The Synthesis and Characterization of Fullerene Hydrides

Jamie Nossal,[a] Rajesh K. Saini,[a] Lawrence B. Alemany,[a] Mark Meier,[b] and W. E. Billups*[a]

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The syntheses and characterization of fullerene hydrides prepared from C_{60} and C_{70} are reviewed. Methods of isolation and characterization are discussed, particularly MS and NMR, including ^{3}He nuclear magnetic resonance spectroscopy. The higher hydrides are discussed in terms of novel structural features and their unusual spectroscopic properties.

Introduction

The discovery of buckminsterfullerene (C_{60}) and related substances in 1985 stimulated enormous interest in the new carbon allotropes.[1] Although available initially only in vanishingly small quantities in the gas phase, an important breakthrough came in 1990, when it was found that these compounds could be synthesized in gram quantities by laser vaporization of graphite.[2] With an abundant supply of these fascinating new materials at hand, a flurry of activity directed at establishing a preliminary picture of fullerene chemistry soon followed. Despite some initial reservations,[3] the fullerenes proved to be excellent substrates for addition reactions, including hydrogenation by several different methods.[4−21]

Jamie Nossal (left, top) received his Bachelor of Science degree in chemistry from the University of Denver in 1990. He received his Ph.D. in organic chemistry from Rice University in 2001, working under the guidance of Prof. W. E. Billups. His research interests include the synthesis and characterization of fullerene hydrides. His current work involves the development of novel analytical methods for the petrochemical industry in Houston, Texas.

Rajesh Kumar Saini (right, top) was born in Ambala, India in 1966. He obtained his masters degree (chemistry) in 1989 and his Ph.D. in organic chemistry in 1996 from Kurukshetra University under the directions of Prof. Om Prakash and Prof. Shiv P. Singh, studying the synthetic utility of hypervalent iodine reagents in organic synthesis. After his doctorate he moved to the United States for his postdoctoral studies. After a brief stay at Sam Houston State University with Dr. Rajender S. Varma, he joined Rice University, where he is working with Prof. W. E. Billups and Prof. Richard E. Smalley on the development and chemistry of carbon nanotubes.

Lawrence Alemany (left, center) received his Ph.D. in chemistry in 1980 from the University of Chicago, working in the research group of Professor Leon M. Stock. He subsequently did postdoctoral research in solid-state NMR at the University of Utah, working with Professors David M. Grant and Ronald J. Pugmire. After 11 years as an NMR spectroscopist at Mobil Research and Development Corp., Alemany moved in 1994 to Rice University, where he now is NMR Manager, Senior Research Scientist, and Lecturer in the chemistry department. He takes an active role in teaching NMR and collaborating in research projects involving solution-state and solid-state NMR. In 1999 he received Rice University's Distinguished Service Award.

Mark S. Meier (left, bottom) was born in 1959 in Tacoma, Washington. He received his A.B. degree from Dartmouth College in 1982 before moving back to the west coast for graduate study. He received his Ph.D. in 1988 at the University of Oregon, working with Prof. Bruce P. Branchaud. After postdoctoral work with Marye Anne Fox at the University of Texas at Austin, he joined the faculty at the University of Kentucky in 1990, where he currently holds the rank of Professor. His research has concentrated on fullerene and carbon nanotube chemistry.

W. E. Billups (right, bottom) was born in 1939 in Huntington, West Virginia. He received his B.S. degree in chemistry from Marshall University in 1961. This was followed by a period in industry, after which he entered the graduate school of the Pennsylvania State University in 1968 and received his Ph.D. in 1970. He then joined the chemistry department at Rice University. He served as the Department Chair from July 1985 until December 1991. His research interests are divided among the areas of small-ring compounds, reactive intermediates, chemistry of free metal atoms, and more recently fullerene and carbon nanotube chemistry.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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[a] Department of Chemistry, Rice University
6100 Main Street, Houston, Texas 77005-1892, USA
Fax: (internat.) + 1-713/348-5155
E-mail: billups@rice.edu
[b] Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506-0055, USA

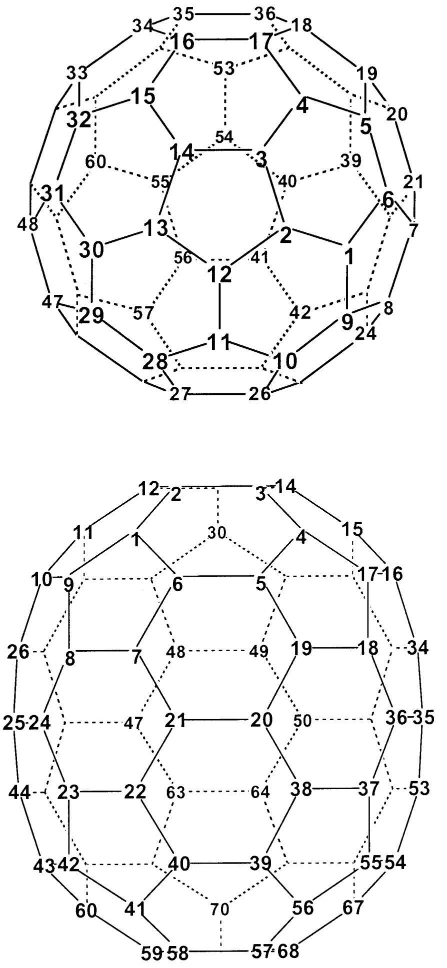


Figure 1. IUPAC-suggested numbering system for C_{60} and C_{70}; some of the numbers on the back side of the cages are omitted for clarity; see: E. W. Godly, R. Taylor, *Pure Appl. Chem.* **1997**, *69*, 1411−1434

The IUPAC numbering system for C_{60} and C_{70} is presented in Figure 1. The adjacent carbon atoms in the fusion of two six-membered rings are given the C(1) and C(2) designation; then the numbering continues in a clockwise fashion.

The first reported derivative was a highly reduced fullerene formed by the Birch reduction of C_{60}.[4] Subsequent work with C_{60}, and to a lesser extent with C_{70}, has resulted in the synthesis and characterization of many other fullerene hydrides. Activity in this area has been spurred on in part by the suggestion that fullerene hydrides might have useful applications as batteries, as catalysts, or as media for storage of dihydrogen. In this review, we present an up-to-date account of progress on the synthesis and characterization of the fullerene hydrides.

Purification and Characterization

Purification of even the simplest derivatized fullerene reaction mixture is often difficult and may require extensive use of preparative high pressure liquid chromatography. $C_{60}H_2$ is the simplest C_{60} derivative, yet it has 23 energetically distinct isomeric possibilities[22,23] without considering any isomers with one or more substituents bonded to the inner surface of the cage. Thus, the preponderance of active sites frequently results in a correspondingly large number of products.[24−26]

Exceptional care in avoiding plasticizers and silicone greases is necessary,[7] as there is a strong tendency for fullerenes and fullerene derivatives to retain these materials.[27a] The fullerene hydrides are significantly less soluble than the parent fullerenes in common solvents, and in some cases this has presented a major obstacle to the isolation of samples suitable for spectral characterization.[8,9,28] Carbon disulfide is frequently used,[7] although the more highly reduced hydrides have been observed to form insoluble precipitates upon dissolution in carbon disulfide.[27] Although chemical shifts are found to be solvent-dependent,[7] NMR spectra of the lower hydrides can be obtained readily. Methylcyclohexane has been used to extract C_{60} and C_{70} hydrides from the unchanged parent fullerenes, which are only slightly soluble in this solvent.[5]

Exclusion of oxygen and light is important, as light-catalyzed oxidation of the higher hydrides appears to be a facile process.[6,15,27−30] Samples kept in the dark may be stored without decomposition for several weeks.[27,29a] Exclusion of oxygen is, of course, important, and even the use of deoxygenated solvents fails at times, due to the ease with which oxygen becomes trapped in the fullerene lattice.[27b] C_{60} has been reduced in deuterated solvents to minimize the rapid oxidation process.[27] Galvinoxyl has been reported to retard the degradation of $C_{60}H_{36}$.[27a]

Although the lower hydrides can be analyzed readily by mass spectrometry, the higher hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$ often fragment under EI conditions.[10] Acceptable EI-MS spectra of C_{60}, C_{70}, C_{76}, C_{78}, and C_{84} hydrides have been obtained immediately after workup through use of carefully prepared samples.[27,29−31]

FAB has been successfully used as a mild MS ionization technique by some workers,[8,13] but others have observed a range of hydrides below the M^+ peak and additional lines appearing at higher masses as well,[10] a phenomenon that prevented definitive analysis of the hydrides resulting from reduction of C_{60} by diimide.[7]

Rüchardt and Lobach and their co-workers have each reported field desorption mass spectrometry as a preferred method. They secured spectra with strong M^+ peaks and substantially less fragmentation of the molecular ions of $C_{60}H_{36}$ and $C_{70}H_{36}$.[10,29] It has also been reported that mass spectra obtained by laser desorption ionization reveal weak M^+ peaks along with a range of partially dehydrogenated products.[8,10,32] Ballenweg and co-workers used LD-TOF mass spectrometry to characterize $C_{60}H_2$,[9] but fragmentation was presumably a minor problem with the dihydrofullerene. Banks and co-workers cited LD-TOF data in support of their contention that the principal product of the C_{60} Birch reduction was actually $C_{60}H_{32}$ and not $C_{60}H_{36}$[33] as originally reported.[4] The LD-TOF spectra published by this group are remarkably similar to the LD-MS spectra of $C_{60}H_{18}$ and $C_{60}H_{36}$ published by Rüchardt, which show that the maxima have been shifted to smaller masses compared to those obtained by other MS methods.[10,32]

A major advance in the identification of fullerene hydrides was achieved when Saunders and co-workers reported the inclusion of noble gas atoms inside fullerenes.[34] These "carcerands" − fullerene molecules containing a second, discrete species such as a noble gas atom − are produced by subjecting the fullerene and the gas to be incorporated to high pressure and temperatures. ^{3}He is an excellent NMR nucleus, with a spin of $^1/_2$ and a high gyromagnetic ratio, which allows He@C_{60} and its derivatives to be examined by ^{3}He NMR spectroscopy. The technique is quite sensitive, and a large amount of empty fullerene does not interfere with the spectrum. The utility of the ^{3}He NMR technique becomes evident when it is considered that each product will produce a single distinct peak in the ^{3}He NMR spectrum. This information, coupled with ^{3}He shifts determined computationally for He@C_{60} derivatives, makes it possible to determine the number of isomers present in a mixture while providing some evidence for structural characterization purposes.

The UV/Vis[4,5,9,11,15,17,19,27,29,35−39] and IR spectra[4,5,8−11,15,19−21,27,29,32,35−38,40] of various fullerene hydrides have been published. The spectra of substituted fullerenes are sometimes similar to the UV spectrum of the parent fullerene, which is consistent with the preservation of an intact cage following addition. FT-IR spectra show the common features of C−H and C−D bonds and C=C skeletal vibrations.

C_{60} Hydrides

(a) $C_{60}H_2$

Henderson and Cahill reported the synthesis of $C_{60}H_2$, the simplest fullerene hydride, in 1993.[11] Hydrolysis of the borane resulting from addition of BH_3 in THF to a solution of C_{60} in dry toluene gave the dihydride in 10−30% yield. Addition across the 6,6-ring fusion (Figure 2) was based on previously published computational results[23] that show that addition across a 6,5-ring is energetically unfavorable. Preparative high pressure liquid chromatography using a "buckyclutcher" column[41] was employed to separate the $C_{60}H_2$ from unchanged C_{60} and $C_{60}O$. Elemental composition was verified by high-resolution positive-ion mass spectrometry.

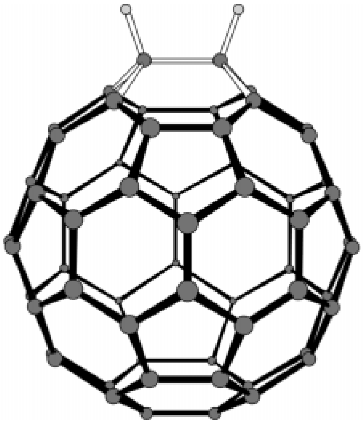


Figure 2. $C_{60}H_2$

$C_{60}H_2$ exhibits a sharp singlet at $\delta = 5.93$ when its ^{1}H NMR spectrum is recorded in [D_8]toluene.[11] This signal remains sharp between −80 °C and +100 °C, showing that the structure of $C_{60}H_2$ is static on the NMR timescale. Because of the asymmetric environment of the ^{11}B nucleus and consequent rapid relaxation of both nuclei, resonances for ^{1}H or ^{11}B nuclei in the presumed intermediate $C_{60}(H)(BH_2)$ could not be obtained. When D_2O was used to hydrolyze the borane, a mixture of $C_{60}H_2$ and $C_{60}HD$ was formed. The ^{1}H NMR spectroscopic data observed for these compounds were consistent with vicinal *cis*-hydrogen substitution.[42]

The 750-MHz ^{1}H NMR spectrum of $C_{60}H_2$ (1:1, [D_6]benzene/CS_2) revealed an unusual 0.30 Hz splitting, not readily observed in spectra taken with a 500-MHz instrument (Figure 3).[43] This splitting is believed to be the result of a residual anisotropic dipole−dipole interaction between the two chemically and magnetically equivalent protons in $C_{60}H_2$. At the time, such phenomena had only rarely been observed, due to the small magnitude of such interactions, which are proportional to the square of the magnetic field strength, and the necessity to use a solvent that can be partially aligned by the magnetic field, thereby allowing alignment transfer to the solute.[44] This effect was not observed when $CDCl_3$ or [D_6]acetone were used as solvents.

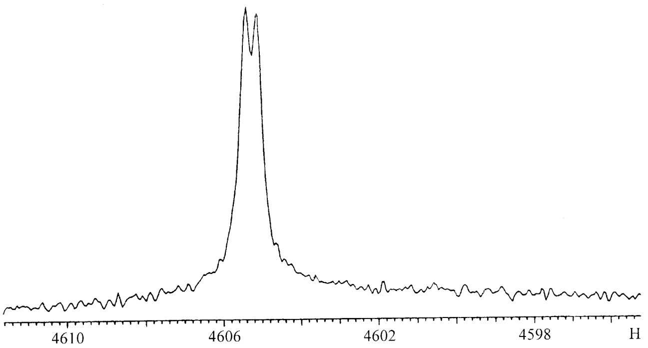


Figure 3. 750-MHz ^{1}H NMR spectrum of $C_{60}H_2$ (1:1, [D_6]benzene/CS_2) with 0.30 Hz splitting

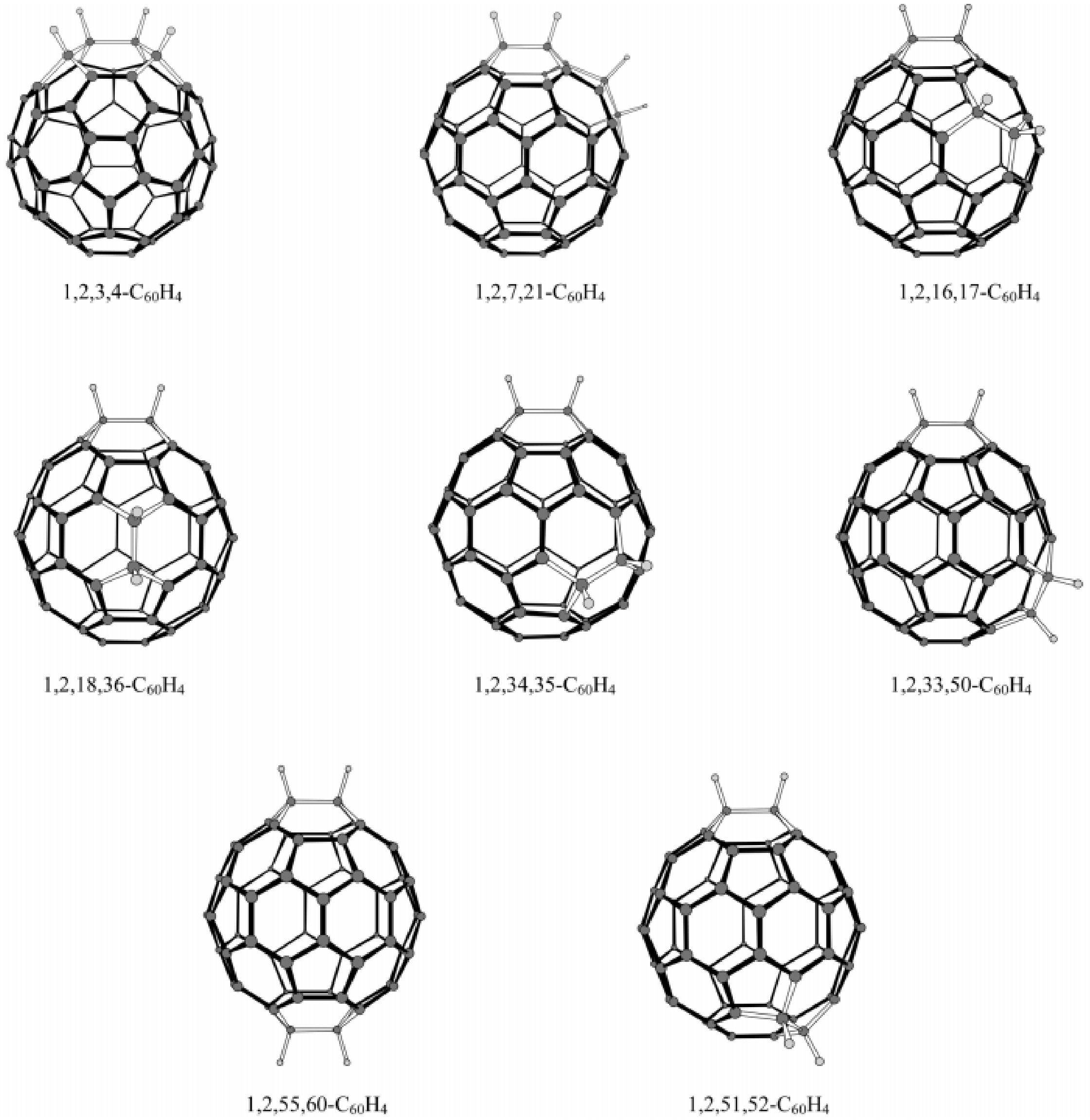
The report by Henderson and Cahill was soon followed by another synthesis in which Zn/HCl in refluxing toluene was used to synthesize $C_{60}H_2$.[13] Oxidation of the hydride by DDQ allowed smooth conversion of the product back to C_{60}. The synthesis of both the 1,2- and 1,4-dihydrofullerenes by reduction of C_{60} using diimide has been reported.[7] Singlet peaks at $\delta = 6.97$ and 7.23 (CS_2 solvent, $CDCl_3$ as lock signal) were assigned to the 1,2- and 1,4-dihydrofullerene isomers, respectively. ^{1}H NMR signals that were upfield with respect to the $C_{60}H_2$ singlets were assigned to more highly reduced C_{60}. It is interesting that anhydrous hydrazine[12] can be used without addition of the usual oxidant that is required to form diimide. In this case the hydrazine is oxidized by the fullerene.

Other methods that have been used to synthesize the dihydride include hydrozirconation,[9] Zn(Cu) reduction,[14b,14c] sonication of a mixture of C_{60} and decahydronaphthalene,[17] catalytic hydrogenation with ruthenium on carbon,[5] rhodium(0) on alumina,[6] palladium and palladium on carbon,[20] protonation of $C_{60}{}^{2-}$ generated by bulk electrolysis,[45] and photoinduced electron transfer from 10-methyl-9,10-dihydroacridine to the triplet excited state of C_{60} by irradiation with visible light in the presence of trifluoroacetic acid in benzonitrile.[46] Solid-state synthesis of $C_{60}H_2$ has been achieved with palladium hydride[18] and with solid-phase C_{60} under H_2 without a catalyst.[16] The 1,4-isomer has not been reported as a component of the reaction products from these reactions.

Reduction of $^3He@C_{60}$ by hydroboration/protonation produced $^3He@C_{60}H_2$, which gave a ^3He NMR signal at $\delta = -9.66$, relative to dissolved helium at $\delta = 0$.[47] The chemistry of $C_{60}H_2$ has remained largely unexplored. Electrochemical reduction has been reported by several groups.[48−50] Meier and co-workers found that C_{60} is a product of cyclic voltammetry of the dihydride in benzonitrile solution;[48] Boulas and co-workers observed the same in 80:20 toluene/DMF.[49] $C_{60}H_2$ therefore undergoes a net oxidation under "reducing" conditions. The photophysical characterization and singlet oxygen yield of dihydrofullerene has been reported by Anderson and Bensasson and their co-workers.[51,52]

(b) $C_{60}H_4$

Henderson and co-workers isolated a mixture of $C_{60}H_4$ isomers in 10% yield from the reduction of $C_{60}H_2$ with borane as the reducing agent.[53] Six of the eight possible isomers that would result from addition to 6,6-bonds (Figure 4) could be detected by ^1H NMR spectroscopy. The major isomer, which accounted for approximately 50% of the crude mixture, could be isolated from the reaction mixture



1,2,3,4-$C_{60}H_4$

1,2,7,21-$C_{60}H_4$

1,2,16,17-$C_{60}H_4$

1,2,18,36-$C_{60}H_4$

1,2,34,35-$C_{60}H_4$

1,2,33,50-$C_{60}H_4$

1,2,55,60-$C_{60}H_4$

1,2,51,52-$C_{60}H_4$

Figure 4. Isomers of $C_{60}H_4$

by high pressure liquid chromatography using a buckyclutcher I stationary phase[41] and toluene/hexane (1:1) isocratic mobile phase. An AA′BB′ spin system centered at $\delta = 5.03$ ([D$_8$]toluene) could readily be assigned to 1,2,3,4-$C_{60}H_4$, which has two pairs of hydrogen atoms bonded to adjacent 6,6-ring fusions. This isomer has been shown to be the most stable tetrahydrofullerene at two levels of ab initio theory and is favored over the next lowest lying isomer, 1,2,18,36-$C_{60}H_4$, by 4.0 kcal/mol.[53] Henderson et al. have also shown that a mixture of tetrahydrofullerenes can be equilibrated to give predominantly the more stable 1,2,3,4-$C_{60}H_4$ isomer. A second isomer was identified as 1,2,18,36-$C_{60}H_4$ by its ^{1}H NMR spectroscopic data [$\delta = 5.36$ (2 H, s) and 5.05 (2 H, AB q)]. Structural assignment of the three other AB quartets present was not possible.

A singlet at $\delta = 6.33$ was tentatively identified as the 1,2,55,60-$C_{60}H_4$ isomer, but this could not be isolated. Avent and co-workers noted that this singlet consists of two almost coincident peaks of equal intensity and that this isomer could be present in two conformations as a result of adjacent hydrogen atoms being very slightly *trans* to one another, due to the inflexibility of the cage.[7] If this were the case, *meso* and (±) isomers would be present and differentiated by a very small chemical shift difference. This explanation would require that other isomers would likewise be affected, and it is notable that Avent reported that similar, very small splittings were present in two other AB quartets. However, in reviewing these results in another report on the ^{1}H spectra of isomers of $C_{60}H_4$, Billups and co-workers proposed alternative explanations, including residual anisotropic dipole−dipole interactions, for the origins of these extra signals.[43b]

C_{60} can also be reduced with anhydrous hydrazine in benzene to give a mixture of fullerene hydrides $C_{60}H_n$ ($n = 2$, 4, 6, 8, 18, 36).[12] The relative ratio of the different hydrides was similar to that obtained by the Cu^{2+}-catalyzed diimide reduction employed by Avent,[7] and the yield of the more reduced fullerenes could be improved by increasing the molar excess of anhydrous hydrazine.[54] The $C_{60}H_4$ isomers eluted from a buckyclutcher column in two fractions: a single, discrete peak and a collection of peaks that were closely spaced and inseparable under the conditions used. 1,2,3,4-$C_{60}H_4$ was found under the single peak. The collection of isomers recovered from the other bands was analyzed carefully by 500-MHz ^{1}H NMR, and at least five, possibly as many as seven, of the remaining isomers were observed (Figure 5).[12] Two AB quartets not reported in previous studies were also observed, but these isomers constituted only a very small percentage of the mixture.

A mixture of ^{3}He@$C_{60}H_4$ isomers was obtained by reduction of ^{3}He@C_{60}[34] with anhydrous hydrazine and analyzed by ^{3}He NMR spectroscopy.[12] Each $C_{60}H_4$ isomer should produce a single distinct peak in the ^{3}He NMR spectrum. Six signals were observed, indicating that six of the possible eight isomers were present in the mixture. The two remaining isomers that were tentatively identified in the 500-MHz ^{1}H NMR spectrum were present in such low concentrations that detection by ^{3}He NMR was not possible. Others have also reported six signals in the ^{3}He NMR spectrum of ^{3}He@$C_{60}H_4$.[47]

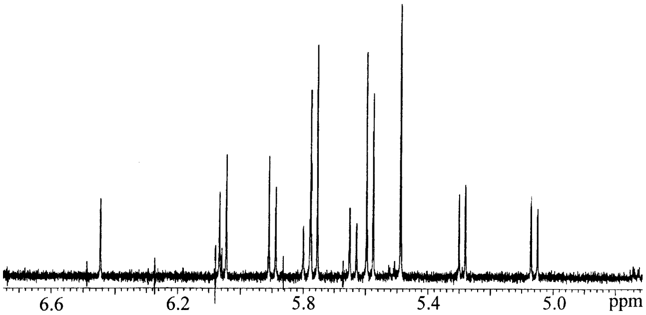


Figure 5. 500-MHz ^{1}H-NMR spectrum of a mixture of $C_{60}H_4$ isomers

Three $C_{60}H_4$ isomers were formed in a 6:6:1 ratio on treatment of C_{60} with a Zn(Cu) couple.[14b] The two major products have been identified as the 1,2,18,36- and 1,2,33,50-$C_{60}H_4$ isomers.

Synthesis of macroscopic amounts of tetrahydrofullerenes has also been achieved by diimide reduction,[7] Zn/HCl reduction,[13] hydroboration,[53] and ruthenium-catalyzed hydrogenation[5] of C_{60}. 1,2,3,4-$C_{60}H_4$ has been synthesized by heating C_{60} and palladium hydride wrapped in gold foil.[18] Its photophysical characterization has also been reported.[52]

(c) $C_{60}H_6$

Two isomers of $C_{60}H_6$ have been isolated in a 6:1 ratio, with a Zn(Cu) couple acting as the reducing agent.[14a,14c] The major product was shown to be 1,2,33,41,42,50-$C_{60}H_6$,[14a−14c] and the minor product was identified as 1,2,18,22,23,36-$C_{60}H_6$[14b,14c] (Figure 6). These are kinetic products derived from 1,2-addition to 1,2,41,42-$C_{60}H_4$ and 1,2,18,36-$C_{60}H_4$, respectively. Zn(Cu) reduction of ^{3}He@C_{60} produced ^{3}He@1,2,33,41,42,50-$C_{60}H_6$ (which gave a ^{3}He NMR signal at $\delta = -15.31$), ^{3}He@1,2,18,22,23,36-$C_{60}H_6$ (which gave a ^{3}He NMR signal at $\delta = -16.35$), and a third, as yet unidentified ^{3}He@$C_{60}H_6$ isomer (which gave a signal at $\delta = -14.24$).[14e]

Curiously, an effort to obtain the $C_{60}H_6$ isomers by hydroboration of their $C_{60}H_4$ precursors failed.[14b] Attempts to isomerize 1,2,33,41,42,50-$C_{60}H_6$ to a thermodynamically

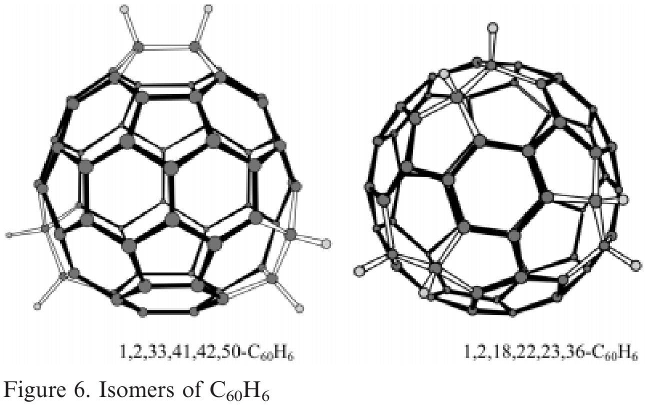
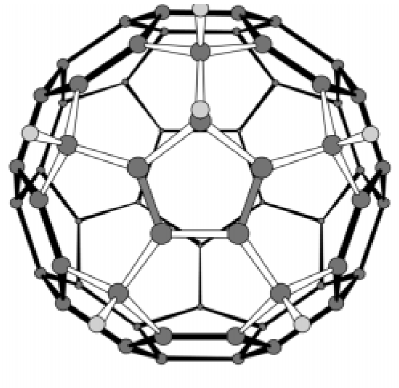

1,2,33,41,42,50-$C_{60}H_6$ 1,2,18,22,23,36-$C_{60}H_6$

Figure 6. Isomers of $C_{60}H_6$

more stable isomer resulted in dehydrogenation to give a mixture of C_{60}, $C_{60}H_2$, and $C_{60}H_4$.[14a]

Geometry-optimized ab initio calculations have been published[55] on the relative energies of 18 $C_{60}H_6$ isomers that can be derived from 1,2-addition to the two lowest energy $C_{60}H_4$ structures 1,2,3,4- and 1,2,4,15-$C_{60}H_4$. (The latter isomer is calculated to be only 0.1 kcal·mol^{-1} lower in energy than the 1,2,18,36-$C_{60}H_4$ isomer, for which calculations had been carried out previously,[53] as discussed above.) Unfortunately, the isomers observed experimentally by Meier and co-workers are not included in this group of 18 $C_{60}H_6$ isomers. However, 1,2,33,50-$C_{60}H_4$ is calculated to be only 0.3 kcal·mol^{-1} higher in energy than 1,2,4,15-$C_{60}H_4$,[53,55] and, as Meier and co-workers noted,[14b] reduction of 1,2,33,50-$C_{60}H_4$ at $C_{41}{=}C_{42}$ would generate the observed 1,2,33,41,42,50-$C_{60}H_6$ major product. In comparison, at the Hartree−Fock/3-21G level of theory, 1,2,4,11,15,30-$C_{60}H_6$ (Figure 7) is the thermodynamically most stable of the 18 isomers that can be derived from 1,2-addition to only the two lowest-energy $C_{60}H_4$ structures 1,2,3,4- and 1,2,4,15-$C_{60}H_4$.[55] This pattern of addition was also observed for the hexabromo- and hexachlorofullerenes, $C_{60}X_6$,[56a,56b] as well as for $C_{60}Cl(C_6H_5)_5$ and $C_{60}H(C_6H_5)_5$.[56c]



1,2,4,11,15,30-$C_{60}H_6$

Figure 7. At the Hartree−Fock/3-21G level of theory, the thermodynamically most stable isomer of $C_{60}H_6$

$C_{60}H_6$ is a minor product in the hydrazine reduction of C_{60}.[7,12] The catalytic hydrogenation of a mixture of C_{60} and C_{70} in toluene with a 5% ruthenium on carbon catalyst[5] produced $C_{60}H_6$ as the major product when the reduction was performed at 100 °C and 2 kg/cm^2 H_2 pressure.

(d) $C_{60}H_{36}$ and $C_{60}H_{18}$

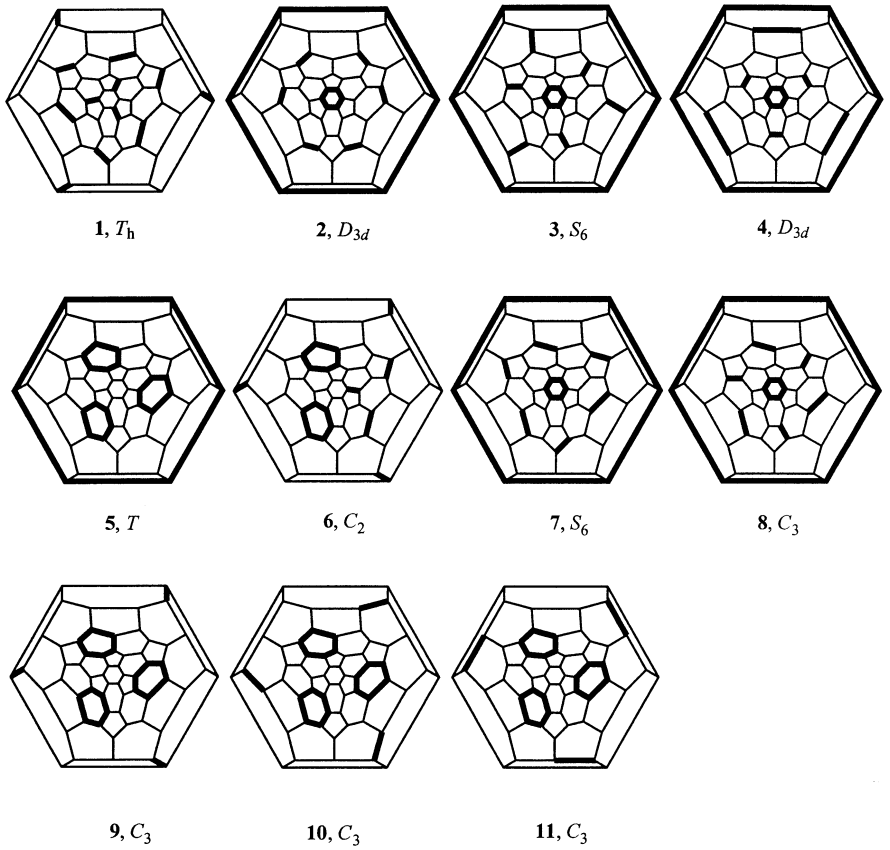
Mass spectrometric analysis of the buff-colored product prepared by the Birch reduction of C_{60} showed that the major product was $C_{60}H_{36}$.[4] When the crude product was treated with DDQ in refluxing toluene, a rapid discharge of the red color of the DDQ−toluene complex with concomitant formation of C_{60} was observed.[4,29b] Mass spectral analysis confirmed that the product was C_{60} and that the Birch reduction had not involved alteration of the fullerene skeleton. Nevertheless, the result was received with considerable skepticism, and it was suggested in one instance that the product was the result of addition of ammonia to the fullerene skeleton.[57]

The addition of 36 hydrogen atoms was not considered surprising, as unconjugated double bonds[58] are not reduced under the conditions of the Birch reduction, and 36 is the minimum number of hydrogen atoms required to leave unconjugated double bonds within each of the pentagons. This arrangement results in $C_{60}H_{36}$ isomer **1** (Figure 8), with twelve unconjugated double bonds. This structure is now known to be a high-energy isomer relative to many of the other possible structures illustrated in the figures.[59−65] It has been established that with increasing hydrogenation of $C_{60}H_n$, the bond angle strain resulting from sp^2 to sp^3 hybridization will decrease as strain due to hydrogen−hydrogen repulsion increases, and that the combined strain reaches a minimum when $n = 36$.[66] Balasubramanian estimated that there are $6.0 \cdot 10^{14}$ isomers of $C_{60}H_{36}$,[26] and Clare and Kepert have catalogued over 100 $C_{60}H_{36}$ isomers.[60,61,65,67]

Characterization of highly reduced fullerenes has proved to be difficult. They are unstable toward light and air,[6,15,27−30] especially in solution.[27,29a] Identification of the molecular ions under electron impact conditions requires[8,10,32] that the spectra be obtained using carefully prepared samples immediately after workup.[27,30] Field desorption mass spectrometry has been reported to give spectra with minimal fragmentation of the molecular ion, relative to other techniques.[10,29] Difficulties with product stability resulted in some debate as to whether $C_{60}H_{36}$ was the primary product of the reaction,[33] but subsequent work has confirmed that $C_{60}H_{36}$ is indeed the major product.[30,68]

Since the initial report describing the Birch reduction, several other routes to $C_{60}H_{36}$ have been reported.[8,10,27] Rüchardt and co-workers have shown that it is possible to synthesize either $C_{60}H_{18}$ or $C_{60}H_{36}$ selectively by transfer hydrogenation.[10,32] A comparison of experimental and simulated infrared and Raman spectra of five $C_{60}H_{36}$ isomers led Rüchardt and co-workers to conclude that the products of this reaction are a mixture of D_{3d} **2** and S_6 **3**.[38,40] A recent comparison of Raman spectra of $C_{60}H_{36}$ samples prepared by high pressure hydrogenation with the results of molecular dynamics calculations prompted Meletov and co-workers to conclude that the three most abundant isomers have D_{3d}, S_6, and T symmetries.[69]

Attalla and co-workers treated fullerite (ca. 85% C_{60}, remainder C_{70} and higher fullerenes) with iodoethane and hydrogen under rather extreme conditions of pressure and temperature.[8] The FAB-MS spectrum showed strong signals at m/z = 757 and 877, which correspond to the M + 1 adducts of $C_{60}H_{36}$ and $C_{70}H_{36}$, respectively. Although detailed analysis was complicated by poor solubility and the presence of products formed from C_{70}, isomer **4**, with D_{3d} symmetry, was proposed. Other work including electron and X-ray diffraction studies[70] also supported the assignment of the D_{3d} structure **4**. It is interesting that a se-



1, T_h **2**, D_{3d} **3**, S_6 **4**, D_{3d}

5, T **6**, C_2 **7**, S_6 **8**, C_3

9, C_3 **10**, C_3 **11**, C_3

Figure 8. Schlegel diagrams of eleven isomers of $C_{60}H_{36}$

cond D_{3d} structure **2** is among the most stable isomers known.[61–63,65]

Darwish and co-workers used zinc and hydrochloric acid to reduce C_{60}.[27] Although the *T* isomer **5** had previously been proposed as the major product,[57,71] analysis of the infrared spectrum led Rüchardt and co-workers to conclude that isomer **3** was the best candidate.[40]

An important advance in the characterization of $C_{60}H_{36}$ came recently when several isomers from the Birch reduction and the transfer hydrogenation method of Rüchardt were isolated by preparative HPLC.[72] Analysis of four bands from the Birch reduction by mass spectrometry indicated that $C_{60}H_{36}$ is the sole product in the two major bands (Figure 9).

Although the broad, featureless spectra obtained by using ^{1}H and solid-state ^{13}C NMR spectroscopy were rather uninformative, the ^{3}He spectra obtained by use of samples prepared by the reduction of $^{3}He@C_{60}$ proved to be somewhat more useful. [D$_4$]-*o*-Dichlorobenzene was found to be a superior solvent for this work, since the fullerene hydrides display greater solubility in this solvent than in other common solvents such as benzene or toluene. Extensive decomposition, observed when carbon disulfide was used for earlier work[27] with the crude product, can be avoided if [D$_4$]-*o*-dichlorobenzene is used.

The ^{3}He NMR spectra of the purified fractions gave slightly broadened but distinctly different signals for each band. The experimentally determined ^{3}He NMR shifts of the different bands were compared with computationally determined values. ^{3}He NMR shifts calculated at the B3LYP/6-31G* level are regarded as the most accurate.[73] Isomers that fall in the range observed for one of the two major fractions (band B) include C_2 **6**, S_6 **7**, C_3 **8**, and S_6 **3** (Figure 8). The chemical shifts calculated for these isomers are $\delta_{He} = -5.1, -5.0, -4.9$, and -4.7, respectively.[74] Calculations predicted[65,74] that each isomer is among the most stable isomers of $C_{60}H_{36}$.

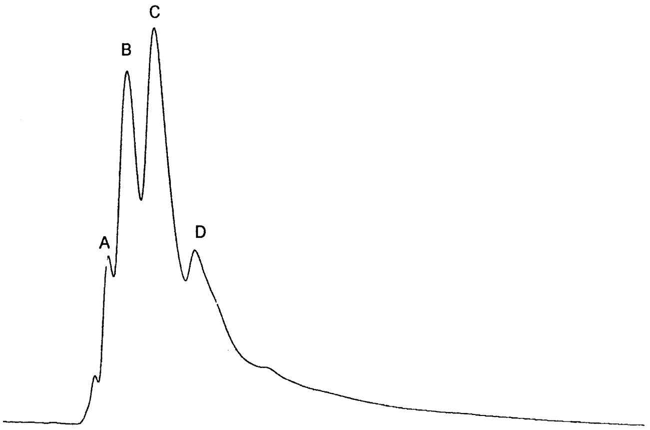


Figure 9. HPLC chromatogram of the products of the Birch reduction of C_{60}

Two benzene rings are a common feature of isomers **3**, **6**, **7**, and **8**. Isomers **7** and **3** each have six equatorial double bonds located at 6,5-ring fusions that are either parallel (**7**) or perpendicular (**3**) to the pair of benzene rings located at the poles. Isomer **8** can be described as a "hybrid" of **7** and **3**, with three equatorial double bonds oriented parallel, as in isomer **7**, and three double bonds oriented perpendicularly, as in **3**. The S_6 isomer **3** has been reported to be one of the $C_{60}H_{36}$ isomers formed by the dihydroanthracene reduction of C_{60}.[38,40] Isomer **6** is structurally similar to the celebrated T $C_{60}H_{36}$ **5** isomer, with two of the four benzenoid moieties present in **5** having been converted into 1,3,5-C_6H_3 rings.

The ^{3}He NMR shift of the other major fraction (band C) is in agreement with calculated values of δ_{He}: $\delta_{He} = -6.1$ for D_{3d} **2**, -6.8 for C_3 **9**, -6.3 for C_3 **11**.[74] The chromatogram (Figure 10) has a trailing shoulder, which confirms that at least two isomers are present. Calculations indicated that C_3 **9** is the second lowest energy $C_{60}H_{36}$ isomer.[65,74]

The mass spectrum of the minor fraction (band D) showed the presence of hydrides other than $C_{60}H_{36}$, although $C_{60}H_{36}$ appeared to be the major component. The observed δ_{He} shift (-8.1) most closely matches the δ_{He} shift of -8.8 predicted at two levels of theory for T $C_{60}H_{36}$ **5**;[74] however, the ^{3}He NMR shift predicted for C_3 $C_{60}H_{36}$ **10**, at $\delta_{He} = -7.0$[73] or -6.9,[74] should also be considered. Previously published ^{3}He NMR spectra of ^{3}He@$C_{60}H_{36}$ obtained both by Birch reduction and by dihydroanthracene reduction of ^{3}He@C_{60} produced two signals at $\delta_{He} = -7.7$ and -7.8.[30] This is approximately the same shift as observed for band D (Figure 9). The slight differences in chemical shifts may be attributed to the use of a 1:1 solution of [D$_6$]benzene and carbon disulfide in the earlier work.[30] An attempt to obtain ^{3}He NMR spectra of a major Birch reduction fraction with a [D$_6$]benzene/CS_2 NMR solvent produced no signal at all, a phenomenon that was attributed to decomposition of the sample during the ten-hour acquisition time.

If band D contains T $C_{60}H_{36}$ **5**, it would confirm the prediction that hydrogenation and fluorination of C_{60} favor isostructural products, since T $C_{60}F_{36}$ **5** has been identified as a minor $C_{60}F_{36}$ isomer.[73] On the other hand, C_3 $C_{60}F_{36}$ **10** was identified as the major $C_{60}F_{36}$ isomer, and consequently C_3 $C_{60}H_{36}$ **10** is possibly a component of band D. Note that C_3 $C_{60}H_{36}$ **10** is significantly less stable than T $C_{60}H_{36}$ **5** (46 kcal·mol^{-1}) according to B3LYP/6-31G* computations.[74] Application of HPLC analysis to the products obtained from the Rüchardt synthesis[10] yielded a major band (band 2, Figure 11) that was found to co-elute with band D from the Birch reduction (Figure 9).[72]

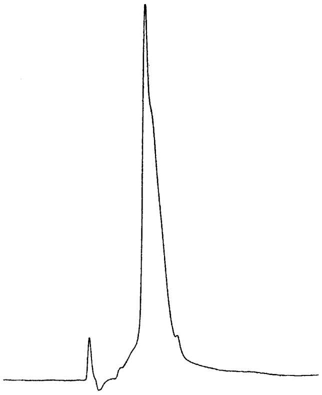


Figure 10. HPLC chromatogram of purified band C; note the trailing shoulder on the main band, indicative of a second $C_{60}H_{36}$ isomer; the small band to the left of the main band is a solvent peak

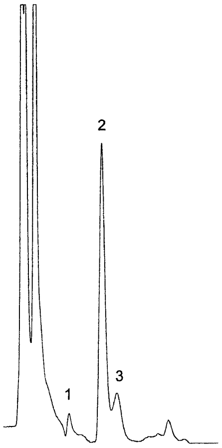


Figure 11. HPLC chromatogram of crude C_{60} dihydroanthracene reduction product mixture; the two large leading bands are due to solvent and residual dihydroanthracene and anthracene

The ^{3}He NMR spectrum of band 2 displayed two sharp signals in a 3:1 ratio at $\delta_{He} = -8.014$ and -8.139.[74] The similarity of these two ^{3}He signals to the two signals reported earlier[30] suggested that the same two isomers are responsible for the signals in each case. The 126 MHz ^{13}C NMR spectrum of band 2 showed 32 signals of sp^2-hybridized carbon atoms and 48 signals of sp^3-hybridized carbon atoms for the solute, with all 80 solute signals having similar intensities.[74] The ^{3}He and ^{13}C spectra imposed severe constraints on the types of isomers that might be present and led Billups and co-workers to conclude that two similar isomers were present in a 3:1 ratio, with one isomer having no symmetry (24 sp^2- and 36 sp^3-hybridized carbon atoms) and the other isomer having C_3 symmetry (8 sp^2- and 12 sp^3-hybridized carbon atoms).

The 500-MHz ^{1}H-NMR spectrum of band 2[74] had a level of spectral detail considerably better than that previously reported at an unspecified field strength for a sample of $C_{60}H_{36}$ prepared by catalytic hydrogenation of C_{60} in the presence of Pd/C in toluene.[75] However, the overall similarity of the spectra obtained by the two groups[74,75] is obvious. While Sui and co-workers[75] did not propose any structures, the spectral similarity suggests that catalytic hydrogenation[75] and dihydroanthracene reduction[74] yielded very similar products. The level of spectral detail shown in the 500-MHz spectrum[74] is far greater than that previously shown[5a,27a,29a,76,77] or indicated[4,10,27b,78] in other samples of $C_{60}H_{36}$. With extensive overlap of the ^{1}H signals expected and no method to separate the two isomers readily apparent, a 900-MHz ^{1}H spectrum (Figure 12) and 800-MHz COSY and TOCSY spectra were obtained as a first step toward resolving signals and determining the identity of the two isomers.[74] Examination of the ^{1}H spectra of this and other samples of $C_{60}H_{36}$ and the ^1H spectrum of $C_{60}H_{18}$[35] showed that the protons in these C_{60} derivatives are significantly deshielded compared to their counterparts in "ordinary" organic molecules. Calculations have shown that three relatively long C−C bonds are associated with the exceptionally deshielded β-proton in $C_{60}H_{18}$;[79] preliminary calculations of ^1H chemical shifts and C−C bond lengths in some isomers of $C_{60}H_{36}$ have also shown that exceptionally deshielded β-proton signals are associated with sites possessing relatively long C−C bonds.[74] Taken together, the calculations and experimental data clearly indicate that the spectrum of $C_{60}H_{36}$ cannot be interpreted solely in terms of the proton chemical shifts exhibited by "ordinary" organic molecules. Billups and co-workers outlined a plan of attack[74] involving extensive calculations and multidimensional NMR that might yield the precise structures of the two isomers present in the dihydroanthracene reduction.

Numerous calculations,[59−65,67,80,81] particularly at higher levels of theory, indicate that *T* $C_{60}H_{36}$ **5** is among the most stable $C_{60}H_{36}$ isomers, but it has yet to be unequivocally detected.[69] These calculations, the observation that a $C_{60}H_{36}$ isomer with no symmetry is 75% abundant,[74] and the absence of the long expected[57,71,73] *T* $C_{60}H_{36}$ **5** all suggest that, in the dihydroanthracene reduction of C_{60}, a significant energy barrier exists for the conversion of the C_3 and C_1 symmetry isomers of $C_{60}H_{36}$ to *T* $C_{60}H_{36}$ **5**. A remarkable difference between $C_{60}H_{36}$ and $C_{60}F_{36}$ is the reported presence of the *T* isomer (about 25%) in $C_{60}F_{36}$.[73] Calculations indicate that *T* $C_{60}F_{36}$ **5** is among the most stable $C_{60}F_{36}$ isomers.[64,65] (The remaining 75% of the $C_{60}F_{36}$ sample was assigned to the C_3 isomer **10**.)

$C_{60}H_{18}$ was found to be a minor component of the crude product from the Birch reduction;[1] however, there is still some uncertainty as to whether $C_{60}H_{18}$ is a co-product of the Birch reduction or an artifact formed by pyrolysis of $C_{60}H_{36}$ during the mass spectrometric analysis. The structure of $C_{60}H_{18}$[35] (Figure 13) has been determined by NMR spectroscopy using a sample of $C_{60}H_{18}$ obtained from M.E.R. (Tucson, Arizona). A structure corresponding to a crown-shaped molecule with C_{3v} symmetry is entirely consistent with the complicated spin system observed for a purified sample. Calculations indicate that this is a particularly stable structure.[60]

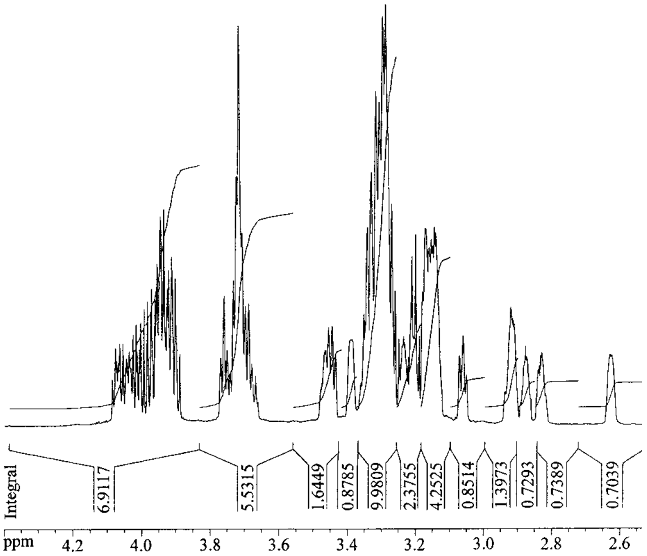


Figure 12. 900-MHz ^1H-NMR spectrum of $C_{60}H_{36}$ band 2 (3:1, $CDCl_3/CS_2$)

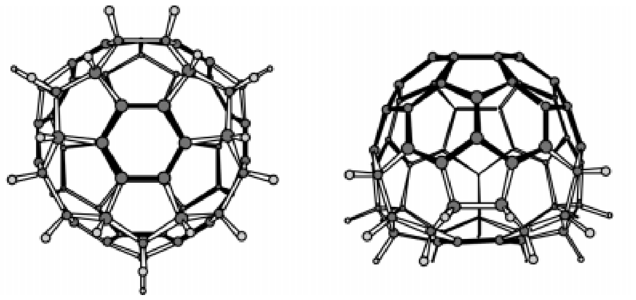


Figure 13. Structure of $C_{60}H_{18}$

Nearly pure $C_{60}H_{18}$ can be prepared when dihydroanthracene (Rüchardt procedure) is used as the reducing agent.[10] The ^3He NMR spectrum of $^3He@C_{60}H_{18}$ exhibits a singlet at $\delta_{He} = -16.45$.[30] Ruthenium-catalyzed hydrogenation[5] of C_{60} has also been reported to yield $C_{60}H_{18}$ as the main product. Some of the photophysical properties of $C_{60}H_{18}$ and $C_{60}H_{36}$ have been reported.[38,39]

(e) $C_{60}H_{60}$

The stability of fullerene hydrides with endohedral hydrogen atoms has been addressed computationally. Dunlap and co-workers calculated that the presence of one, twelve, or 24 hydrogen atoms inside the C_{60} cage was energetically unfavorable for $C_{60}H_{36}$, but that a $C_{60}H_{60}$ structure with at least one endohedral hydrogen atom was more stable than $C_{60}H_{60}$ with all hydrogens pointing outward.[82] Saunders predicted (MM3 optimization) that the lowest-energy isomer of $C_{60}H_{60}$ should have C_1 symmetry with ten hydrogen atoms inside the cage so as to allow each H−C−C−H fragment corresponding to a C−C shared edge to adopt a chair conformation with one hydrogen atom pointing inside the cage and one pointing outward.[83] Subsequent semiempirical calculations by Bakowies and Thiel also indicated that this C_1 symmetry isomer with ten hydrogen atoms inside the cage is much more stable than the I_h isomer.[84] Isomers of $C_{60}H_{12}$, $C_{60}H_{24}$, $C_{60}H_{36}$, and $C_{60}H_{48}$ with endohedral hydrogen atoms were all higher in energy than those isomers with all hydrogen atoms outside the fullerene cage.[85]

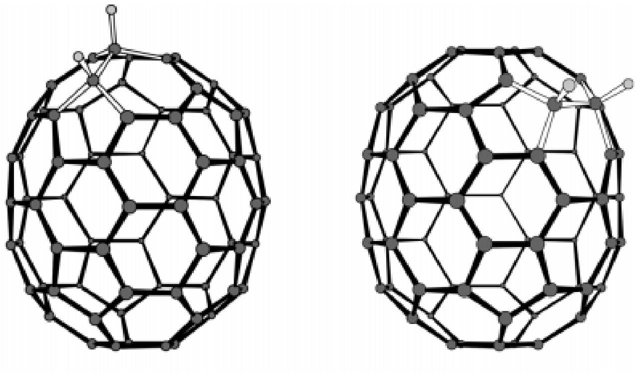
C_{70} Hydrides

In contrast to C_{60}, C_{70} has five sets of carbon atoms,[86] and this enhances the number of possible isomers that result from addition reactions.[87] There are 23 possible exohedral $C_{60}H_2$ isomers, whereas 143 possible structures for $C_{70}H_2$ may exist.[88] In general, however, the methods that have been used to reduce C_{60} may also be used to synthesize hydrides from C_{70}.

Hartree−Fock SCF calculations suggest that the central region of the C_{70} molecule should be unreactive, since the five conjugated, benzene-like rings should give rise to significant delocalization.[63,89] In contrast, the bonds at the poles of the rugby-ball-like molecule have significant double-bond character, and they are predicted to be the most susceptible to hydrogenation reactions. Other studies suggest that the regiochemistry of addition to C_{70} is driven largely by steric factors rather than by electronic effects.[64] Semiempirical MNDO, AM1, and PM3 calculations indicate that aromaticity is negatively correlated with stability in highly substituted C_{70}: a result substantially different from the situation with C_{60}.[90,91]

(a) $C_{70}H_2$

In 1994 Henderson and co-workers reported the first synthesis of $C_{70}H_2$.[37] Two equiv. of BH_3 in THF were added to a toluene solution of C_{70}, and the products were separated by HPLC using a buckyclutcher I column.[41] The two principal products were identified as $C_{70}H_2$ isomers by high resolution FAB MS. The ^{1}H NMR spectrum of the more rapidly eluting isomer exhibited a singlet at $\delta = 3.91$ in [D$_8$]toluene. The corresponding $C_{70}HD$ isomer was produced by hydrolysis of the intermediate organoborane with D_2O, and displayed a $^3J_{HD}$ of 2.3±0.2 Hz and a small upfield isotope shift $^3\Delta H(D)$ of 8.4 ppb. These results were found to be consistent with the presence of vicinally equivalent hydrogen atoms, and so the structure was assigned as the 5,6-isomer (Figure 14).



1,2-$C_{70}H_2$ 5,6-$C_{70}H_2$

Figure 14. Isomers of $C_{70}H_2$

The ^{1}H NMR spectrum of the second dihydride consisted of an AB quartet centered at $\delta = 4.00$ in [D$_8$]toluene. The $^3J_{HD}$ of the corresponding $C_{70}HD$ isomer was 2.2±0.2 Hz, and a small upfield isotope shift $^3\Delta H(D)$ of 7.8 ppm was observed; both suggested the presence of non-equivalent, vicinal hydrogen atoms. These results were found to be consistent with the lowest-energy 1,2-isomer (Figure 14).

Although these isomers failed to interconvert upon standing in solution at room temperature, analysis of the mixture formed by equilibration in the presence of a platinum-on-silica catalyst provided a free energy of 1.4±0.2 kcal/mol, in agreement with a previously calculated value.[88] Ab initio calculations for the $C_{70}H_2$ derivatives indicate that 1,2-additions at 6,6-ring fusions and 1,4-additions across six-membered rings are the preferred modes of addition.[88] The 1,2- and 5,6-dihydro isomers are the two lowest-energy isomers, and both result from 1,2-additions to 6,6-ring fusions located near the C_{70} pole. The 1,2-isomer is favored over the 5,6-isomer by 0.2−1.3 kcal/mol, although semiempirical MNDO/PM-3 calculations reverse the ordering.

The ^{13}C NMR spectrum of 1,2-$C_{70}H_2$ has been investigated.[14b,14d] The sp^3-C resonances appeared at $\delta = 44.06$ and 46.37. In the ^{1}H-coupled ^{13}C NMR spectrum, the associated $^1J_{CH}$ and $^2J_{CH}$ coupling constants, as well as numerous other long-range coupling constants, were determined. Interestingly, while the magnitudes of the $^2J_{CH}$ constants are smaller in 1,2-$C_{70}H_2$ (5.02 Hz, 4.71 Hz) than in 1,2-$C_{60}H_2$ (6.7 Hz), the longer distance coupling constants are larger in 1,2-$C_{70}H_2$, extending out to five bonds. Indeed, while only a few ^{13}C resonances in 1,2-$C_{60}H_2$ exhibited resolvable long-range couplings, 26 of the 37 ^{13}C resonances in 1,2-$C_{70}H_2$ displayed measurable couplings.

Reduction of C_{70} by diimide yields[7] the 1,2- and 5,6-dihydrofullerene-C_{70} isomers in an 8:1 ratio (Figure 14). Higher hydrides, which were not identified, are thought to result from addition to the 1,2-isomer rather than to the 5,6-isomer, since this isomer is a relatively minor product and the yield of any higher hydrides derived from this isomer would be small.

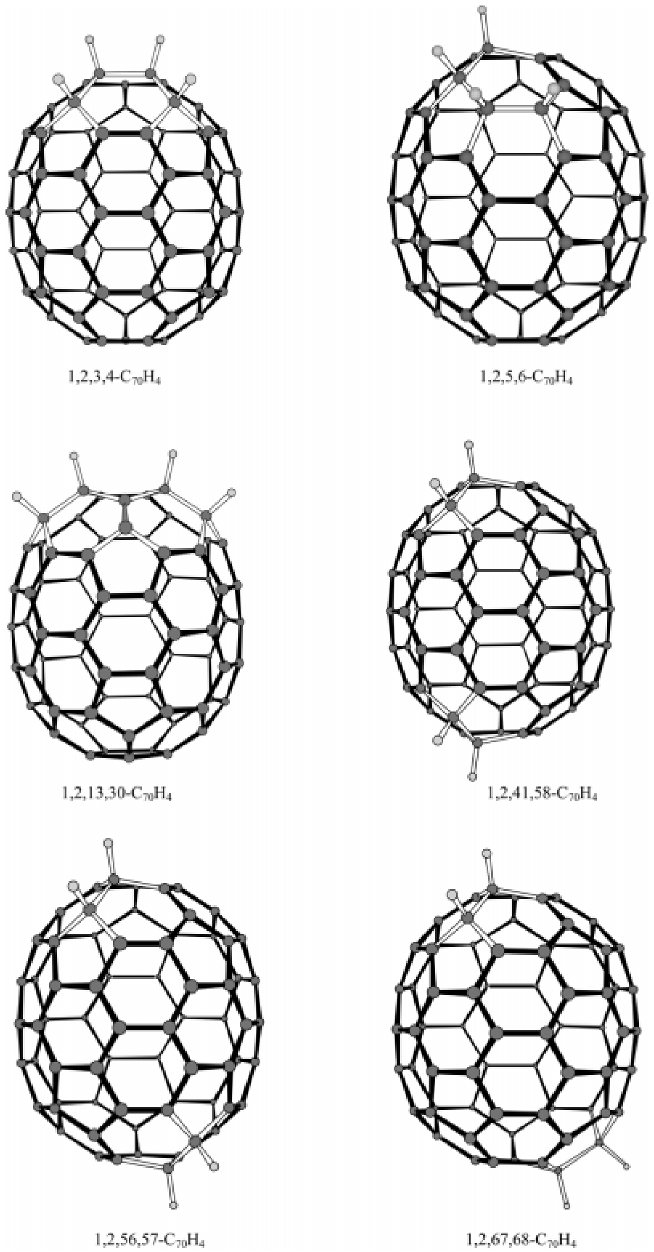
Zn(Cu) reduction of ^{3}He@C_{70} produced ^{3}He@1,2-$C_{70}H_2$, which gave a ^{3}He NMR signal at $\delta = -27.18$.[14e] The electrochemical reduction of 1,2-$C_{70}H_2$ and 5,6-$C_{70}H_2$ has been reported.[49] Each isomer undergoes three reductions in a toluene/DMF solution. The three $E_{1/2}$ values for the 1,2-isomer are nearly the same as those for the 5,6-isomer. Photophysical studies of 1,2-$C_{70}H_2$ have also been reported.[92,93]

(b) $C_{70}H_4$

Several isomers of $C_{70}H_4$ have been characterized. Reduction by diimide or anhydrous hydrazine provides a convenient route to these hydrides.

The AA′BB′ spin system was noted as being rather similar to that of 1,2,3,4-tetrahydrofullerene-C_{60} and was assigned to the 1,2,3,4-$C_{70}H_4$ isomer, which also has hydrogen atoms bonded to four adjacent carbon atoms in a six-membered ring (Figure 15).[7] The ABCD spin system showed couplings very similar to those found for the AA′BB′ spin systems in 1,2,3,4-$C_{60}H_4$ and 1,2,3,4-$C_{70}H_4$, and this was postulated as the result of an unsymmetrical $C_{70}H_4$ isomer. This was assigned as 1,2,5,6-tetrahydrofullerene-C_{70}, which probably forms primarily by the 5,6-addition of two hydrogen atoms to the 1,2-isomer, though it can also be obtained by 1,2-addition to the minor 5,6-isomer.

1,2,3,4- and 1,2,5,6-tetrahydrofullerene-C_{70} result from addition to a previously substituted six-membered ring, and this supports the argument that this pattern of addition is favored by increasing delocalization. The remaining possible $C_{70}H_4$ isomers that derive from addition to the 1,2-position and its equivalents are 1,2,13,30-, 1,2,41,58-,



$1,2,3,4\text{-}C_{70}H_4$ $1,2,5,6\text{-}C_{70}H_4$

$1,2,13,30\text{-}C_{70}H_4$ $1,2,41,58\text{-}C_{70}H_4$

$1,2,56,57\text{-}C_{70}H_4$ $1,2,67,68\text{-}C_{70}H_4$

Figure 15. Isomers of $C_{70}H_4$

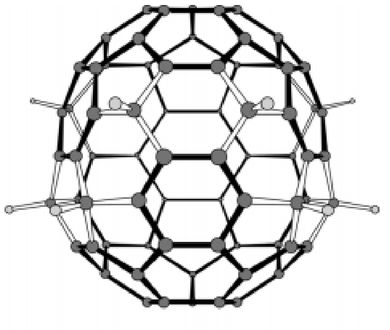
1,2,56,57-, and 1,2,67,68-tetrahydrofullerene-C_{70} (Figure 15). Each is predicted to give an AB quartet, and there are indeed four AB quartets present in the ^1H NMR spectrum.[7] Although definitive assignments could not be made, the 1,2,13,30-isomer is probably responsible for the most upfield AB quartet, since this isomer has all four sp^3-carbon atoms in close proximity.

The selective reduction of C_{70} with Zn(Cu) yields 1,2-$C_{70}H_2$ as well as several isomers of $C_{70}H_4$ and one isomer of $C_{70}H_8$.[14d] The major $C_{70}H_4$ isomer was isolated and determined to be the 1,2,56,57-isomer by a combination of ^1H NMR [AB pattern composed of resonances at $\delta = 5.43$ ($J = 16.1$ Hz) and 5.01 ($J = 16.1$ Hz)], ^1H-decoupled ^{13}C NMR (35 resonances of equal intensity, indicative of C_2 symmetry), and ^1H-coupled ^{13}C NMR spectroscopy. Since only one- and two-bond couplings were observed at the sp^3-carbon resonances, the symmetry-equivalent pairs of adjacent protonated carbon atoms are located more than five bonds apart, placing them at opposite poles of the molecule. Several ^{13}C resonances in the ^1H-coupled experiment showed no sign of ^1H coupling, and only the 1,2,56,57-$C_{70}H_4$ isomer has carbon atoms more than five bonds away from a protonated carbon atom.

A minor isomer of $C_{70}H_4$ isolated from the Zn(Cu) reaction displayed ^1H-coupled and ^1H-decoupled ^{13}C NMR spectra similar to those of the 1,2,56,57-$C_{70}H_4$ isomer.[14d] However, the presence of additional signals exhibiting long-range ^1H-^{13}C coupling suggested that this minor isomer was 1,2,67,68-$C_{70}H_4$ (Figure 15). Zn(Cu) reduction of $^3He@C_{70}$ produced $^3He@1,2,56,57\text{-}C_{70}H_4$, which gave a ^3He NMR signal at $\delta = -25.33$.[14e]

(c) $C_{70}H_8$, $C_{70}H_{10}$, and $C_{70}H_{12}$

The purification and characterization of the $C_{70}H_8$ species formed in the Zn(Cu) reduction has been reported.[14d] The ^1H-decoupled ^{13}C NMR spectrum and ^1H-^1H DQF-COSY spectrum indicated that the protons of this hydride are bonded to non-adjacent carbon atoms and therefore cannot be the direct reduction product of either the $C_{70}H_2$ or $C_{70}H_4$ isomers. This was demonstrated by isolation of 1,2-$C_{70}H_2$ and reduction of this compound with Zn(Cu). Only $C_{70}H_4$ and more highly reduced species ($C_{70}H_{10}$+) were formed. The structure of the $C_{70}H_8$ compound was assigned as 7,19,23,27,33,37,44,53-$C_{70}H_8$, and a complete description of the spin system has been worked out (Figure 16). Zn(Cu) reduction of $^3He@C_{70}$ produced the corresponding $^3He@7,19,23,27,33,37,44,53\text{-}C_{70}H_8$, which gave a ^3He NMR signal at $\delta = -17.84$.[14e]



$7,19,23,27,33,37,44,53\text{-}C_{70}H_8$

Figure 16. Isomer $C_{70}H_8$ formed by Zn(Cu) reduction

This $C_{70}H_8$ species is the precursor to two of the three $C_{70}H_{10}$ species formed in the Zn(Cu) reduction of C_{70}.[94] The structure of the major $C_{70}H_{10}$ species has been determined as the 7,8,19,26,33,37,45,49,53,63-isomer, resulting from reduction of 7,19,23,27,33,37,44,53-$C_{70}H_8$ in such a manner as to preserve the maximum amount of aromaticity (Figure 17). The last pair of hydrogen atoms adds to adjacent carbon atoms, as demonstrated by the presence of a $^2J_{CH}$ (5.6 Hz) at one of the five sp^3-C resonances. This $C_{70}H_{10}$ species has the same addition pattern as in $C_{70}Cl_{10}$[95a] and $C_{70}(C_6H_5)_{10}$.[95b] Each of these compounds has a chromophore that is reduced to a pair of corranulene units, one at each pole and separated by an insulating belt of protonated carbon atoms. Zn(Cu) reduction of $^{3}He@C_{70}$ produced $^{3}He@7,8,19,26,33,37,45,49,53,63\text{-}C_{70}H_{10}$, which gave a ^{3}He NMR signal at $\delta = -17.17$, the most deshielded ^{3}He NMR signal thus far observed in neutral C_{70} derivatives.[14e] Taylor and co-workers have reported the unexpected co-elution of $C_{70}H_{12}$ with C_{84} and proposed some possible structures.[96]

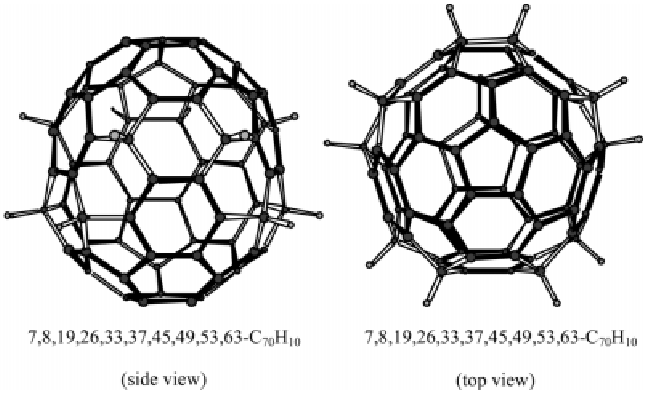


Figure 17. Major isomer of $C_{70}H_{10}$ by Zn(Cu) reduction

(d) $C_{70}H_{36}$

More highly reduced C_{70} derivatives have been prepared in several ways: by hydrogenation in the presence of iodoethane[8] or a ruthenium-on-carbon catalyst,[5] reduction with 9,10-dihydroanthrancene,[29a,32] and treatment with Zn and concentrated HCl.[27] With the Zn/HCl approach, $C_{70}H_{36}$ and a mixture of hydrides ($C_{70}H_{38-44}$) were major constituents of the product mixture, which were shown by EI-MS to be $C_{70}H_{36-44}$.

The ^{1}H NMR spectrum of these hydrides features a wide band between $\delta = 2.4$ and 4.0 ([D$_6$]benzene), which strongly resembles the spectrum of the analogous $C_{60}H_{36}$. The more upfield location of the band compared to the C_{60} derivative is in keeping with the pattern previously noted for the di- and tetrahydro derivatives.

The structure of $C_{70}H_{36}$ has not yet been determined. Book and Scuseria calculated the relative energies of several $C_{70}H_{36}$ isomers with their hydrogen addends concentrated at the poles of the C_{70} cage.[63] Two isomers with C_2 symmetry were reported to be slightly favored, but the semiempirical methods employed did not completely rule out other isomers with relative energies within a few kcal/mol of the C_2 isomers.

The UV spectrum of $C_{70}H_{36}$ obtained by Darwish and co-workers showed a broad band centered at 275 nm and a pronounced shoulder at 223.5 nm.[27a] These features closely resemble the 221 and 258−286 nm absorptions for naphthalene, consistent with a structure with two naphthalene-like moieties and one phenanthrene-like unit in the equatorial region of $C_{70}H_{36}$[97] (rather than a band of five *para*-linked benzenoid rings[32,63]).

$C_{70}H_{36}$ has also been reported as the major product obtained by Birch reduction of C_{70}.[36] However, the product mixture was analyzed by EI-MS, and other studies have noted that $C_{70}H_{36}$ is unstable under these conditions and decomposes into a series of hydrides with lower hydrogen content.[27] $C_{70}H_{36}$ is the major product of the reduction of C_{70} by dihydroanthracene, but substantial amounts of $C_{70}H_{38}$, $C_{70}H_{40}$, $C_{70}H_{42}$, $C_{70}H_{44}$, and $C_{70}H_{46}$ also formed and could be detected by field desorption MS.[29a] Similarly, $C_{70}H_{36}$ and $C_{70}H_{38}$ are formed when a mixture of C_{60} and C_{70} in toluene was hydrogenated catalytically with 5% ruthenium-on-carbon catalyst.[5]

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