Formation, Isolation, and Spectroscopic Properties of Some Isomers of $C_{60}H_{38}$, $C_{60}H_{40}$, $C_{60}H_{42}$, and $C_{60}H_{44}$ − Analysis of the Effect of the Different Shapes of Various Helium-Containing Hydrogenated Fullerenes on Their ^{3}He Chemical Shifts

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A complex mixture of $C_{60}H_{38}$ to $C_{60}H_{44}$ has been prepared by a much milder procedure (Benkeser reduction) than the hydrogenation procedures that have frequently been used to produce such highly hydrogenated derivatives of C_{60}. ^{1}H and ^{13}C NMR spectra of fractions isolated by HPLC showed that more highly hydrogenated fullerenes exhibited signals that were shifted upfield. The opposite trend appears to hold in ^{3}He NMR spectra of the corresponding endohedral helium compounds. The changes in the ^{1}H, ^{13}C, and ^{3}He chemical shifts are reasonable for fullerenes hydrogenated to different extents. In particular, previously reported substantial changes in the shapes of the various hydrogenated fullerenes can reasonably account for the interesting trends apparent both in the ^{3}He chemical shifts of He@$C_{60}H_x$ ($x = 0$–44) and in the HPLC retention times of the corresponding non-helium-containing species.

Introduction

The chemistry of benzene and other aromatics is now a substantial portion of organic chemistry. The chemistry of C_{60} and other fullerenes is at a much earlier stage. While a large portion of aromatic chemistry involves substitution of other groups for hydrogen atoms, C_{60} and other fullerenes have no hydrogen atoms. Until now, most of the chemistry has been concerned with addition reactions. A large number of different functional groups have been added, but a considerable fraction of the reactions which have produced multiple adducts have involved hydrogen or fluorine. For example, fluorine adds readily to such molecules producing a large variety of products with many fluorine atoms. A number of different reduction procedures can add multiple hydrogen atoms. In many cases, there are striking parallels between hydrogenation and fluorination products.

Thus far, only a single isomer of $C_{60}H_2$ has been reported. In principle, two hydrogen atoms can add to C_{60} to produce a number of isomers. Either only a single isomer is produced by the reaction conditions used, or other isomers are produced but rapidly become the single reported substance. In this isomer, the two hydrogen atoms are adjacent on a fusion between six-membered rings. We can think of this substance as the result of hydrogenating one of the 30 double bonds of the fullerene. When additional reduction is carried out, multiple isomers are produced. The hydrogen atoms are, therefore, not moving freely over the surface of the fullerene in these compounds.

How can these materials be studied? Chromatography can be used to separate either pure substances or mixtures of products. Mass spectroscopy yields formulas, but does not distinguish among isomers. Proton and carbon NMR can yield further valuable information but the spectra are complex. Once the high symmetry of C_{60} is broken, each isomer of each substance yields a large number of carbon peaks. If there are many hydrogen atoms, the ^{1}H NMR spectrum of each isomer can also become complex. A further NMR nucleus can be applied to this problem. If ^{3}He is incorporated into the fullerene before reduction or fluorination, helium NMR spectra can be taken of the product mixtures. Each separate isomer yields a single sharp helium peak. Even though there is no bond to the helium atom, the helium shifts are observed over a wide range. The helium atom therefore reports the magnetic field that it experiences. This magnetic field is, in turn, strongly affected by the diamagnetic π bonds and, to a lesser extent, the σ bonds of the fullerene. While the helium atom can move relatively freely inside the fullerene and indeed there is room for more than one helium atom, one can, to a good

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approximation, think of the helium atom as occupying an averaged position in the center of the fullerene cavity.

As far as we have seen, each isomer of a reduced or fluorinated fullerene gives a separate distinguishable helium peak and we can therefore count the number of isomers present in a mixture. Where partial separation has been achieved by chromatography, we can easily see how the different chromatographic peaks contain different relative amounts of the different isomers. Furthermore, it is possible to do theoretical calculations in order to predict the helium chemical shifts of the isomers with reasonable accuracy. In particular, in cases of low symmetry the calculations required to do this are very time-consuming. Qualitative generalizations can also be drawn concerning the areas where helium shifts are found to be correlated to different types of structural change.

The study of highly reduced C_{60} has been limited largely to $C_{60}H_{18}$ and $C_{60}H_{36}$ since there are several methods available for the synthesis of these species in quantities suitable for subsequent studies.[1] In contrast, relatively few reports have appeared on more highly hydrogenated C_{60}. There is a report of a Birch reduction[2] of C_{60} yielding a small amount of $C_{60}H_{38}$ and $C_{60}H_{40}$ in addition to $C_{60}H_{36}$.[3] The attempted reduction of $C_{60}H_{36}$ by hydrogen in the presence of a rhodium/alumina catalyst at room temperature for 10 d did not reveal any further hydrogenation of the cage.[4] However, both transfer hydrogenation[5,6] and direct hydrogenation[7−10] under more severe conditions do cause further hydrogenation. Analysis (most commonly by mass spectrometry) of the products from these various hydrogenation reactions indicated the presence of species ranging from $C_{60}H_{40}$[8] to $C_{60}H_{52}$.[10] Mass spectral analysis of the products obtained from the ambient reduction of C_{60} with Zn/conc. HCl indicated the presence of $C_{60}H_{36}$ (82%), $C_{60}H_{38}$ (15%), and $C_{60}H_{40}$ (3%); additional reduction occurred when DCl was used instead, as mass spectral analysis of the products indicated the presence of $C_{60}D_{36}$ (32%), $C_{60}D_{38}$ (31%), $C_{60}D_{40}$ (22%), $C_{60}D_{42}$ (11%), and $C_{60}D_{44}$ (4%).[11]

The Birch reduction of aromatic substrates such as benzene, naphthalene, and anthracene has been studied extensively.[2] A modification of this dissolving-metal reduction was developed by Benkeser,[12] who obtained more highly reduced products relative to the classic Birch reduction by replacing the ammonia solvent with a low-molecular-weight amine such as ethylenediamine, ethylamine, *tert*-butylamine, or diethylamine.

In this paper, we describe the synthesis of $C_{60}H_{38}$ to $C_{60}H_{44}$ in high yield by the Benkeser reduction of $C_{60}H_{36}$, separation of the products by HPLC, molecular weight characterization of the products in each fraction by FD-MS, and spectroscopic analysis of each fraction by ^{1}H and ^{13}C NMR spectroscopy. We also present an analysis of the ^{3}He NMR spectroscopic data obtained on the material from the Benkeser reduction of He@$C_{60}H_{36}$. There do not appear to be any reports involving ^{13}C or ^{3}He NMR analyses of such highly hydrogenated fullerenes. In addition, upon examination of previously reported ^{3}He chemical shift data for samples of helium-containing hydrogenated C_{60} and HPLC retention time data for the corresponding non-helium-containing fluorinated samples, it becomes apparent that substantial changes in the shapes of the various hydrogenated fullerenes can reasonably account both for the relative ^{3}He chemical shifts and the relative HPLC retention times.

Results and Discussion

A mixture of $C_{60}H_{36}$ prepared by the Birch reduction of C_{60}, then subjected to a second Birch reduction, resulted only in recovery of $C_{60}H_{36}$. Using lithium in ethylenediamine to reduce the mixture of $C_{60}H_{36}$ isomers obtained by Birch reduction of C_{60} produced a $C_{60}H_{36}$ to $C_{60}H_{44}$ product mixture that eluted in five fractions (Figure 1).

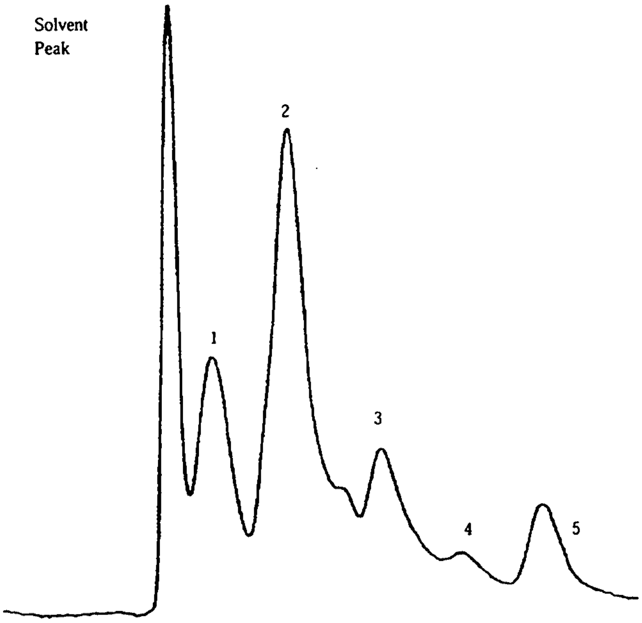

Figure 1. HPLC chromatogram of the $C_{60}H_{36}$ to $C_{60}H_{44}$ product mixture from Benkeser reduction of $C_{60}H_{36}$; peaks labeled 1−5 were isolated by preparative HPLC

FD-MS analysis of these non-helium-containing products showed that the crude product mixture contained the fullerene hydrides $C_{60}H_{36}$, $C_{60}H_{38}$, $C_{60}H_{40}$, $C_{60}H_{42}$, and $C_{60}H_{44}$. Separation of each fraction from the mixture by preparative HPLC and characterization by FD-MS of the five purified fractions showed that the bands that eluted earlier had higher fullerene hydrides, while the last fraction was the unreduced $C_{60}H_{36}$ from the Birch reduction. A steady increase in elution time with decreasing extent of hydrogenation has also been noted in HPLC separation of a mixture of $C_{60}H_{52}$, $C_{60}H_{48}$, and $C_{60}H_{42}$.[10] (Similarly, $C_{60}F_{38}$ elutes before $C_{60}F_{36}$, and $C_{60}F_{36}$ elutes before $C_{60}F_{34}$.[13]) According to the FD-MS analysis of non-helium-containing Benkeser-reduced products, Fraction 1 contained mostly $C_{60}H_{42}$ with some $C_{60}H_{44}$, Fraction 2 contained mostly $C_{60}H_{42}$ with some $C_{60}H_{40}$, Fraction 3 contained mostly $C_{60}H_{40}$ with some $C_{60}H_{38}$, Fraction 4 contained mostly $C_{60}H_{38}$ with some $C_{60}H_{36}$, while Fraction 5 contained only unchanged $C_{60}H_{36}$. Clearly, almost all of the $C_{60}H_{36}$ had been reduced further and under relatively mild conditions compared to transfer or direct hydrogenation.[5−10] The presence of a mixture of different molecular weight products in each of Fractions 1−4 was verified by measuring the relative intensities of the M^+ and $[M + 2]^+$ peaks.

In order to determine the number of isomers present in each fraction, $He@C_{60}H_{38-44}$ was synthesized by Benkeser reduction of $He@C_{60}H_{36}$ and separated by HPLC (Figure 2) for characterization by ^3He NMR spectroscopy (Figure 3), as endohedral ^3He chemical shifts are very sensitive to the structure of the fullerene.[14]

Fraction 5 gave ^3He NMR signals in the intensity ratio of 3:1 at $\delta = -8.03$ and -8.16 ppm (relative to the signal at $\delta = 0$ ppm for helium gas dissolved in the solvent). These signals are consistent with what was previously reported for two isomers of $He@C_{60}H_{36}$ produced by dihydroanthracene reduction.[3] The ^3He NMR spectra of Fractions 1−5 showed that hydrogenation of $He@C_{60}H_{36}$ shifts the signals downfield, with the signals clustered near $\delta = -6.4$ ppm believed to be mostly from isomers of $He@C_{60}H_{36}$ and $He@C_{60}H_{38}$, while the signals clustered near $\delta = -3.0$ ppm are believed to be mostly from isomers of $He@C_{60}H_{40}$ and $He@C_{60}H_{42}$ and possibly $He@C_{60}H_{44}$. ^3He NMR spectra of the individual fractions show that all the signals observed in Fraction 2 are also observed in the same ratio in the spectrum of Fraction 1 (Figure 4). However, only Fraction 1 gives the two weak, most downfield signals ($\delta = -2.85$ and -2.76 ppm). Because Fraction 1 is a minor component on the front end of Fraction 2 (Figure 2), these two weak signals apparently result only from Fraction 1. These ^3He

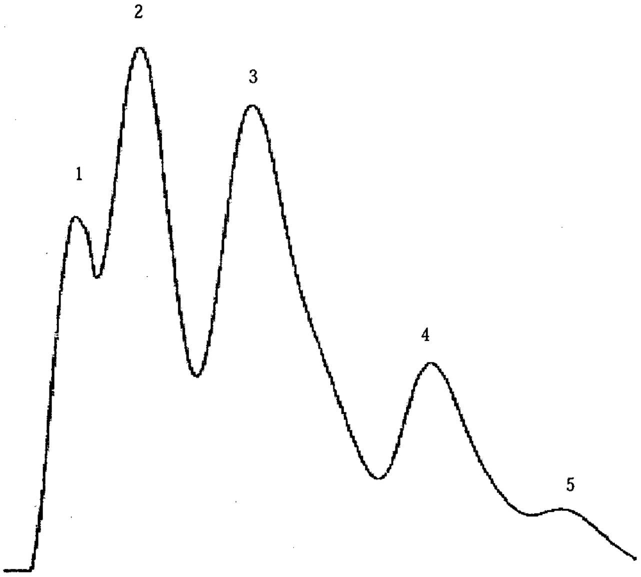

Figure 2. HPLC chromatogram of the $He@C_{60}H_{36}-C_{60}H_{44}$ product mixture from Benkeser reduction of $He@C_{60}H_{36}$; peaks labeled 1−5 were isolated by preparative HPLC

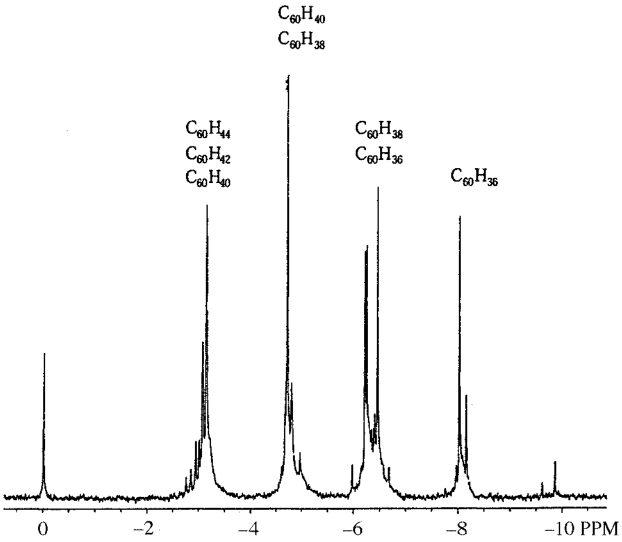

Figure 3. ^3He NMR spectrum of the product obtained by Benkeser reduction of $He@C_{60}H_{36}$; subsequent isolation by HPLC gave individual fractions whose spectra were identified by comparing the ^3He NMR spectra before and after fractionation; the cluster of peaks at $\delta = -3.0$ ppm is of a mixture of Fraction 1 and Fraction 2

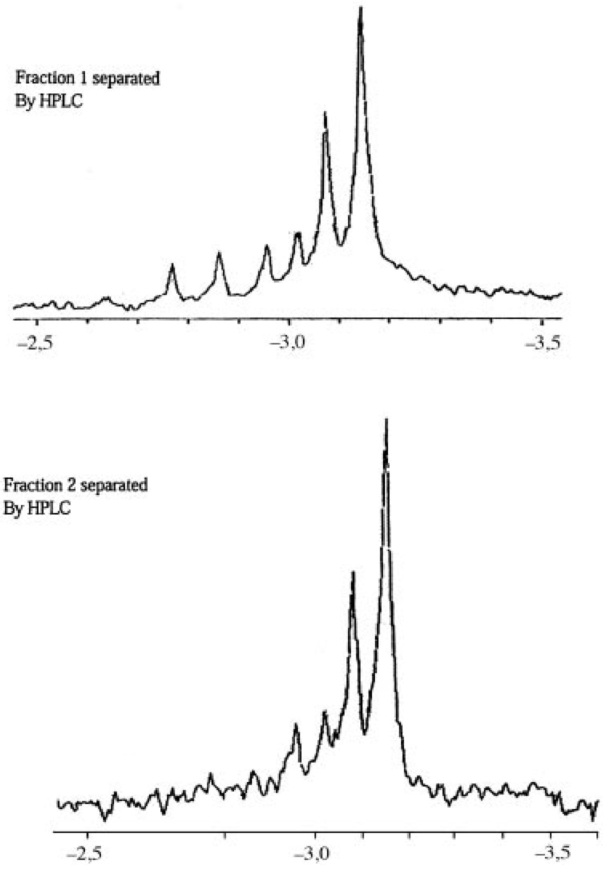

Figure 4. ^3He NMR spectrum of Fraction 1 (top) and Fraction 2 (bottom) after HPLC separation; Fraction 1 is composed of $C_{60}H_{44}$, $C_{60}H_{42}$ and $C_{60}H_{40}$, while Fraction 2 contains only $C_{60}H_{42}$ and $C_{60}H_{40}$

NMR signals appear to be the most deshielded signals reported for any endohedral neutral fullerene. Only the ^{3}He NMR signal for $^3He@C_{70}^{6-}$ is more deshielded (δ = +8.3 ppm).[15]

For a given level of hydrogenation, multiple isomers are clearly present. A steady downfield shift with increasing hydrogenation would parallel the trend previously observed with $He@C_{60}H_{32}/He@C_{60}H_{36}$, $He@C_{60}H_{36}$, and $He@C_{60}H_{38}/He@C_{60}H_{40}$ produced by Birch reduction of $He@C_{60}$.[3] It is not possible to determine the extent of hydrogenation just from the ^{3}He chemical shift because at a given level of hydrogenation, different isomers frequently give ^{3}He chemical shifts spread over a range of several ppm.[3,16–19]

An interesting trend is emerging in the ^{3}He chemical shifts of hydrogenated fullerenes. Hydrogenation causes a steady *upfield* shift in proceeding from $He@C_{60}$ (δ = −6.3 ppm[16]) to $He@C_{60}H_2$ (δ = −9.66 ppm[16]) to $He@C_{60}H_4$ (δ = −9.3 to −12.8 ppm[16,17]) to $He@C_{60}H_6$ (δ = −14.2 to −16.3 ppm[19]) to $He@C_{60}H_{18}$ (δ = −16.4 ppm[18]). Further hydrogenation reverses this trend. In addition to the ^{3}He NMR signals shown in Figure 3, other work has reported ^{3}He NMR signals for a mixture of $He@C_{60}H_{32}$ and $He@C_{60}H_{36}$ ranging from δ = −8.4 to −7.6 ppm,[3] $He@C_{60}H_{36}$ from δ = −8.1 to −4.6 ppm,[3,18] and a mixture of $He@C_{60}H_{38}$ and $He@C_{60}H_{40}$ from δ = −4.0 to −3.2 ppm.[3] Clearly, the ^{3}He chemical shift of a highly hydrogenated fullerene is extremely sensitive to the structure of the fullerene. A proposed explanation now follows for the increased shielding and then deshielding of the helium environment as the extent of hydrogenation of C_{60} increases.

The helium chemical shift of $He@C_{60}F_{36}$ (δ = −10.49 to −10.52 ppm) is downfield of that for $He@C_{60}F_{18}$ (δ = −16.66 ppm),[20] just as is observed with the corresponding hydrogenated species. Further comparison of ^{3}He chemical shifts between fluorinated and hydrogenated C_{60} is not possible, as no ^{3}He NMR spectroscopic data appear to be available for other fluorinated C_{60} species.

However, there is a remarkable parallel between the ^{3}He chemical shifts noted above for hydrogenated C_{60} species and the HPLC retention times of a mixture of fluorinated C_{60} species all of which are isostructural with the known H analogs $C_{60}H_2$, $C_{60}H_4$, $C_{60}H_{18}$, and $C_{60}H_{36}$, except for the structure proposed for $C_{60}F_6$. These retention times steadily and significantly increase in the order C_{60} (8.5 min), $C_{60}F_2$ (11.3 min), $C_{60}F_4$ (16.2 min), $C_{60}F_6$ (24 min), $C_{60}F_8$ (31.6 min), and $C_{60}F_{16}$ (84.0 min),[21,22] but further fluorination steadily and significantly decreases retention times in the order $C_{60}F_{18}$ (38.0 min), $C_{60}F_{36}$ (3.5 min), and $C_{60}F_{48}$.[21,23] When these retention times were reported, the authors stated that "There is presently no clear explanation for this behaviour."[21]

In each of $C_{60}F_2$, $C_{60}F_4$, $C_{60}F_6$, $C_{60}F_8$,[21] $C_{60}F_{16}$ and $C_{60}F_{18}$,[24] all the fluorine atoms are in just one-half of the molecule. Clearly, adding successive pairs of fluorine atoms to just one-half of the molecule should result in a steady increase in polarity through $C_{60}F_8$ (although very recent work indicates that uncertainty exists concerning the precise structure of $C_{60}F_8$[25]), and a steady increase in retention time is consistent with a steady increase in polarity.

Of course, it is not possible for all the fluorine atoms to be in just one-half of the molecule for $C_{60}F_{36}$ and $C_{60}F_{48}$. Thus, it is not surprising that $C_{60}F_{18}$ is more polar than $C_{60}F_{36}$.[26] The much longer retention time of $C_{60}F_{18}$ is consistent with its greater polarity.[27] The C_s symmetry of $C_{60}F_{16}$,[24] the precursor to $C_{60}F_{18}$,[26] is lower than the C_{3v} symmetry of $C_{60}F_{18}$, which would account for the still higher polarity of $C_{60}F_{16}$.

An analysis of the structures of C_{60}, $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$ is essential for understanding the increased shielding and then deshielding of the helium environment upon increasing hydrogenation of C_{60}. In contrast to C_{60} with its icosahedral symmetry (soccerball geometry), $C_{60}F_{18}$ has C_{3v} symmetry. One half of the cage is flattened. The six-carbon hexagonal face at the center of the $C_{18}F_{18}$ fluorinated crown has equal bond lengths, which shows that this six-carbon ring is fully aromatic. The remaining C_{36} part of the molecule contains an undistorted fullerene hemisphere.[28] With all 18 fluorine atoms in one hemisphere, the molecule is highly polar.[23]

$C_{60}F_{48}$ exists as D_3 and S_6 isomers with six isolated double bonds. Each isomer consists of two equivalent hemispheres related by C_2 rotation or inversion, respectively. Each hemisphere has indentations resulting from the double bonds.[29] $C_{60}F_{36}$ exists as *T*, C_3, and C_1 isomers (as well as an uncharacterized fourth isomer) with distorted cage shapes intermediate between those for $C_{60}F_{18}$ and $C_{60}F_{48}$.[26,30–34]

Thus, C_{60}, a nonpolar, essentially spherical molecule, becomes highly polar and nearly hemispherical upon fluorination to $C_{60}F_{18}$, which re-expands and becomes nonpolar and much more spherical than hemispherical upon fluorination to $C_{60}F_{36}$ or $C_{60}F_{48}$. We believe that the much longer retention time for $C_{60}F_{18}$ compared to C_{60}, $C_{60}F_{36}$, or $C_{60}F_{48}$ is a direct result of this increase in polarity. A similar increase in HPLC retention times with increasing polarity has been noted for another series of closely related fluorinated C_{60} derivatives.[35,36]

$C_{60}H_{18}$ is isostructural with $C_{60}F_{18}$.[27,37] Calculations indicate that $C_{60}H_{18}$ has a slightly less planar, slightly less aromatic ring surrounded by the $C_{18}H_{18}$ crown.[38] Thus, in $He@C_{60}H_{18}$, the helium atom is confined to little more than a hemisphere and is situated directly above a nearly flat, essentially aromatic ring in the center of the $C_{18}H_{18}$ crown. Since the region directly above an aromatic ring is known to be shielded,[39] it is reasonable for $He@C_{60}H_{18}$ to give the most upfield ^{3}He NMR signal among the hydrogenated C_{60} species. This signal is only 0.2 ppm downfield of that for $^3He@C_{60}F_{18}$. After further hydrogenation, roughly spherical and only slightly polar $C_{60}H_{36}$–$C_{60}H_{44}$ species form, and the ^{3}He NMR signal shifts back downfield.

Because the central benzene ring in $C_{60}H_{18}$ and $C_{60}F_{18}$ is nearly flat, [*n*]paracyclophanes with $n \geq 9$ are a better model system than [*n*]paracyclophanes with $n \leq 8$[40] for the effect of a ring current on the chemical shift of a nucleus above the central benzene ring in $C_{60}H_{18}$ and $C_{60}F_{18}$. For these larger [*n*]paracyclophanes ($n = 9-12, 14$), the ^{13}C nuclei of the interior CH_2 groups experience only a modest ring current effect (as evidenced from their modestly increased shieldings), but the ^{1}H nuclei of these interior CH_2 groups experience a very noticeable ring current effect (as evidenced from the correspondingly increased shieldings).[41]

The complexity of the ^{3}He, ^{1}H, and ^{13}C NMR spectra for each fraction precludes identifying the specific structure of any of the compounds present. Others have calculated the heats of formation and relative stabilities of some isomers of $C_{60}H_x$, where $x > 36$.[42−49] Most of these calculations have been limited to isomers with a threefold or higher symmetry element, as is possible for $C_{60}H_{42}$, $C_{60}H_{48}$, $C_{60}H_{54}$, and $C_{60}H_{60}$, to allow the calculations to be done in a reasonable amount of time. The relatively recent and extensive calculations by Clare and Kepert on the relative stabilities of numerous isomers of $C_{60}H_{36}$[50] and numerous isomers of $C_{60}H_{42}$, $C_{60}H_{48}$, and $C_{60}H_{54}$[49] are particularly noteworthy. Developing methods to separate and characterize similar highly hydrogenated derivatives of C_{60} remains a formidable challenge. Once it becomes possible to identify the specific structure of any of the $C_{60}H_{42}$ species produced in this work (or any $C_{60}H_{42}$, $C_{60}H_{48}$, or $C_{60}H_{54}$ species that might be formed subsequently), it will be extremely interesting to see if the structure is among those calculated to be relatively stable.

In any event, these initial results demonstrate the utility of the Benkeser reduction for reducing $C_{60}H_{36}$ under relatively mild conditions. Subsequent reduction by direct or transfer hydrogenation might yield still more highly reduced species, as might direct or transfer hydrogenation of $C_{60}H_{36}$ followed by Benkeser reduction. In particular, the synthesis and characterization of $C_{60}H_{48}$ remains to be accomplished, with the objective of comparing its structure against the known D_3 and S_6 isomers of $C_{60}F_{48}$. The synthesis of $C_{60}H_{60}$ remains the ultimate challenge, with the fascinating possibility of inward-pointing hydrogen atoms to relieve strain.[42,44,45,51−54]

Experimental Section

Spectroscopy and Chromatography: 400 and 500 MHz ^{1}H (Figure S1) and 126 MHz ^{13}C (Figure S2) NMR spectra were obtained at Rice and 381 MHz ^{3}He NMR spectra (Figures 3 and 4) were obtained at Yale with instrumentation previously described[3] on samples dissolved in *o*-$C_6D_4Cl_2$ containing TMS as a ^{1}H and ^{13}C chemical shift reference. Mass spectra were obtained using a Finnigan MAT 95 spectrometer. HPLC analyses were performed using a Waters 501 pump and a Waters 486 tunable absorbance detector connected to a Waters data module equipped with a Regis Technologies 10 mm × 25 cm Buckyclutcher I stationary phase column using a toluene/hexanes (7:3) isocratic mobile phase. A flow rate of 2.2 mL/min and a wavelength of 280 nm were employed. All solvents were HPLC grade. The Buckyclutcher I column uses a Trident-Tri-DNP, selective tripodal π-acidic stationary phase ([2,4-$(NO_2)_2C_6H_3{-}O{-}CH_2]_3C{-}(CH_2)_9{-}Si(CH_3)_2{-}O{-}$]) for highly selective π−π complexation with fullerenes.[55,56]

Benkeser Reduction of $C_{60}H_{36}$: $C_{60}H_{36}$ (180 mg, 86% yield) was synthesized as described previously[3] from C_{60} (200 mg, 0.278 mmol) and placed in a 250-mL one-neck flask. The flask was equipped with a magnetic stirring bar and a condenser, placed in an oil bath and 100 mL of ethylenediamine was then added. The mixture was stirred until the temperature reached 90 °C. After heating, small pieces of lithium metal (6 g, 0.857 mol) were added to the mixture over a period of 1.5 h in order to sustain the deep blue color. After all the lithium metal was added, the reaction mixture was refluxed for 2 h, whereupon the reaction was stopped and the contents left to cool to room temperature. The flask was then further cooled in an ice bath, and excess lithium metal was destroyed by slow addition of distilled water. The water layer was then extracted with freshly distilled benzene (3 × 75 mL). The organic layer was further washed with 10% HCl (2 × 25 mL) followed by saturated NaCl (2 × 25 mL). The organic layer was dried with sodium sulfate to obtain a colorless solution. The solvent was stripped under vacuum; a whitish powder was obtained. The product was then analyzed by HPLC, and the five bands (Fraction 1−5) were isolated by preparative HPLC in toluene/hexanes (7:3) using a Buckyclutcher I preparative column.

Band 1: (7.80 min retention time). FD-MS for $C_{60}H_{44}$: calcd. 764.2, found 764.2. FD-MS for $C_{60}H_{42}$: calcd. 762.3, found 762.1. ^{3}He NMR: $\delta = -3.15, -3.08, -3.03, -2.96, -2.85$, and -2.76 ppm.

Band 2: (9.17 min retention time). FD-MS for $C_{60}H_{42}$: calcd. 762.3, found 762.2. FD-MS for $C_{60}H_{40}$: calcd. 760.2, found 760.1. ^{3}He NMR: $\delta = -3.15, -3.08, -3.03$, and -2.96 ppm.

Band 3: (11.20 min retention time). FD-MS for $C_{60}H_{40}$: calcd. 760.2, found 760.1. FD-MS for $C_{60}H_{38}$: calcd. 758.3, found 758.1. ^{3}He NMR: $\delta = -4.97, -4.81$, and -4.73 ppm.

Band 4: (12.57 min retention time). FD-MS for $C_{60}H_{38}$: calcd. 758.3, found 758.2. FD-MS for $C_{60}H_{36}$: calcd. 756.2, found 756.1. ^{3}He NMR: $\delta = -6.47, -6.41, -6.39, -6.27$, and -6.23 ppm.

Band 5: (14.46 min retention time). FD-MS for $C_{60}H_{36}$: calcd. 756.2, found 756.2. ^{3}He NMR: $\delta = -8.03$ and -8.16 ppm (ratio 3:1).

Electronic Supporting Information Available: ^{1}H and DEPT-135 ^{13}C NMR spectra and discussion of the five fractions obtained from HPLC separation of the $C_{60}H_{36}$ to $C_{60}H_{44}$ product mixture, which had been obtained by Benkeser reduction of the mixture of $C_{60}H_{36}$ isomers obtained by Birch reduction of C_{60} (see footnote on the first page of this article).

Acknowledgments

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[1] For a review citing many different syntheses of $C_{60}H_{18}$ and $C_{60}H_{36}$, see: J. Nossal, R. K. Saini, L. B. Alemany, M. Meier, W. E. Billups, *Eur. J. Org. Chem.* **2001**, 4167−4180.

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