY, *Acc. Chem. Res.* **1992**, *25*, 98.
- 182 A. J. STONE, D. J. WALES, *Chem. Phys. Lett.* **1986**, *128*, 501.
- 183 G. VON HELDEN, N. G. GOTTS, M. T. BOWERS, *Nature* **1993**, 363, 60.
- 184 M. T. BOWERS, P. R. KEMPER, G. VON HELDEN, P. A. M. VAN KOPPEN, *Science* **1993**, *260*, 1446.
- 185 G. VON HELDEN, N. G. GOTTS, M. T. BOWERS, *J. Am. Chem. Soc.* **1993**, *115*, 4363.
- 186 D. BABIC, N. TRINAJSTIC, *J. Mol. Struct.* **1996**, *376*, 507.
- 187 D. H. PARKER, K. CHATTERJEE, P. WURZ, K. R. LYKKE, M. J. PELLIN, L. M. STOCK, *Carbon* **1992**, *30*, 1167.
- 188 S. IIJIMA, *Nature* **1991**, 354, 56.
- 189 T. W. EBBESEN, P. M. AJAYAN, *Nature* **1992**, 358, 220.
- 190 K. FOSTIROPOULOS, Dissertation, University of Heidelberg, **1991**.
- 191 C. YERETZIAN, J. B. WILEY, K. HOLCZER, T. SU, S. NGUYEN, R. B. KANER, R. L. WHETTEN, *J. Phys. Chem.* **1993**, *97*, 10097.
- 192 W. MÜLLER, U. WIRTH, H. MOHN, K. ALBERTI, *Fullerenes '93* **1993**.
- 193 J. THEOBALD, M. PERRUT, J.-V. WEBER, E. MILLON, J.-F. MULLER, *Separation Sci. Technol.* **1995**, *30*, 2783.
- 194 T. JOVANOVIĆ, D. KORUGA, B. JOVANCICEVIC, J. SIMIC-KRSTIC, *Fullerenes, Nanotubes, Carbon Nanostruct.* **2003**, *11*, 383.
- 195 R. TAYLOR, J. P. HARE, A. A. K. ABDULSADA, H. W. KROTO, *J. Chem. Soc., Chem. Commun.* **1990**, 1423.
- 196 R. D. JOHNSON, G. MEIJER, D. S. BETHUNE, *J. Am. Chem. Soc.* **1990**, *112*, 8983.
- 197 K. CHATTERJEE, D. H. PARKER, P. WURZ, K. R. LYKKE, D. M. GRUEN, L. M. STOCK, *J. Org. Chem.* **1992**, *57*, 3253.

- 198 K. C. KHEMANI, M. PRATO, F. WUDL, *J. Org. Chem.* **1992**, *57*, 3254.
- 199 A. M. VASSALLO, A. J. PALMISANO, L. S. K. PANG, M. A. WILSON, *J. Chem. Soc., Chem. Commun.* **1992**, 60.
- 200 I. N. KREMENSKAYA, M. A. NUDELMAN, I. G. SHLYAMINA, V. I. SHLYAMIN, *Mendeleev Commun.* **1993**, 9.
- 201 W. A. SCRIVENS, P. V. BEDWORTH, J. M. TOUR, *J. Am. Chem. Soc.* **1992**, *114*, 7917.
- 202 L. ISAACS, A. WEHRIG, F. DIEDERICH, *Helv. Chim. Acta* **1993**, *76*, 1231.
- 203 N. KOMATSU, T. OHE, K. MATSUSHIGE, *Carbon* **2004**, *42*, 163.
- 204 R. TAYLOR, J. P. PARSONS, A. G. AVENT, S. P. RANNARD, T. J. DENNIS, J. P. HARE, H. W. KROTO, D. R. M. WALTON, *Nature* **1991**, *351*, 277.
- 205 M. S. MEIER, J. P. SELEGUE, *J. Org. Chem.* **1992**, *57*, 1924.
- 206 A. GÜGEL, M. BECKER, D. HAMMEL, L. MINDACH, J. RAEDER, T. SIMON, M. WAGNER, K. MÜLLEN, *Angew. Chem.* **1992**, *104*, 666; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 644.
- 207 A. GÜGEL, K. MÜLLEN, *J. Chromatogr.* **1993**, *628*, 23.
- 208 W. A. SCRIVENS, A. M. RAWLETT, J. M. TOUR, *J. Org. Chem.* **1997**, *62*, 2310.
- 209 A. MITTELBACH, W. HOENLE, H. G. VON SCHNERING, J. CARLSEN, R. JANIÁK, H. QUAST, *Angew. Chem.* **1992**, *104*, 1681; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1642.
- 210 R. Ettl, I. CHAO, F. DIEDERICH, R. L. WHETTEN, *Nature* **1991**, *353*, 149.
- 211 F. DIEDERICH, R. L. WHETTEN, C. THILGEN, R. Ettl, I. CHAO, M. M. ALVAREZ, *Science* **1991**, *254*, 1768.
- 212 J. M. HAWKINS, T. A. LEWIS, S. D. LOREN, A. MEYER, J. R. HEATH, Y. SHIBATO, R. J. SAYKALLY, *J. Org. Chem.* **1990**, *55*, 6250.
- 213 W. H. PIRKLE, C. J. WELCH, *J. Org. Chem.* **1991**, *56*, 6973.
- 214 C. J. WELCH, W. H. PIRKLE, *J. Chromatogr.* **1992**, *609*, 89.
- 215 K. CABRERA, G. WIELAND, M. SCHAEFER, *J. Chromatogr.* **1993**, *644*, 396.
- 216 K. KIMATA, K. HOSOYA, T. ARAKI, N. TANAKA, *J. Org. Chem.* **1993**, *58*, 282.
- 217 B. NIE, V. M. ROTELLO, *J. Org. Chem.* **1996**, *61*, 1870.
- 218 K. JINNO, K. YAMAMOTO, T. UEDA, H. NAGASHIMA, K. ITOH, J. C. FETZER, W. R. BIGGS, *J. Chromatogr.* **1992**, *594*, 105.
- 219 C. THILGEN, F. DIEDERICH, R. L. WHETTEN, *Buckminsterfullerenes* **1993**, 59.
- 220 A. HIRSCH, I. LAMPARTH, H. R. KARFUNKEL, *Angew. Chem.* **1994**, *106*, 453; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 437.
- 221 A. HIRSCH, T. GRÖSSER, A. SKIEBE, A. SOI, *Chem. Ber.* **1993**, *126*, 1061.
- 222 A. HIRSCH, O. VOSTROWSKY, *Eur. J. Org. Chem.* **2001**, 829.
- 223 A. HIRSCH, *Top. Curr. Chem.* **1999**, *199*, 1.
- 224 F. DJOJO, A. HIRSCH, *Chem. Eur. J.* **1998**, *4*, 344.
- 225 F. DJOJO, A. HIRSCH, S. GRIMME, *Eur. J. Org. Chem.* **1999**, 3027.
- 226 B. GROSS, V. SCHURIG, I. LAMPARTH, A. HIRSCH, *J. Chromatogr., A* **1997**, *791*, 65.
- 227 B. GROSS, V. SCHURIG, I. LAMPARTH, A. HERZOG, F. DJOJO, A. HIRSCH, *Chem. Commun.* **1997**, 1117.
- 228 U. REUTHER, T. BRANDMÜLLER, W. DONAUBAUER, F. HAMPEL, A. HIRSCH, *Chem. Eur. J.* **2002**, *8*, 2833.
- 229 I. BUCSI, R. ANISZELD, T. SHAMMA, G. K. S. PRAKASH, G. A. OLAH, *Proc. Natl. Acad. Sci.* **1994**, *91*, 9019.
- 230 R. J. DOOME, A. FONSECA, H. RICHTER, J. B. NAGY, P. A. THIRY, A. A. LUCAS, *J. Phys. Chem. Solids* **1997**, *58*, 1839.
- 231 N. KOMATSU, *Org. Biomol. Chem.* **2003**, *1*, 204.
- 232 D. E. MANOLOPOULOS, J. C. MAY, S. E. DOWN, *Chem. Phys. Lett.* **1991**, *181*, 105.
- 233 P. W. FOWLER, R. C. BATTEN, D. E. MANOLOPOULOS, *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3103.
- 234 J. M. SCHULMAN, R. L. DISCH, M. A. MILLER, R. C. PECK, *Chem. Phys. Lett.* **1987**, *141*, 45.
- 235 H. P. LÜTHI, J. ALMLOF, *Chem. Phys. Lett.* **1987**, *135*, 357.
- 236 D. DUNLAP, B. SAMORI, C. BUSTAMANTE, *NATO ASI Ser., Ser. C: Math. Phys. Sci.* **1988**, *242*, 275.s
- 237 G. E. SCUSERIA, *Chem. Phys. Lett.* **1991**, *176*, 423.
- 238 M. HASER, J. ALMLOF, G. E. SCUSERIA, *Chem. Phys. Lett.* **1991**, *181*, 497.
- 239 C. S. YANNONI, P. P. BERNIER, D. S. BETHUNE, G. MEIJER, J. R. SALEM, *J. Am. Chem. Soc.* **1991**, *113*, 3190.
- 240 W. I. F. DAVID, R. M. IBBERSON, J. C. MATTHEWMAN, K. PRASSIDES, T. J. S. DENNIS, J. P. HARE, H. W. KROTO,

- R. TAYLOR, D. R. M. WALTON, *Nature* **1991**, 353, 147.
- 241 K. HEDBERG, L. HEDBERG, D. S. BETHUNE, C. A. BROWN, H. C. DORN, R. D. JOHNSON, M. DE VRIES, *Science* **1991**, 254, 410.
- 242 S. LIU, Y. J. LU, M. M. KAPPES, J. A. IBERS, *Science* **1991**, 254, 408.
- 243 T. G. SCHMALZ, D. J. KLEIN, *Buckminsterfullerenes* **1993**, 83.
- 244 M. S. DRESSELHAUS, G. DRESSELHAUS, P. C. EKLUND, *Science of Fullerenes and Carbon Nanotubes*. Academic Press, San Diego, **1996**.
- 245 G. E. SCUSERIA, *Chem. Phys. Lett.* **1991**, 180, 451.
- 246 A. L. BALCH, V. J. CATALANO, J. W. LEE, M. M. OLMSTEAD, S. R. PARKIN, *J. Am. Chem. Soc.* **1991**, 113, 8953.
- 247 H. B. BÜRGI, P. VENUGOPALAN, D. SCHWARZENBACH, F. DIEDERICH, C. THILGEN, *Helv. Chim. Acta* **1993**, 76, 2155.
- 248 D. E. MANOLOPOULOS, *J. Chem. Soc., Faraday Trans.* **1991**, 87, 2861.
- 249 D. E. MANOLOPOULOS, P. W. FOWLER, *Chem. Phys. Lett.* **1991**, 187, 1.
- 250 R. TAYLOR, *Tetrahedron Lett.* **1991**, 32, 3731.
- 251 R. TAYLOR, *J. Chem. Soc., Perkin Trans. 2: Phys. Org. Chem. (1972–1999)* **1992**, 3.
- 252 M. D. DIENER, J. M. ALFORD, *Nature* **1998**, 393, 668.
- 253 F. H. HENNRICH, R. H. MICHEL, A. FISCHER, S. RICHARD-SCHNEIDER, S. GILB, M. M. KAPPES, D. FUCHS, M. BÜRK, K. KOBAYASHI, S. NAGASE, *Angew. Chem.* **1996**, 108, 1839; *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 1732.
- 254 K. BALASUBRAMANIAN, *Chem. Phys. Lett.* **1993**, 206, 210.
- 255 F. DIEDERICH, R. Ettl, Y. RUBIN, R. L. WHETTEN, R. BECK, M. ALVAREZ, S. ANZ, D. SENSARMA, F. WUDL, et al., *Science* **1991**, 252, 548.
- 256 K. KIKUCHI, N. NAKAHARA, T. WAKABAYASHI, S. SUZUKI, H. SHIROMARU, Y. MIYAKE, K. SAITO, I. IKEMOTO, M. KAINOSHO, Y. ACHIBA, *Nature* **1992**, 357, 142.
- 257 R. TAYLOR, G. J. LANGLEY, T. J. S. DENNIS, H. W. KROTO, D. R. M. WALTON, *J. Chem. Soc., Chem. Commun.* **1992**, 1043.
- 258 R. TAYLOR, G. J. LANGLEY, A. G. AVENT, J. S. DENNIS, H. W. KROTO, D. R. M. WALTON, *J. Chem. Soc., Perkin Trans. 2: Phys. Org. Chem.* **1993**, 1029.
- 259 R. H. MICHEL, M. M. KAPPES, P. ADELMANN, G. ROTH, *Angew. Chem.* **1994**, 106, 1742; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1651.
- 260 A. L. BALCH, A. S. GINWALLA, J. W. LEE, B. C. NOLL, M. M. OLMSTEAD, *J. Am. Chem. Soc.* **1994**, 116, 2227.
- 261 T. J. S. DENNIS, T. KAI, T. TOMIYAMA, H. SHINOHARA, *Chem. Commun.* **1998**, 619.
- 262 A. G. AVENT, D. DUBOIS, A. PENICAUD, R. TAYLOR, *J. Chem. Soc., Perkin Trans. 2: Phys. Org. Chem.* **1997**, 1907.
- 263 C. THILGEN, F. DIEDERICH, *Top. Curr. Chem.* **1999**, 199, 135.
- 264 A. GORYUNKOV, V. Y. MARKOV, I. N. IOFFE, D. BOLSKAR ROBERT, M. D. DIENER, I. KUVYTCHKO, S. H. STRAUSS, V. BOLTA-LINA OLGA, *Angew. Chem.* **2004**, 116, 1015; *Angew. Chem. Int. Ed. Engl.* **2004**, 43, 997.
- 265 C. THILGEN, A. HERRMANN, F. DIEDERICH, *Helv. Chim. Acta* **1997**, 80, 183.
- 266 R. KESSINGER, J. CRASSOUS, A. HERMANN, M. RÜTTIMANN, L. ECHEGOYEN, F. DIEDERICH, *Angew. Chem.* **1998**, 110, 2022; *Angew. Chem. Int. Ed. Engl.* **1998**, 37, 1919.
- 267 J. CRASSOUS, J. RIVERA, N. S. FENDER, L. SHU, L. ECHEGOYEN, C. THILGEN, A. HERRMANN, F. DIEDERICH, *Angew. Chem.* **1999**, 111, 1716; *Angew. Chem. Int. Ed. Engl.* **1999**, 38, 1613.
- 268 H. GOTO, N. HARADA, J. CRASSOUS, F. DIEDERICH, *J. Chem. Soc., Perkin Trans. 2* **1998**, 1719.
- 269 R. TAYLOR, D. R. WALTON, *Nature* **1993**, 363, 685.
- 270 B. L. ZHANG, C. H. XU, C. Z. WANG, C. T. CHAN, K. M. HO, *Phys. Rev. B: Condensed Matter Mater. Phys.* **1992**, 46, 7333.
- 271 J. TERSOFF, *Phys. Rev. B: Condensed Matter Mater. Phys.* **1992**, 46, 15546.
- 272 C. CHRISTIDES, T. J. S. DENNIS, K. PRASSIDES, R. L. CAPPELLETTI, D. A. NEUMANN, J. R. D. COPLEY, *Phys. Rev. B: Condensed Matter Mater. Phys.* **1994**, 49, 2897.
- 273 D. L. LICHTENBERGER, K. W. NEBESNY, C. D. RAY, D. R. HUFFMAN, L. D. LAMB, *Chem. Phys. Lett.* **1991**, 176, 203.
- 274 A. TOKMAKOFF, D. R. HAYNES, S. M. GEORGE, *Chem. Phys. Lett.* **1991**, 186, 450.

- 275 G. DRESSELHAUS, M. S. DRESSELHAUS, J. G. MAVROIDES, *Carbon* **1966**, *4*, 433.
- 276 J. DE VRIES, H. STEGER, B. KAMKE, C. MENZEL, B. WEISSER, W. KAMKE, I. V. HERTEL, *Chem. Phys. Lett.* **1992**, *188*, 159.
- 277 A. V. NIKOLAEV, T. J. S. DENNIS, K. PRASSIDES, A. K. SOPER, *Chem. Phys. Lett.* **1994**, *223*, 143.
- 278 S. SAITO, A. OSHIYAMA, *Phys. Rev. B: Condensed Matter Mater. Phys.* **1991**, *44*, 11532.
- 279 T. KUYOYASHI, M. SAKIYAMA, *Fullerene Sci. Technol.* **1993**, *1*, 269.
- 280 O. V. BOLTALINA, L. N. SIDOROV, A. Y. BORSHCHEVSKY, E. V. SUKHANOVA, E. V. SKOKAN, *Rapid Commun. Mass Spectrom.* **1993**, *7*, 1009.
- 281 P. WURZ, K. R. LYKKE, M. J. PELLIN, D. M. GRUEN, *J. Appl. Phys.* **1991**, *70*, 6647.
- 282 K. HARIGAYA, *Chem. Phys. Lett.* **1992**, *189*, 79.
- 283 W. ANDREONI, F. GYGI, M. PARRINELLO, *Phys. Rev. Lett.* **1992**, *68*, 823.
- 284 K. NAKAO, N. KURITA, M. FUJITA, *Phys. Rev. B: Condensed Matter Mater. Phys.* **1994**, *49*, 11415.
- 285 G. ONIDA, W. ANDREONI, J. KOHANOFF, M. PARRINELLO, *Chem. Phys. Lett.* **1994**, *219*, 1.
- 286 N. SIVARAMAN, R. DHAMODARAN, I. KALIAPPAN, T. G. SRINIVASAN, P. R. V. RAO, C. K. MATHEWS, *J. Org. Chem.* **1992**, *57*, 6077.
- 287 R. S. RUOFF, D. S. TSE, R. MALHOTRA, D. C. LORENTS, *J. Phys. Chem.* **1993**, *97*, 3379.
- 288 W. A. SCRIVENS, J. M. TOUR, *J. Chem. Soc., Chem. Commun.* **1993**, 1207.
- 289 M. V. KOROBV, A. L. SMITH, *Fullerene: Chem. Phys. Technol.* **2000**, 53.
- 290 Z. GASZYNA, P. N. SCHATZ, J. P. HARE, T. J. DENNIS, H. W. KROTO, R. TAYLOR, D. R. M. WALTON, *Chem. Phys. Lett.* **1991**, *183*, 283.
- 291 S. LEACH, M. VERVLOET, A. DESPRES, E. BREHERET, J. P. HARE, T. J. DENNIS, H. W. KROTO, R. TAYLOR, D. R. M. WALTON, *Chem. Phys.* **1992**, *160*, 451.
- 292 H. IMAHORI, Y. SAKATA, *Adv. Mater.* **1997**, *9*, 537.
- 293 H. IMAHORI, Y. SAKATA, *Eur. J. Org. Chem.* **1999**, 2445.
- 294 D. M. GULDI, *Chem. Soc. Rev.* **2002**, *31*, 22.
- 295 D. M. GULDI, P. V. KAMAT, *Fullerenes: Chem. Phys. Technol.* **2000**, 225.
- 296 R. D. JOHNSON, G. MEIJER, J. R. SALEM, D. S. BETHUNE, *J. Am. Chem. Soc.* **1991**, *113*, 3619.
- 297 R. M. FLEMING, B. HESSEN, T. SIEGRIST, A. R. KORTAN, P. MARSH, R. TYCKO, G. DABBAGH, R. C. HADDON, *ACS Symp. Ser.* **1992**, *481*, 25.
- 298 A. R. KORTAN, N. KOPYLOV, S. GLARUM, E. M. GYORGY, A. P. RAMIREZ, R. M. FLEMING, F. A. THIEL, R. C. HADDON, *Nature* **1992**, *355*, 529.
- 299 P. W. STEPHENS, L. MIHALY, P. L. LEE, R. L. WHETTEN, S. M. HUANG, R. KANER, F. DEIDERICH, K. HOLCZER, *Nature* **1991**, *351*, 632.
- 300 C. S. YANNONI, R. D. JOHNSON, G. MEIJER, D. S. BETHUNE, J. R. SALEM, *J. Phys. Chem.* **1991**, *95*, 9.
- 301 R. TYCKO, R. C. HADDON, G. DABBAGH, S. H. GLARUM, D. C. DOUGLASS, A. M. MUJSCE, *J. Phys. Chem.* **1991**, *95*, 518.
- 302 R. D. JOHNSON, C. S. YANNONI, H. C. DORN, J. R. SALEM, D. S. BETHUNE, *Science* **1992**, *255*, 1235.
- 303 P. A. HEINEY, J. E. FISCHER, A. R. MCGHIE, W. J. ROMANOW, A. M. DENENSTEIN, J. P. MCCAULEY, JR., A. B. SMITH, III, D. E. COX, *Phys. Rev. Lett.* **1991**, *66*, 2911.
- 304 A. DWORKIN, H. SZWARC, S. LEACH, J. P. HARE, T. J. DENNIS, H. W. KROTO, R. TAYLOR, D. R. M. WALTON, *Comp. Rend. Acad. Sci., Ser. II: Mecan., Phys., Chim., Sci. la Terre et de l'Univers* **1991**, *312*, 979.
- 305 J. S. TSE, D. D. KLUG, D. A. WILKINSON, Y. P. HANDA, *Chem. Phys. Lett.* **1991**, *183*, 387.
- 306 P. A. HEINEY, *J. Phys. Chem. Solids* **1992**, *53*, 1333.
- 307 M. F. MEIDINE, P. B. HITCHCOCK, H. W. KROTO, R. TAYLOR, D. R. M. WALTON, *J. Chem. Soc., Chem. Commun.* **1992**, 1534.
- 308 A. L. BALCH, J. W. LEE, B. C. NOLL, M. M. OLMSTEAD, *J. Chem. Soc., Chem. Commun.* **1993**, 56.
- 309 S. M. GORUN, K. M. CREEGAN, R. D. SHERWOOD, D. M. COX, V. W. DAY, C. S. DAY, R. M. UPTON, C. E. BRIANT, *J. Chem. Soc., Chem. Commun.* **1991**, 1556.

- 310 J. D. CRANE, P. B. HITCHCOCK, H. W. KROTO, R. TAYLOR, D. R. M. WALTON, *J. Chem. Soc., Chem. Commun.* **1992**, 1764.
- 311 A. IZUOKA, T. TACHIKAWA, T. SUGAWARA, Y. SUZUKI, M. KONNO, Y. SAITO, H. SHINOHARA, *J. Chem. Soc., Chem. Commun.* **1992**, 1472.
- 312 D. V. KONAREV, R. N. LYUBOVSKAYA, A. Y. KOVALEVSKY, P. COPPENS, *Chem. Commun.* **2000**, 2357.
- 313 J. D. CRANE, P. B. HITCHCOCK, *J. Chem. Soc., Dalton Trans.: Inorg. Chem.* **1993**, 2537.
- 314 V. KONAREV DMITRI, S. KHASANOV SALAVAT, G. SAITO, I. VORONTOV IVAN, A. OTSUKA, N. LYUBOVSKAYA RIMMA, M. ANTIPIN YURY, *Inorg. Chem.* **2003**, 42, 3706.
- 315 P. D. W. BOYD, M. C. HODGSON, C. E. F. RICKARD, A. G. OLIVER, L. CHAKER, P. J. BROTHERS, R. D. BOLSKAR, F. S. THAM, C. A. REED, *J. Am. Chem. Soc.* **1999**, 121, 10487.
- 316 D. R. EVANS, N. L. P. FACKLER, Z. XIE, C. E. F. RICKARD, P. D. W. BOYD, C. A. REED, *J. Am. Chem. Soc.* **1999**, 121, 8466.
- 317 D. SUN, F. S. THAM, C. A. REED, L. CHAKER, M. BURGESS, P. D. W. BOYD, *J. Am. Chem. Soc.* **2000**, 122, 10704.
- 318 A. L. BALCH, *Fullerenes: Chem. Phys. Technol.* **2000**, 177.
- 319 D. SUN, F. S. THAM, C. A. REED, L. CHAKER, P. D. W. BOYD, *J. Am. Chem. Soc.* **2002**, 124, 6604.
- 320 F. MICHAUD, M. BARRIO, D. O. LOPEZ, J. L. TAMARIT, V. AGAFONOV, S. TOSCANI, H. SZWARC, R. CEOLIN, *Chem. Mater.* **2000**, 12, 3595.
- 321 P. R. BIRKETT, C. CHRISTIDES, P. B. HITCHCOCK, H. W. KROTO, K. PRASSIDES, R. TAYLOR, D. R. M. WALTON, *J. Chem. Soc., Perkin Trans. 2: Phys. Org. Chem.* **1993**, 1407.
- 322 O. ERMER, *Helv. Chim. Acta* **1991**, 74, 1339.
- 323 G. ROTH, P. ADELMANN, *J. Phys. I* **1992**, 2, 1541.
- 324 T. ANDERSSON, K. NILSSON, M. SUNDAHL, G. WESTMAN, O. WENNERSTROEM, *J. Chem. Soc., Chem. Commun.* **1992**, 604.
- 325 L. J. BARBOUR, G. W. ORR, J. L. ATWOOD, *Chem. Commun.* **1998**, 1901.
- 326 J. L. ATWOOD, L. J. BARBOUR, M. W. HEAVEN, C. L. RASTON, *Angew. Chem.* **2003**, 115, 3376; *Angew. Chem. Int. Ed. Engl.* **2003**, 42, 3254.