DOI: 10.1002/anie.200705450

Fullerenes

Synthesis and Structural Characterization of $C_{70}H_{38}$**

*Thomas Wågberg, Mattias Hedenström, Alexandr V. Talyzin, Ingmar Sethson, Yury O. Tsybin, Jeremiah M. Purcell, Alan G. Marshall, Dag Noréus, and Dan Johnels**

Theoretical and experimental studies[1] on addition reactions of fullerenes have been reported over the last few years as these reactions can lead to many different materials with various chemical and optical properties. The report of improved efficiency in photovoltaic cells through the use of fullerene-based materials has further increased the interest in this research field.[2] We have shown that the high-pressure hydrogenation of C_{60} at 100 bar and 400 °C results in the direct synthesis of predominantly a C_{3v} isomer of $C_{60}H_{18}$ in more than 95 % purity without any further purification.[3] We now report the successful synthesis and structural determination of the far more complex $C_{70}H_{38}$ structure. Theoretically, the number of isomers for a specific hydrogenated fullerene structure is enormous. For example, $C_{60}H_{18}$ has been calculated to have 6×10^{14} such isomers[4] and $C_{60}H_{36}$ roughly 1×10^{13},[4,5] but in practice stability constraints reduce that number significantly. For fullerene structures such as C_{60} and C_{70}, the stability is mainly determined by the combination of π-electronic and steric contributions to the total energy, whereas most of the isomers of hydrogenated structures are thought to be stabilized by pair-wise addition of hydrogen atoms.[6] According to semiempirical calculations, the initial pair-wise hydrogenation should occur at hex-hex edges.[7] The aromaticity of the different isomers is also an important parameter, and it has been shown that particularly stable isomers exist for structures containing separated benzenoid rings.[8] Hydrofullerenes that have isomers with separated benzenoid rings are $C_{60}H_{36}$[5,9] and $C_{70}H_{36}$.[10] The importance of the separated benzenoid rings for stability has, however, been questioned for $C_{70}H_{36}$ by Fowler et al., who conclude on the basis of MNDO calculations that the most stable structure of $C_{70}H_{36}$ does not contain benzenoid rings.[8] From these results, it is clear that further experimental studies are needed to fully explain the stability of hydrogenated fullerenes and related compounds.

Hydrogenated fullerenes have been synthesized by several methods,[1a,11] with the resulting structures and compositions depending on the specific method used. In many cases the produced material needs significant purification, which is both costly and time-consuming. Our present study and earlier studies have shown that the hydrogenation of fullerenes at appropriate pressures and temperatures results in the selective preparation of materials with particular stoichiometries and consisting of only a small number of isomers.[3] This result can, at least partly, be explained by a rearrangement of the hydrogen atoms on the fullerene surface as a result of the extreme experimental conditions, thereby leading to the formation of the most stable structure. However, prolonged hydrogenation of C_{60} results in fragmentation and partial collapse of the fullerene cage with formation of, for example, $C_{59}H_x$ and $C_{58}H_x$.[12]

Figure 1 shows the mass spectral analysis obtained by 9.4 T high-resolution atmospheric-pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry (APPI FT-ICR MS) of a C_{70} sample hydrogenated at 673 K and an H_2 pressure of 100 bar for 72 h. Figure 1 a shows a base signal that corresponds to the singly charged molecular ion of $C_{70}H_{37}$. As hydrocarbons have only an even number of hydrogen atoms in the solid state, the $C_{70}H_{37}$ ions must originate either from protonation of $C_{70}H_{36}$ during ionization or from loss of a hydrogen atom from $C_{70}H_{38}^{+\bullet}$. In contrast to NMR spectroscopic results, the high-resolution mass spectrum shows abundant non-hydrogenated C_{70} radical ions and oxidized $C_{70}H_{38}$ ions.

Figure 1 b indicates the presence of the $C_{70}H_x$ ($x = 36, 38, 40, \ldots$) series of hydrocarbons that undergo both protonation and radical-ion formation upon APPI. The splitting of the signals shown in Figure 1 c confirms the presence of $C_{70}H_{38}$ in the mixture of hydrogenated fullerenes. Specifically, the monoisotopic $[^{12}C_{70}H_{38}]^{+\bullet}$ species is resolved from $[^{12}C_{69}{}^{13}CH_{37}]^{+}$ (^{12}CH and ^{13}C differ in mass by 4.4 mDa), and

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[*] Dr. M. Hedenström, Dr. I. Sethson, Prof. D. Johnels
Umeå University
Department of Chemistry
901 87 Umeå (Sweden)
Fax: (+46) 90-786-66-73
E-mail: Dan.Johnels@chem.umu.se
Dr. T. Wågberg, Dr. A. V. Talyzin
Umeå University
Department of Physics
901 87 Umeå (Sweden)
Dr. J. M. Purcell, Prof. A. G. Marshall
Ion Cyclotron Resonance Program
National High Magnetic Field Laboratory
Tallahassee, FL 32310-4005 (USA)
Prof. Y. O. Tsybin
Biomolecular Mass Spectrometry Laboratory
Ecole Polytechnique Federale de Lausanne
1015 Lausanne (Switzerland)
Prof. D. Noréus
Stockholm University
Department of Chemistry
Stockholm (Sweden)

[**] T.W. thanks the Wenner-Gren foundations, Carl Tryggers foundation, and Magnus Bergvalls foundation for generous support. We thank the Swedish NMR center for support. FTICR experiments were supported by the USA National Science Foundation (DMR-0084173), Florida State University, and the National High Magnetic Field Laboratory in Tallahasse, FL.

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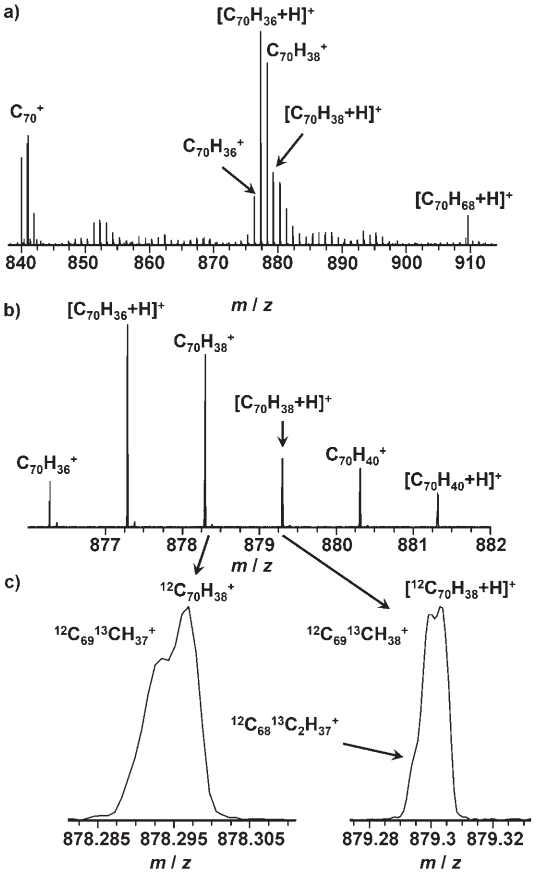

Figure 1. High-resolution atmospheric pressure photo-ionization Fourier transform ion cyclotron resonance mass spectrum of hydrogenated C_{70}: a) broadband spectrum, demonstrating the presence of C_{70} and a series of $C_{70}H_x$ isomers with $x = 36, 38, 40$; b) spectrum segment, showing both protonated and radical hydrocarbon cations; c) resolution of overlapping signals, thereby confirming the presence of $C_{70}H_{38}$.

$[^{12}C_{70}H_{38}+H]^+$ from $[^{12}C_{69}{}^{13}CH_{38}]^{+\bullet}$ (mass difference: 4.4 mDa) and $[^{12}C_{68}{}^{13}C_2H_{37}]^+$ (mass difference: 8.9 mDa).

The presence of a $C_{70}H_{38}$ hydrofullerene in our samples is a bit surprising. The stability of $C_{60}H_{36}$ has been shown to be particularly high, and most theoretical considerations focused on the corresponding $C_{70}H_{36}$ moiety. However, the research groups of Clare[10b] and Fowler[8] found that $C_{70}H_{40}$ can form a structure with nearly the same stability as $C_{70}H_{36}$. Furthermore, the synthesis of $C_{70}H_{38}$ by reduction of C_{70} with Zn/HCl in benzene has been reported,[13] and under some conditions it even dominates over the formation of $C_{70}H_{36}$ and $C_{70}H_{40}$.[14] A recent report by Hitchcock et al.[15] of $C_{70}F_{38}$ and the similarity between hydrogenation and fluorination reactions of fullerenes implies that the stability of $C_{70}H_{38}$ could be higher than that of $C_{70}H_{36}$ under certain conditions.

The structural elucidation was based on NMR spectroscopic investigations. As in the case of $C_{60}H_{36}$,[16] 2D methods were required to assign the structure. The most crucial experiments were HSQC, HSQC-TOCSY, and primarily ^{13}C INADEQUATE.

Figure 2 shows an overlay of the HSQC and HSQC-TOCSY spectra. From the interpretation of the HSQC spectrum it is evident that the sample consists mainly of a major isomer of C_2 symmetry that carries 19 inequivalent hydrogen atoms. By integration of the HSQC spectrum it can be estimated that the major isomer constitutes about 50 % of the material. The remaining signals arise from several other isomers of hydrogenated fullerenes, as also indicated by the mass spectrometric analysis.

A short TOCSY mixing time was used to emphasize correlations between neighboring protons, thereby simplifying the spectrum. Some correlations between non-neighboring protons were, however, also observed and could be used to further support the connectivity.

The complete bonding scheme was obtained by performing an INADEQUATE experiment on 25 % ^{13}C-enriched $C_{70}H_{38}$. The INADEQUATE technique has previously been applied to both hydrogenated fullerenes and other fullerene derivatives, and is used to identify pairs of adjacent ^{13}C atoms.[17] The obtained chemical shifts are shown in Table 1. Only three of the expected signals are missing in the INADEQUATE spectrum, probably as a result of small differences in their chemical shifts relative to their *J* coupling constants, thus resulting in AB spin systems with low signal intensities;[18] this effect was previously observed for fullerene derivatives.[18,19]

The combined information from the different 2D NMR experiments gives the connectivity among the carbon atoms. Theoretical investigations have assumed that the ten carbon atoms on the equator of the C_{70} framework should be unprotonated otherwise excessive steric strain would be introduced.[4] However, recent experimental work on $C_{70}F_{38}$ isomers shows that the equator can, in fact, be fluorinated.[6,15]

The Schlegel diagram of the proposed structure based on the NMR spectroscopic data is presented in Figure 3a (with the same projection as previously employed for the related $C_{70}F_{38}$ isomers). Figure 3b shows a 3D model of the molecular structure. It should be emphasized that the 2D NMR

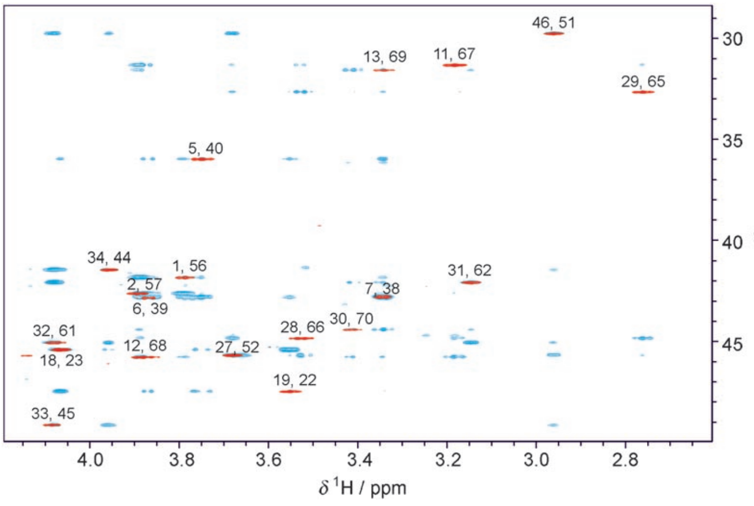

Figure 2. Overlay of the HSQC (red) and HSQC-TOCSY (blue) spectra of $C_{70}H_{38}$.

Table 1: ^{13}C and ^{1}H Chemical shifts of $C_{70}H_{38}$.

Position[a]	δ (^{1}H)[b]	δ (^{13}C)[b]	Position[a]	δ (^{13}C)[b]
46, 51	2.96	29.76	20, 21	123.36
11, 67	3.18	31.32	47, 50	125.28
13, 69	3.34	31.57	9, 55	131.29
29, 65	2.76	32.67	25, 35	131.91
5, 40	3.75	35.99	24, 36	131.94
34, 44	3.96	41.46	26, 53	135.69
1, 56	3.78	41.82	3, 58	136.16
31, 62	3.14	42.08	49, 63	136.16
2, 57	3.89	42.63	48, 64	136.44
7, 38	3.34	42.78	10, 54	136.54
6, 39	3.87	42.85	15, 60	137.22
30, 70	3.41	44.41	4, 41	137.64
28, 66	3.52	44.85	17, 42	139.86
32, 61	4.07	45.05	14, 59	140.69
18, 23	4.06	45.41	8, 37	142.28
27, 52	3.68	45.68	16, 43	144.08
12, 68	3.87	45.78		
19, 22	3.55	47.49		
33, 45	4.08	49.15		

[a] Positions are numbered according to the Schegel diagram (Figure 3 a). [b] Chemical shifts are presented in ppm. Dichlorobenzene was used as an internal reference (^{1}H: $\delta = 7.06$ ppm, and ^{13}C: $\delta = 127.2$ ppm).

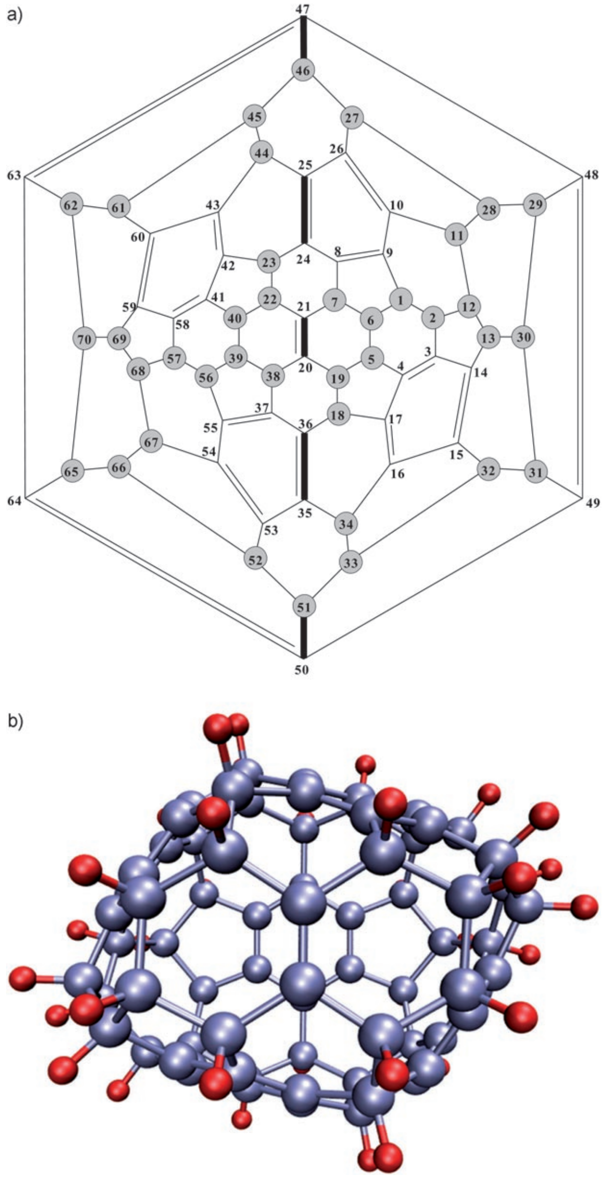

Figure 3. a) Schlegel diagram for $C_{70}H_{38}$ (equator bonds in bold), b) molecular structure of $C_{70}H_{38}$.

spectroscopic data uniquely confirms the proposed isomer, and that no other isomer exists that would fulfill the connectivity scheme determined by NMR spectroscopy.

The crucial finding from the overlay of the connections upon the C_{70} framework is the presence of two five-membered rings on opposite sides of a six-membered ring, which gives rise to an uncommon linear 5,6,5 ring fusion. It should be noted that the C_2 isomer has five benzenoid rings and two protonated sites at the equator. The scheme corresponds well with the initial pair-wise protonation at hex-hex edges, which at some sites proceeds to form symmetry-equivalent S motifs as proposed by Clare and Kepert.[6] Our proposed isomer has the same substitution pattern as the proposed, but not observed "structure X" in the aforementioned study of $C_{70}F_{38}$ by Hitchcock et al.,[15] and is related to their observed isomers by three or six 1,3-hydrogen atom shifts. The dominance of the observed isomer can probably be related to the long exposure time under the extreme synthesis conditions, which leads to rearrangement of the hydrogen atoms on the C_{70} framework and the elimination of less-stable isomers.

DFT calculations on the $C_{70}F_{38}$ isomers show that there is an increased stability on introduction of additional benzenoid structures.[15] We have found that similar DFT calculations give the same result for hydrogenated systems.

In summary we have shown that $C_{70}H_{38}$ can be synthesized effectively by high-pressure hydrogenation. NMR experiments uniquely determine the structure of the main isomer as a C_2-symmetric structure containing five benzenoid rings and two protonated atoms at the equator.

Experimental Section

C_{70} powder (0.5–1 g, 99.5 % pure, MTR Ltd., Cleveland, USA) was loaded into an approximately 3-cm^3 alumina container, followed by hydrogenation in a sealed chamber at an H_2 static gas pressure of 100–120 bar and 673 K for 72 h. Prior to hydrogenation, the samples were degassed by heating at 473 K in a vacuum (10^{-5} Torr) for several hours. Stronger signals for the carbon atoms were obtained in some NMR experiments by synthesizing 25 % ^{13}C-enriched C_{70} (MER, USA) under the same experimental conditions as the non-enriched samples. The reproducibility of the synthesis method was very good: In total, six batches produced on three separate occasions under the same experimental conditions showed almost identical properties. The solubility of our material was less than 0.5 mg mL^{-1} in benzene and more than 5 mg mL^{-1} in chloroform and dichlorobenzene. In most solvents, $C_{70}H_{38}$ decomposed after a few days: a well known problem for hydrogenated fullerenes, especially if the solution is simultaneously exposed to air and light. Therefore, most of our experiments were performed on samples in sealed glass tubes after repeated freeze-pump-thaw cycles and purged with nitrogen gas. This procedure gave yellow/brownish homogeneous solutions that were stable for several months in aromatic solvents. Approximately 5–

7 mg mL^{-1} of the material was dissolved in deuterated chloroform or dichlorobenzene. Sensitivity-enhanced HSQC and HSQC-TOCSY experiments were recorded on a Bruker DRX 600 MHz instrument equipped with a TXI cryoprobe and a Varian INOVA 800 MHz instrument. INADEQUATE experiments were recorded at 600 MHz. All experiments were performed at 25 °C.

X-ray diffraction patterns were recorded on a Siemens D5000 diffractometer using CuK$_\alpha$ radiation. For mass spectrometric analysis, samples were prepared by dissolving the hydrogenated fullerene powder in toluene. Accurate mass measurements were obtained with a custom-built 9.4 T high-resolution atmospheric pressure photoionization Fourier transform ion cyclotron resonance (APPI FTICR) mass spectrometer. Experimental procedures and instrument description can be found elsewhere.[20] Each mass spectrum was internally calibrated from the isotopic signals of the C_{70} radical cation.

Received: November 28, 2007

Keywords: fullerenes · hydrogenation · mass spectrometry · NMR spectroscopy · reaction mechanism

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