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Selective Synthesis of the C_{3v} Isomer of $C_{60}H_{18}$

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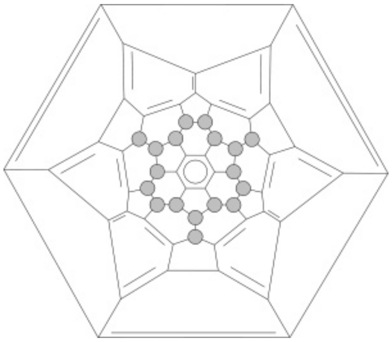
ABSTRACT



$C_{60}H_{18}$ has been produced by hydrogenation of C_{60} at 100 bar H_2 pressure and 673 K for 10 h. We have investigated the crude material without any purification by use of ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry. We show that the crude material consists of 95% of the C_{3v} isomer of $C_{60}H_{18}$.

One of the first derivatives of C_{60} confirmed by mass spectrometry was $C_{60}H_{36}$ together with minor amounts of $C_{60}H_{18}$.[1] Progress in investigation of these materials was slowed by the difficulty in obtaining large amounts of pure single isomeric materials. New techniques for the synthesis of bulk amounts of $C_{60}H_{18}$ could facilitate further work on functionalization of this material. Functionalization of C_{60} is an important direction to obtain new and very promising classes of materials that can be utilized, for example, in solar cell applications.[2]

Of the several techniques available to prepare $C_{60}H_{18}$, most result in materials that require further purification. It is also worth mentioning that the very detailed review on hydrogenated fullerenes by Nossal et al.[3] contains only a very brief section discussing $C_{60}H_{18}$. Recently, however, Briggs et al.[4]

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(1) Banks, M. R.; Dale, M. J.; Gosney, I.; Hodgson, P. K. G.; Jennings, R. C. K.; Jones, A. C.; Lecoultre, J.; Langridge-Smith, P. R. R.; Maier, J. P.; Scrivens, J. H.; Smith, M. J. C.; Smyth, C. J.; Taylor, A. T.; Thorburn, P.; Webster, A. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1149.

(2) Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromherz, T.; Hummelen, J. C. *Appl. Phys. Lett.* **2001**, *78*, 841.

(3) Nossal, J.; Saini, R. K.; Alemany, L. B.; Meier, M.; Billups, W. E. *Eur. J. Org. Chem.* **2001**, 4167.

(4) Briggs, J. B.; Montgomery, M.; Silva, L.; Miller, G. P.; *Org. Lett.* **2005**, *7*, 5553.

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reported a new technique to produce $C_{60}H_{18}$ with high yield, by use of polyamines as hydrogenating agents, without any need for chromatographic purification.

Here we report another technique based on hydrogenation of solid C_{60} at high H_2 gas pressure and high temperature. Careful selection of the reaction conditions, such as pressure, temperature, and treatment period, resulted in synthesis of more than 95 wt % purity of the single C_{3v} isomer of $C_{60}H_{18}$ without additional purification.

The same isomer was earlier reported by Darwish et al.[5] Their material was produced by the M.E.R Corporation with a technique resembling ours, but lacking experimental procedures.

To produce the material, C_{60} powder (0.5−1 g, 99.5% pure, MTR Ltd., Cleveland USA) was loaded into an alumina container of ca. 3 cm^3 size, followed by hydrogenation at 100 bar H_2 gas pressure at 673 K for a period of 10 h. Prior to hydrogenation, samples were degassed by heating at 473 K in vacuum (10^{-5} Torr) for several hours. Hydrogenation was performed in a sealed chamber under a static hydrogen atmosphere.

The final C/H composition of the sample was 2.6 wt %, from elemental analysis based on flush combustion gas chromatography (FC GC) (Mikro Kemi AB, Uppsala, Sweden),[6] compared to 2.44 wt % calculated for pure $C_{60}H_{18}$. The accuracy of hydrogen analysis is estimated to be ~0.1%.

The homogeneous red sample was characterized by X-ray diffraction (XRD), IR and NMR spectroscopy, and atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry (APPI FT-ICR MS). Accurate mass analysis was performed by 9.4 T high-resolution APPI FT-ICR MS. Experimental procedures and instrument description can be found elsewhere.[8]

The NMR data were obtained for saturated C_6D_6 solutions and in the solid state. The NMR data of the saturated C_6D_6 solution were obtained using a Bruker DRX 600 MHz spectrometer equipped with a TXI cryoprobe operating at 600.17 and 150.93 MHz for ^1H and ^{13}C. Cross Polarization/Magic Angle Spinning (CP/MAS) NMR experiments were performed with a Bruker AMX2 500 spectrometer operating at 500.13 and 125.77 MHz for ^1H and ^{13}C. The XRD analysis of our sample gave a face-centered cubic structure with cell parameter $a = 14.55$ Å, compared to $a = 14.17$ Å for pure C_{60}. The increased cell parameter is typical for hydrogenated fullerenes.[7] More details can be found in ref 8. An APPI FT-ICR mass spectrum of the sample is presented in Figure 1 and shows a remarkably pure $C_{60}H_{18}$, considering that no purification was conducted.

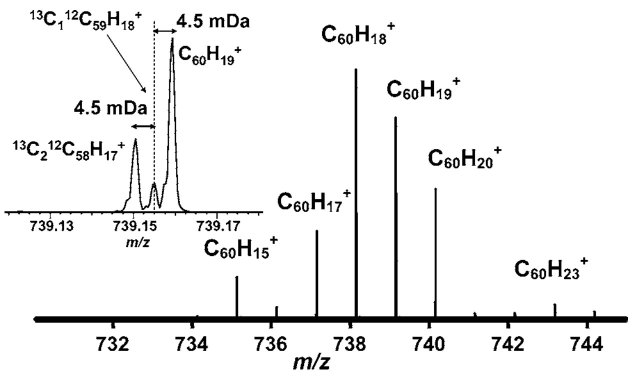

Figure 1. Composition of a hydrogenated sample revealed by APPI FT-ICR MS. Inset shows the close up at *m/z* 739.1−739.2. Both radical and protonated species can be present.

The IR spectrum is in very good agreement with earlier results,[5,9] and C−H vibrations were found at 2925, 2897, 2882 (weak), and 2847 cm^{-1}.

It is well-known that even if mass spectrometry indicates good purity for a hydrogenated sample a large number of different isomers can still exist in the sample. For $C_{60}H_{18}$, the number of possible isomers has been calculated[10] to be on the order of 1.5×10^{13}. To establish the purity of the sample and the type of isomer, we used NMR spectroscopy. The ^1H NMR spectrum for saturated C_6D_6 solution is shown in Figure 2.

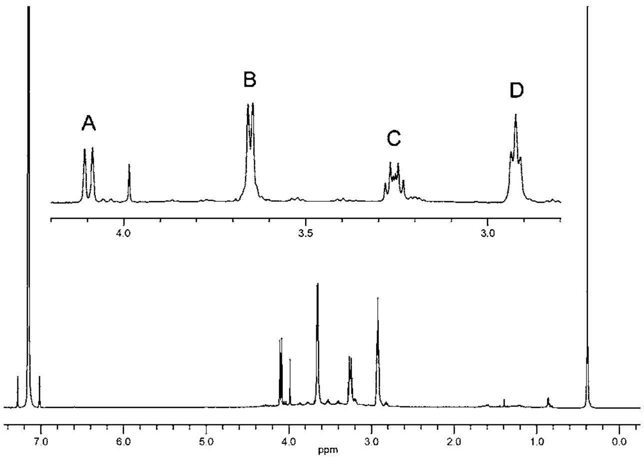

Figure 2. ^1H spectrum (600 MHz) of the crude hydrogenation product; for labeling, see Figure 3.

Figure 2 shows that the measured sample is of very high purity. There are four main signals in the ^1H NMR spectrum originating from hydrogenated C_{60}, except for the residual solvent peak and an unknown impurity at 0.38 ppm. That

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(5) Darwish, A. D.; Avent, A. G.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1996**, *10*, 2051.

(6) For the elemental analysis, the samples are first dried under vacuum, then completely oxidized into gaseous CO_2 and H_2O and subsequently analyzed by gas chromatography. Gas concentration is determined by a thermal conductivity detector, and the accuracy of the hydrogen analysis is estimated to be ~0.1%.

(7) Talyzin, A. V.; Shulga, Y. M.; Jacob, A. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *78*, 1005.

(8) Talyzin, A. V.; Tsybin, Y. O.; Purcell, J. M.; Schaub, T. M.; Schulga, Y. M.; Noreus, D.; Sato, T.; Dzwylewski, A.; Sundqvist, B.; Marshall, A. G. *J. Phys Chem. A*, submitted.

(9) IR spectrum is given as Supporting Information.

(10) Balasubramanian, K. *Chem. Phys. Lett.* **1991**, *182*, 257.

signal stems from protons not connected to any carbon, as concluded from the absence of cross-peaks in the HSQC spectrum. This corresponds well to trace amounts of water in benzene.[11] The main signals are all in the region in which hydrogenated fullerenes are expected to appear and can all be assigned to signals arising from $C_{60}H_{18}$. The integrals are 1:2:1:2, that is, the system has 3-fold symmetry, indicating that our $C_{60}H_{18}$ sample is dominated by the C_{3v} crown isomer of $C_{60}H_{18}$, shown as a Schlegel diagram in Figure 3. The same isomer has been reported to be the dominant component in earlier studies,[4,5] and we confirm the prior ^{1}H assignments. The reason for the dominance of the C_{3v} isomer has been explained by stepwise addition of H_2 and that the next addition occurs in a 1,2 or 1,4 fashion relative to the first.[12] Furthermore, the resulting structure contains an aromatic substructure that counteracts the increased steric repulsion between neighboring hydrogen atoms to form a particularly stable structure.[13]

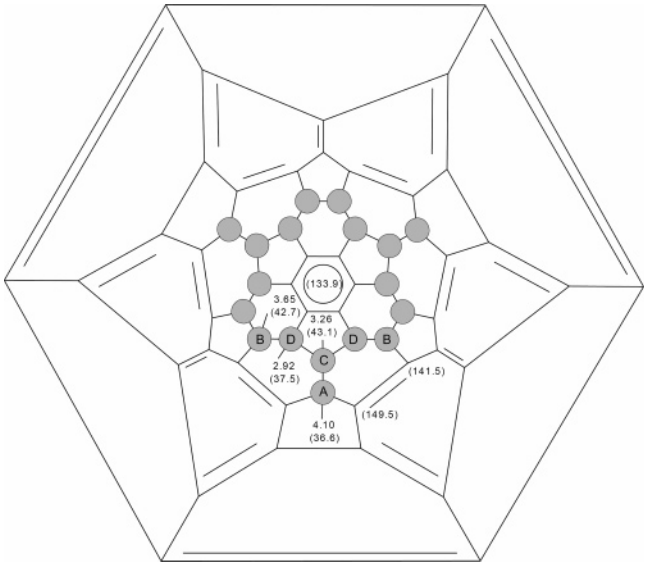

Figure 3. Schlegel diagram of the C_{3v} isomer of $C_{60}H_{18}$ together with the proposed ^{1}H and (^{13}C) NMR assignments. The protonated positions are given in gray.

To strengthen the structural determination and to assign the $C_{60}H_{18}$ NMR spectra, we also performed 2D COSY as well as proton-detected HSQC and HMBC ^{13}C NMR experiments.

The ^{1}H NMR signals for the A, B, C, and D sites in Figure 3 correspond to the signals at 4.10, 3.65, 3.26, and 2.92 ppm, respectively, as reported earlier.[4,5] The HSQC spectrum shows four sp^3 ^{13}C signals at 36.6, 43.1, 37.5, and 42.7 ppm, respectively. The signals are shifted approximately 0.4 ppm to higher field relative to the shifts observed by Briggs et al.[4] That difference can be explained by use of different solvents, $C_6D_4Cl_2$ for theirs versus C_6D_6 for ours. Three sp^2 signals from the carbons located close to protons were observed in the HMBC experiment at 133.9, 141.5, and 149.5 ppm. The full ^{1}H assignment and the partial ^{13}C assignment of the NMR signals of $C_{60}H_{18}$ in solution are shown in Figure 3. Three additional ^{13}C signals were reported by Briggs et al. at 146.1, 151.3, and 151.5 ppm in $C_6D_4Cl_2$.[4]

A complementary solid-state CP/MAS NMR spectrum (see Figure 4) shows the expected signals of the solid material and indicates that the main component even in the solid material is the C_{3v} isomer of $C_{60}H_{18}$.

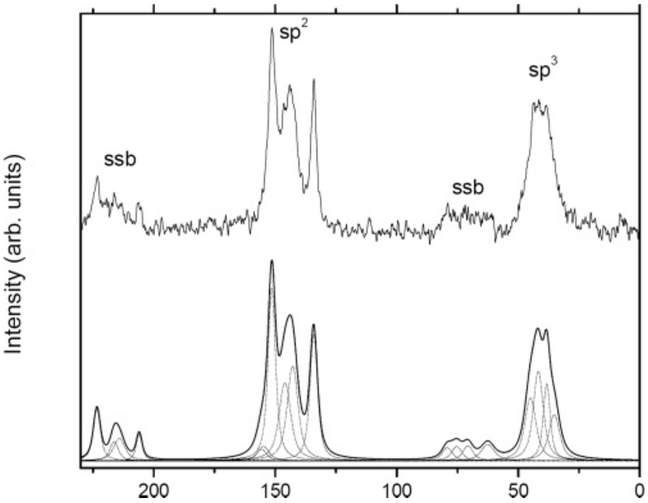

Figure 4. Solid-state 125.77 MHz ^{13}C NMR CP/MAS spectrum of $C_{60}H_{18}$ (ssb denotes spinning side bands).

The issue has been raised of whether the six-membered ring in the top of the $C_{60}H_{18}$ has a true flat aromatic character. Our measurements show that the carbon atoms in the aromatic ring appear at an NMR chemical shift of 133.9 ppm. That value is very close to that for relevant aromatic systems, such as hexamethyl benzene (132.2 ppm),[14] indicating that $C_{60}H_{18}$ indeed contains a planar aromatic subsystem and thus is isostructural to $C_{60}F_{18}$, which has been investigated by single-crystal X-ray crystallography.[15]

To conclude, we have shown that our hydrogenation procedure results in direct synthesis of one major isomer of $C_{60}H_{18}$ of 95% purity. Structural characterization of the $C_{60}H_{18}$ resulted in the identification of only one C_{3v} isomer that is isostructural to the well-characterized C_{3v} isomer of $C_{60}F_{18}$.

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(11) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

(12) Clare, B. W.; Kepert, D. L. *J. Mol. Struct. THEOCHEM* **2003**, *622*, 185.

(13) Clare, B. W.; Kepert, D. L. *J. Mol. Struct. THEOCHEM* **1994**, *303*, 1.

(14) Dalling, D. K.; Ladner, K. H.; Grant, D. M.; Woolfenden, W. R. *J. Am. Chem. Soc.* **1977**, *99*, 7142.

(15) Troyanov, S. I.; Boltalina, O. V.; Kouvytchko, I. V.; Troshin, P. A. Kemnitz, E.; Hitchcock P. B.; Taylor, R. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2002**, *10*, 243.

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Supporting Information Available: Infrared spectrum with a list of absorption peak frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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