[7H]Benzanthrene, a Catalyst for the Transfer Hydrogenation of C_{60} and C_{70} by 9,10-Dihydroanthracene [1]

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Summary: [7H]Benzanthrene 2 was used as a catalyst for the transfer hydrogenation of C_{60} and C_{70} by 9,10-dihydroanthracene 1. The catalyst allowed milder reaction conditions (250 °C) than the non catalyzed procedure did (350 °C).[2] The reaction products identified by EI-MS were $C_{60}H_{36}$, $C_{60}H_{44}$ and $C_{70}H_{36}$ thus a higher degree of hydrogenation could be reached in the case of C_{60}. The method is also suitable for deuteration. A structure proposal for $C_{70}H_{36}$ and its $\Delta H_f(g)$ from molecular mechanics calculations are presented.

In attempts to prepare hydrogenated derivatives of C_{60} several hydrogenation methods were used in the past.[2-5] We have previously reported a new transfer hydrogenation procedure by heating C_{60} with 9,10-dihydroanthracene (DHA) 1 to 350 °C to produce $C_{60}H_{36}$ or $C_{60}H_{18}$ [2] depending on the conditions. We have discovered now that this reaction can be performed at temperatures as low as 250 °C when [7H]benzanthrene 2 is added as a catalyst to C_{60} dissolved in a melt of DHA 1. The catalytic principle for the transfer hydrogenation was recently published for phenalene 3 as catalyst in another context.[6] In addition we report for the first time the hydrogenation and deuteration of C_{70} by the same procedure.
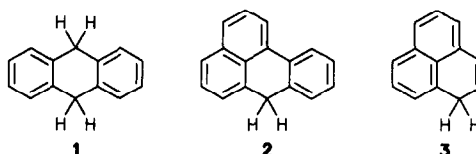
When pure samples C_{60} or C_{70} were heated with 5 molar equivalents 2 and 100 molar equivalents DHA 1 each to 250 °C in an ampoule under N_2 the fullerenes were decolourized and their hydrogenated

derivatives could be isolated by sublimation of residual DHA **1**, catalyst **2** and anthracene. C_{70} reacted more slowly (150 min) than C_{60} (120 min). The deuteration of C_{60} (270 min) und C_{70} (400 min) was also possible when 9,9',10,10'-tetradeuterio-dihydroanthracene and 7,7'-dideuterio-[7H]benzanthrene were used. The spectral properties of the products which were pure according to TLC (n-hexane-CH_2Cl_2 3:1) except for traces of **2** are recorded in table 1.

Table 1: Spectral data of hydrogenated and deuterated products of C_{60} and C_{70}.

MS (EI, 70 EV):	$C_{60}H_x$: x=0-36, 42-44	$C_{60}D_x$: x=0-36
	$C_{70}H_x$: x=0-36	$C_{70}D_x$: x=0-36
MS (UV laser desorption)	see figure 1	
^{1}H-NMR (400 MHz, $CDCl_3$)	$C_{60}H_x$: m = 3.00 - 4.70 ppm, maxima at 4.43, 4.28, 4.20, 4.00, 3.86, 3.45 ppm.	
	$C_{70}H_x$: m = 2.80 - 4.60 ppm, maxima at 4.16, 4.08, 3.73, 3.48 ppm.	
FT-IR (KBr) cm^{-1}	$C_{60}H_x$: 2962, 2921, 2853 (C-H).	
	$C_{60}D_x$: 2153 (C-D).	
	$C_{70}H_x$: 2923, 2853 (C-H).	
	$C_{70}D_x$: 2150 (C-D).	

The ^{1}H NMR and the FT-IR spectra show common features of C-H and C-D bonds, respectively. The deuteration of C_{60} and C_{70} to yield $C_{60}D_x$ and $C_{70}D_x$ resulted in an increase of the molecular weight by about the degree of addition, e.g. M($C_{60}H_{36}$) = 720+36=756 and M($C_{60}D_{36}$) = 720+2*36=792. Thus oxidation products could be excluded. The mass spectra were recorded by EI (70 eV) and laser desorption (LD spectra, λ = 248 nm). With both methods broad mass distributions were found. In the EI experiments M$^+$ peaks $C_{60}H_{36}/C_{60}D_{36}$, $C_{60}H_{44}$ and $C_{70}H_{36}/C_{70}D_{36}$ were detected. The LD spectra were identical to those obtained for the uncatalyzed reaction products, showing the same degree of hydrogenation for C_{60} and C_{70}. As previously observed [2] the maxima in the LD spectra were shifted to smaller masses compared to other MS methods. Odd masses have significantly higher intensities than even masses which becomes even more apparent on taking into account the ^{13}C isotope distribution in the fullerenes and is almost certainly due to the ionisation mechanism involved in the LD experiments. At high laser fluences C_{60} and C_{70} and their typical photofragmentation patterns (C_2 loss) are seen proving that the cage structures were retained after the reductions.

A structure proposal for $C_{70}H_{36}$ from molecular mechanics calculations (MM3) is shown in figure 2. It is based on the expectation that only nonconjugated or aromatic like double bonds are present after the hydrogenation process which are unreactive towards transfer hydrogenation.[6] One double bond is located in each of the twelve five-membred rings of the cluster. Two isolated cyclopentenes form the pole (fig. 2a),[7] ten combine their double bonds to form a pentaphenylene belt around the equator (fig.

2b). The enthalpy of formation of $C_{70}H_{36}$ is calculated as $\Delta H^0_f(g) = 490.2$ kcal mol^{-1}. Further hydrogenation of the two poles to form $C_{70}H_{40}$ leads to an increase of $\Delta H^0_f(g) = 535.7$ kcal mol^{-1}; accordingly $C_{70}H_{36}$ should be thermodynamically preferred.[7]
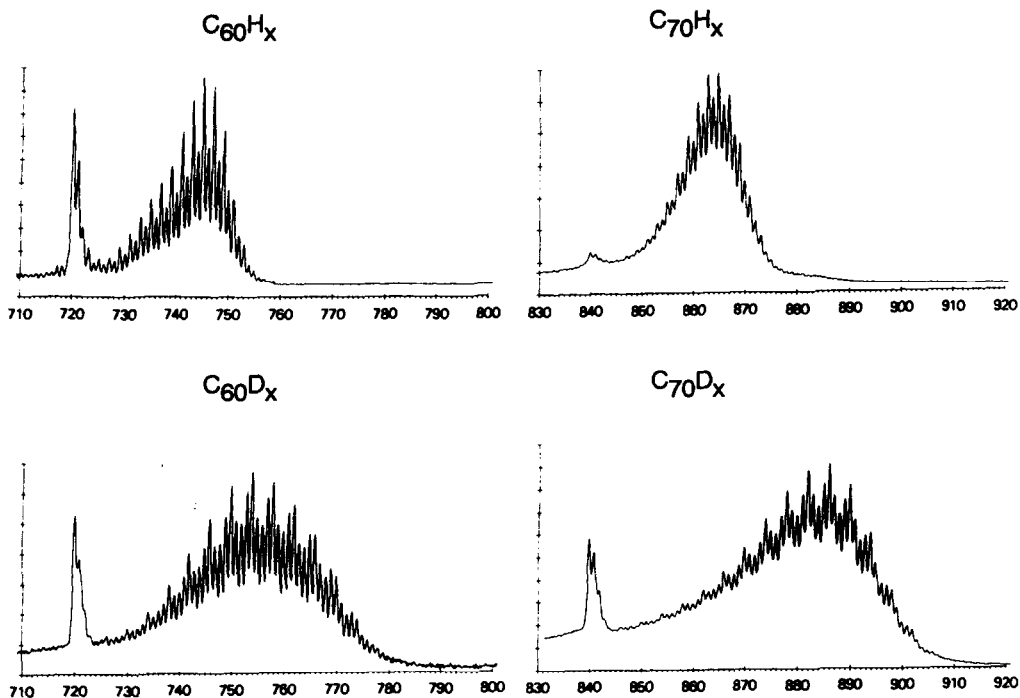

Figure 1: LD-MS spectra ($\lambda = 248$ nm), intensity (arb. units) vs. mass (amu).

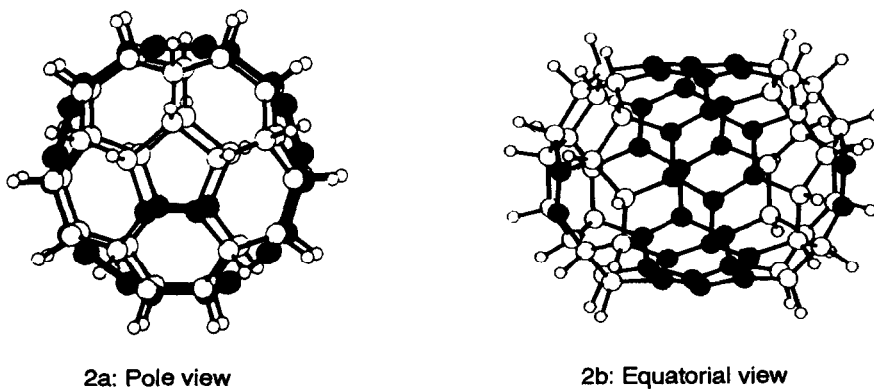2a: Pole view   2b: Equatorial view

Figure 2: Postulated structure of $C_{70}H_{36}$.[7] Symbols for sp^2-carbon atoms are filled.

The results presented in this communication suggest that even higher hydrogenated products of C_{60} may be available when milder reaction conditions could be realized as for catalysis by **2**. They also show that $C_{70}H_{36}$ is obtained with high specificity from C_{70}.

References and Notes

Dedicated to Prof. Hans Bock on the occasion of his 65th birthday.

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7. Due to the regioisomerism of the two double bonds at the poles five isomers could be formulated. In figure 2 the pole double bonds are drawn eclipsed. The differences $\Delta\Delta H^0_f(g)$ between eclipsed and noneclipsed structures should be negligible.