The Chemistry of the Fullerenes

Andreas Hirsch

University of Tübingen

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Dedicated to my wife Almut

Preface

"Buckminsterfullerene: Is it a real thing?" This question was in our heads that evening in November 1990, when Fred Wudl came into the lab and showed us the first 50 mg sample of C_{60}. Although at that time there was evidence for the geometrical structures of this soccer ball shaped molecule and his bigger brother the "American football" C_{70}, no one knew what the chemical and physical properties of these fascinating molecular allotropes of carbon would be. On that same night we started to work on C_{60} and three reversible one electron reductions of the carbon sphere were found – one more than already detected by the Rice group. We were all enthusiastic and Fred projected possible chemical transformations and proposed remarkable electronic properties of fulleride salts – a prediction that shortly thereafter became reality by the discovery of the superconductivity of K_3C_{60} in the Bell labs. It was one of the greatest opportunities in my scientific life, that Fred asked me to participate in the ball game and to investigate organic fullerene chemistry. He also encouraged me to carry on this work in Germany, once I had finished my postdoctoral time in his group in Santa Barbara. The pioneering research of these early days is still a basis of my present work. Fullerene chemistry, which is unique in many respects, has meanwhile exploded. In a very short period of time a huge number of chemical transformations of the "real thing" C_{60} and outstanding properties of fullerene derivatives have been discovered. Many principles of fullerene chemistry are understood. The fullerenes are now an established compound class in organic chemistry.

It is therefore the right time to give a first comprehensive overview of fullerene chemistry, which is the aim of this book. This summary addresses chemists, material scientists and a broad readership in industry and the scientific community. The number of publications in this field meanwhile gains such dimensions that for nonspecialists it is very difficult to obtain a facile access to the topics of interest. In this book, which contains the complete important literature, the reader will find all aspects of fullerene chemistry as well as the properties of fullerene derivatives. After a short description of the discovery of the fullerenes all methods of the production and isolation of the parent fullerenes and endohedrals are discussed in detail (Chapter 1). In this first chapter the mechanism of the fullerene formation, the physical properties, for example the molecular structure, the thermodynamic, electronic and spectroscopic properties as well as solubilities are also summarized. This knowledge is necessary to understand the chemical behavior of the fullerenes. The description of the chemistry of the fullerenes themselves is organized according to the type of chemical transformation, starting from the reduction (Chapter 2), nucleophilic additions (Chapter 3), cycloadditions (Chapter 4), hydrogenation (Chapter 5), radical additions (Chapter 6), transition metal complex formation (Chapter 7) through oxidation and reactions with electrophiles (Chapter 8). Most of the examples presented in these chapters are reactions with C_{60}, since only very little work has been published on C_{70} and the higher fullerenes. It is the aim to provide an understanding of the basic characteristics of fullerene chemistry. This is achieved by a comparative description of both experimental and theoretical investigations in each of these chapters. It is also emphasized in each chapter wherever a reaction type leads to a fullerene derivative with a potential for practical application. In the last chapter (Chapter 9) the emerging principles of fullerene chemistry, such as reactivity and regiochemistry, are evaluated and summarized. The fullerene chemistry is still in an early stage of development. For synthetic chemists a lot of challenging work remains to be done. A prediction of the future directions of fullerene chemistry is therefore also given in Chapter 9 and finally, since from the beginning of the fullerene era many practical uses have been proposed, perspectives for applications are evaluated.

Writing this book prevented me for some time from carrying out practical work with my own hands. Nevertheless, since I have had co-workers like Thomas Grösser, Iris Lamparth, Andreas Skiebe and Antonio Soi, the experimental work on fullerenes in my lab has proceeded, even with much success. I am also indebted to my co-workers for their assistance in preparing figures and illustrations presented in this book. I thank Dr. L. R. Subramanian for reading the entire manuscript and for useful suggestions.

From Georg Thieme Verlag I thank Dr. J. P. Richmond for the excellent co-operation, which enabled the fast realization of this book project.

I am very grateful to my teacher Prof. Dr. Dr. h.c. M. Hanack, who has been supporting me for many years and who provided the starting conditions for writing this book.

It was Prof. Dr. F. Wudl who introduced me to the art of fullerene chemistry and who inspired me to continue with this work, for which I want to thank him very much. On reviewing the manuscript he came up with cogent comments and suggestions.

My special thanks go to my wife Almut, who, despite the fact that for several months she was very often deprived of the company of her husband, responded with warmth and understanding.

Andreas Hirsch
Tübingen, May 1994

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1.1 The 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 played a minor role in the past. 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, the fullerenes are spherical molecules and are soluble in a variety of organic solvents, an important requirement for chemical manipulations.

The fullerenes are built up of fused pentagons and hexagons. The pentagons, absent in graphite, provide the curvature. The smallest stable and at the same time the most abundant fullerene, obtained by usual preparation methods, is the I_h-symmetrical buckminsterfullerene C_{60} [Fig 1.1]. Buckminsterfullerene has the shape of a soccer ball. The next stable homologue is C_{70} [Fig 1.2] followed by the higher fullerenes C_{76}, C_{78}, C_{82}, C_{84}, C_{90}, C_{94} and C_{96}. 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 additionally appeal from an aesthetic point of view. The beauty and the unprecedented spherical architecture of these molecular cages immediately attracted the attention of many scientists. In a very fast development buckminsterfullerene C_{60} became one of the most intensively investigated molecules. For the 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 questions concerning the derivatization of fullerenes have been asked from the beginning: 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 nomenclature method of buckminsterfullerene given below is too lengthly 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),14,16,19,21,23,25,27,29(45),30,32,(44),33,
35(43),36,38(54),39(51),40(48),41,46,49,52,55,57,59-triacontaene.

Furthermore, the enormous number of derivatives including the multitude of possible regioisomers, available by chemical modifications requires the introduction of a simple nomenclature. Already by naming the soccer ball shaped C_{60} as [5,6]-fullerene-60-I_h, its structure is sufficiently described[2]. Thereby the numbers 5 and 6 denote, that C_{60} consists of pentagons and hexagons and the number 60 indicates the number of C-atoms. For [5,6]-fullerene-60-I_h and [5,6]-fullerene-70-D_{5h} there exists only one stable isomer of each, which further simplifies their name to fullerene-60 and fullerene-70. The indication of the symmetry groups however becomes important for the description of the higher fullerenes, where different isomers, for example [5,6]-fullerene-78-D_3 and [5,6]-fullerene-78-C_{2v} coexist. An unambiguous description of exohedrally modified derivatives also requires to introduce a numbering system for the C-atoms in each fullerene[3]. Thereby, the C-atoms are numbered in a spiral clockwise fashion, commencing in a hexagon. This is shown in Figure 1.1 and 1.2 for C_{60} and C_{70}. Although the axis of highest symmetry in C_{60} as well as in C_{70} (S_{10} and C_5) goes through pentagons, it is useful to start the numbering in a hexagon, since none of the other fullerenes have five-fold

symmetry and the bonds of the highest priority (reactivity) in C_{60} and C_{70} are those at the junction of two hexagons [Fig 1.1, Fig 1.2].

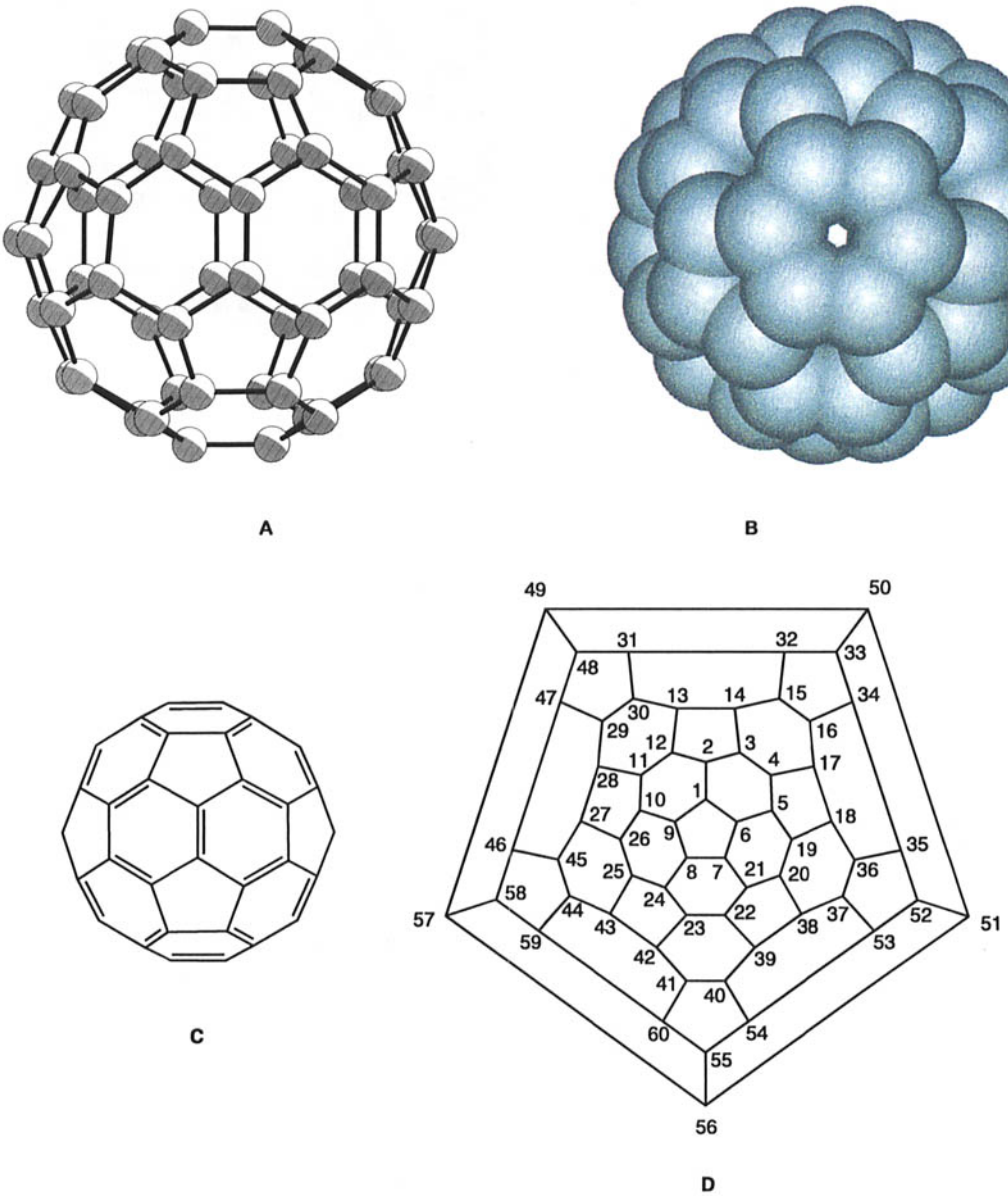
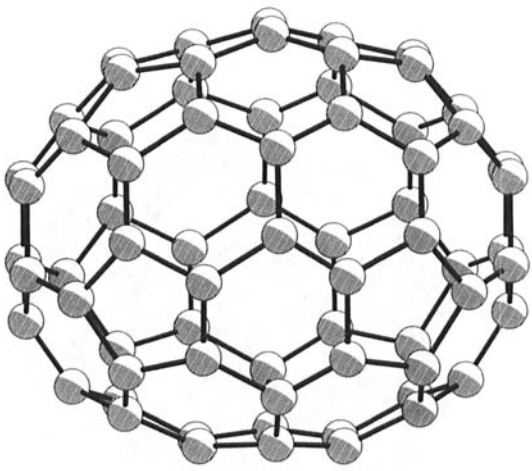


Figure 1.1 Schematic representations of C_{60} (A) ball and stick model, (B) space filling model, (C) front view diagram and (D) Schlegel diagram with numbering of the C-atoms



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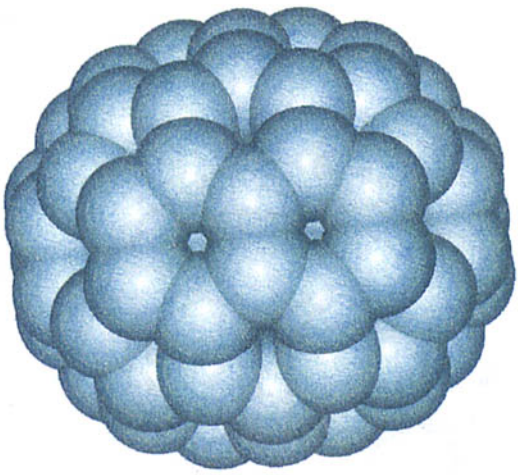

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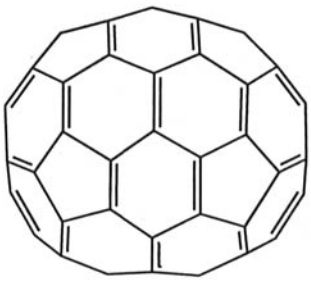

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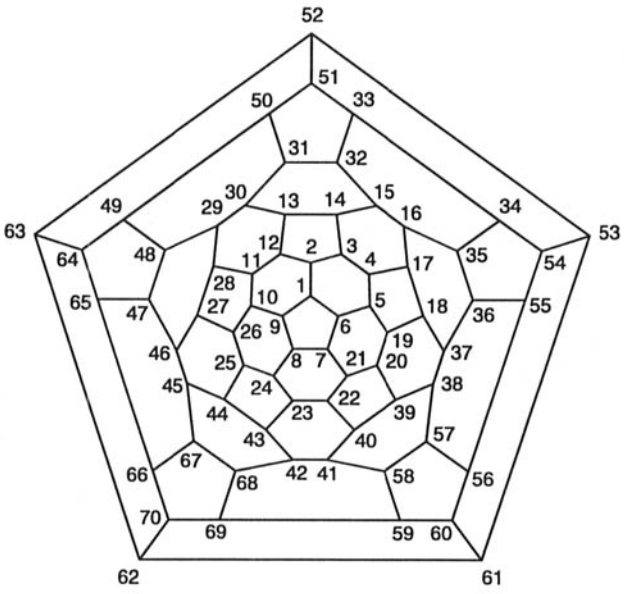


D

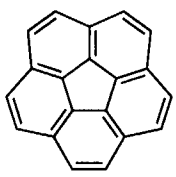
Figure 1.2 Schematic representations of C_{70} (A) ball and stick model, (B) space filling model, (C) front view diagram and (D) Schlegel diagram with numbering of the C-atoms

For simple schematic representations of fullerenes and their derivatives front view formulas or Schlegel diagrams are useful. The front view formulas give a quick impression of the geometry and the bonding situation (double bonds, single bonds) projected in two dimensions. The bonds at the back of the molecule are omitted for clarity. This kind of representation is often used for derivatives with only few adducts bound to the fullerene core. The Schlegel diagram shows each C-atom of the fullerene, which is flattened out in two dimensions. This model is suitable for the consideration of polyadducts for example polyhydrofullerenes.

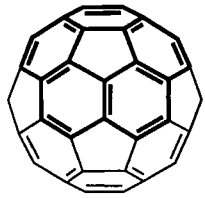
The main type of chemical fullerene derivatizations are addition reactions. Regardless of the relatively large number of possible reaction sites, addition reactions show a remarkable regioselectivity, especially when the number of addents is small. This is another fulfilled requirement, which makes these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

1.2 The Discovery of the Fullerenes

In 1966 Deadalus alias D. E. H. Jones considered the possibility of making large hollow carbon cages, structures, that nowadays are called giant fullerenes[4,5]. This suggestion did not elicit any reaction from the scientific community. Four years later in 1970, simulated by the synthesis of the bowl shaped corannulene **1**[6], Osawa for the first time proposed the spherical I_h-symmetric football structure for the C_{60} molecule (**2**)[7,8]. In the course of his efforts to find new three-dimensional superaromatic π-systems, he recognized the 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} have been reported[9,10,11,12].



1



2

In 1984 it was observed, that upon laser vaporization of graphite, large carbon-only clusters C_n with n = 30-190 can be produced[13]. The mass distribution of the carbon 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 at this time. The breakthrough in the experimental discovery of the fullerenes came in 1985[14] when Kroto visited the Rice University in Houston. Here, Smalley and co-workers developed a technique[15] for studying refractory clusters by mass spectrometry, generated in a plasma by focusing a pulsed laser on a solid, in this case graphite. The original goal of the investigations of Kroto and Smalley 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[16,17] can be simulated by laboratory experiments[18]. During the course of these studies, it was observed, that under

specific clustering conditions the 720 mass peak attributed to C_{60} and to a lesser extent the peak attributed to C_{70} exhibit a pronounced intensity in the spectra [Fig. 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[14]. 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 a synthesis in macroscopic amounts needed to be found.

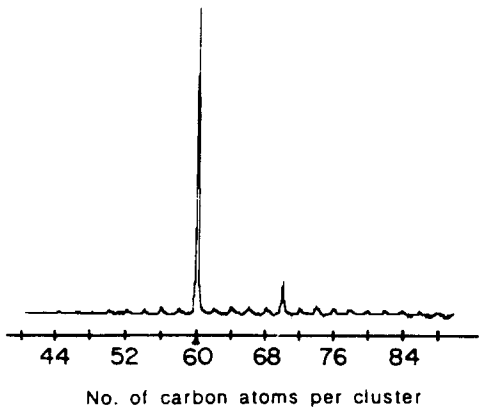


Figure 1.3 Time-of-flight mass spectrum of carbon cluster produced by laser vaporization of graphite under the optimum conditions for observation of a dominant C_{60} signal[14].

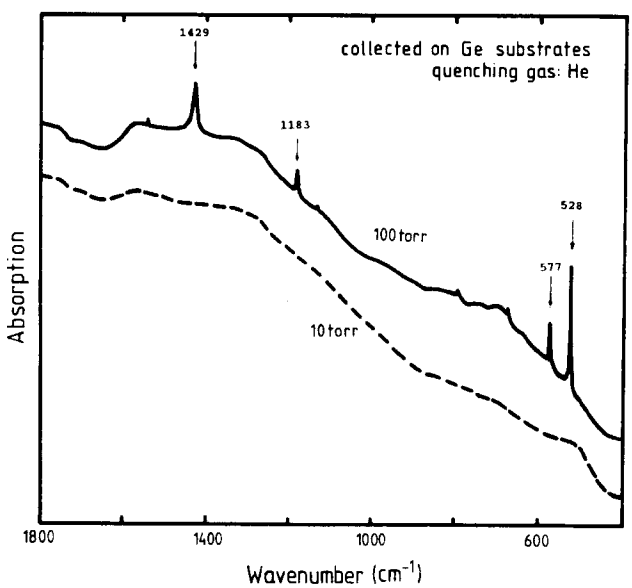


Figure 1.4 IR-spectra of soot particles produced by evaporation of graphite under different helium quenching gas pressures. The occurrence of the four additional sharp peaks at elevated helium pressures turned out to originate from buckminsterfullerene (C_{60})[19].

This second breakthrough in the fullerene research was achieved by Krätschmer and Huffman[19]. Their intention was to produce laboratory analogues of interstellar dust by vaporization of graphite rods in a helium atmosphere[20]. They observed, that upon choosing the right helium pressure, the IR-spectra of the soot, generated by the graphite vaporization, show four sharp stronger absorptions, together with those of the continuum of regular soot [Fig. 1.4][21]. These absorptions were close to the positions predicted by theory for buckminsterfullerene[22]. The isolation of the fullerenes from the soot was then accomplished 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. Next to buckminsterfullerene C_{60}, higher homolgues are also obtained by this technique. Now, the fullerenes were 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

The generation of fullerenes by resistive heating of graphite was the first technique to produce macroscopic quantities[19]. This method is based on the technique for the production of amorphous carbon films in a vacuum evaporator[23]. The apparatus [Fig. 1.5] that Krätschmer and Fostiropoulos used for the first production of fullerenes consisted of a bell jar as recipient, which is connected to a pump system and a gas inlet. In the interior of the recipient two graphite rod 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.

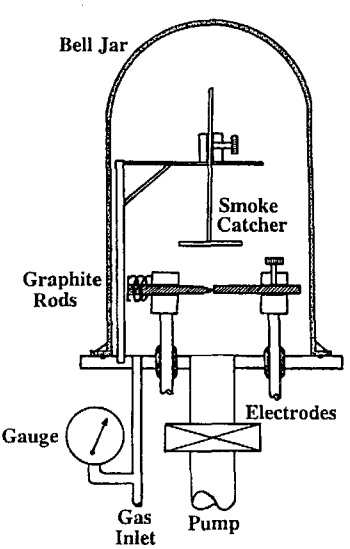


Figure 1.5 Fullerene generator originally used by Krätschmer[19,24].