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Formation, Isolation, Spectroscopic Properties, and Calculated Properties of Some Isomers of $C_{60}H_{36}$

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Abstract: Isomers of $C_{60}H_{36}$ and He@$C_{60}H_{36}$ have been synthesized by the Birch or dihydroanthracene reduction of C_{60} and isolated by preparative high-pressure liquid chromatography. ^{3}He, ^{13}C, and ^{1}H NMR spectroscopic properties were then determined. A comparison of experimental chemical shifts against those computed using density functional theory (B3LYP) with polarized triple- and double-ζ basis sets for He and C,H, respectively, allowed provisional assignment of structure for several isomers to be made. Theoretical calculations have also been carried out to identify low-energy structures. The transfer hydrogenation method using dihydroanthracene gives a major $C_{60}H_{36}$ isomer and a minor $C_{60}H_{36}$ isomer with C_3 symmetry as determined by the ^{13}C NMR spectrum of $C_{60}H_{36}$ and the ^{3}He NMR spectrum of the corresponding sample of ^{3}He@$C_{60}H_{36}$. In view of the HPLC retention times and the ^{3}He chemical shifts observed for the Birch and dihydroanthracene reduction products, the two isomers generated by the latter procedure can be only minor isomers of the Birch reduction. A significant energy barrier apparently exists in the dihydroanthracene reduction of C_{60} for the conversion of the C_3 and C_1 symmetry isomers of $C_{60}H_{36}$ to the T symmetry isomer previously predicted by many calculations to be among the most stable $C_{60}H_{36}$ isomers. Many of the ^{1}H NMR signals exhibited by $C_{60}H_{36}$ (and $C_{60}H_{18}$, previously reported) are unusually deshielded compared to "ordinary" organic compounds, presumably because the unusual structures of $C_{60}H_{36}$ and $C_{60}H_{18}$ result in chemical shift tensors with one or more unusual principal values. Calculations clearly show a relationship between exceptionally deshielded protons beta to a benzene ring in $C_{60}H_{18}$ and $C_{60}H_{36}$ and relatively long C−C bonds associated with these protons. The additional information obtained from 1D and 2D ^{1}H NMR spectra obtained at ultrahigh field strengths (up to 900 MHz) will serve as a critical test of chemical shifts to be obtained from future calculations on different $C_{60}H_{36}$ isomers.

Introduction

The first derivatives of C_{60} were prepared by the Birch reduction of the fullerene in 1990.[1] Mass spectral evidence for $C_{60}H_{36}$ was presented, and despite early skepticism,[2,3] this work has been repeated successfully in several laboratories.[4,5] Extensive studies, both computationally and experimentally, to determine the structure of these hydrides have been reported,[6−14] but characterization has proven to be extremely difficult. In this paper, we present results that show that the product obtained from the Birch reduction is a mixture composed mostly of several isomers of $C_{60}H_{36}$ and the product obtained from the dihydroanthracene reduction consists mostly of a single $C_{60}H_{36}$ isomer with C_1 symmetry and a minor $C_{60}H_{36}$ isomer with C_3 symmetry.

Background. Analysis by mass spectroscopy of the buff-colored solid obtained by the Birch reduction of C_{60} showed that the product was primarily $C_{60}H_{36}$, along with some $C_{60}H_{18}$.[1] When the crude product was treated with DDQ in refluxing toluene, the red color of the DDQ−toluene complex was

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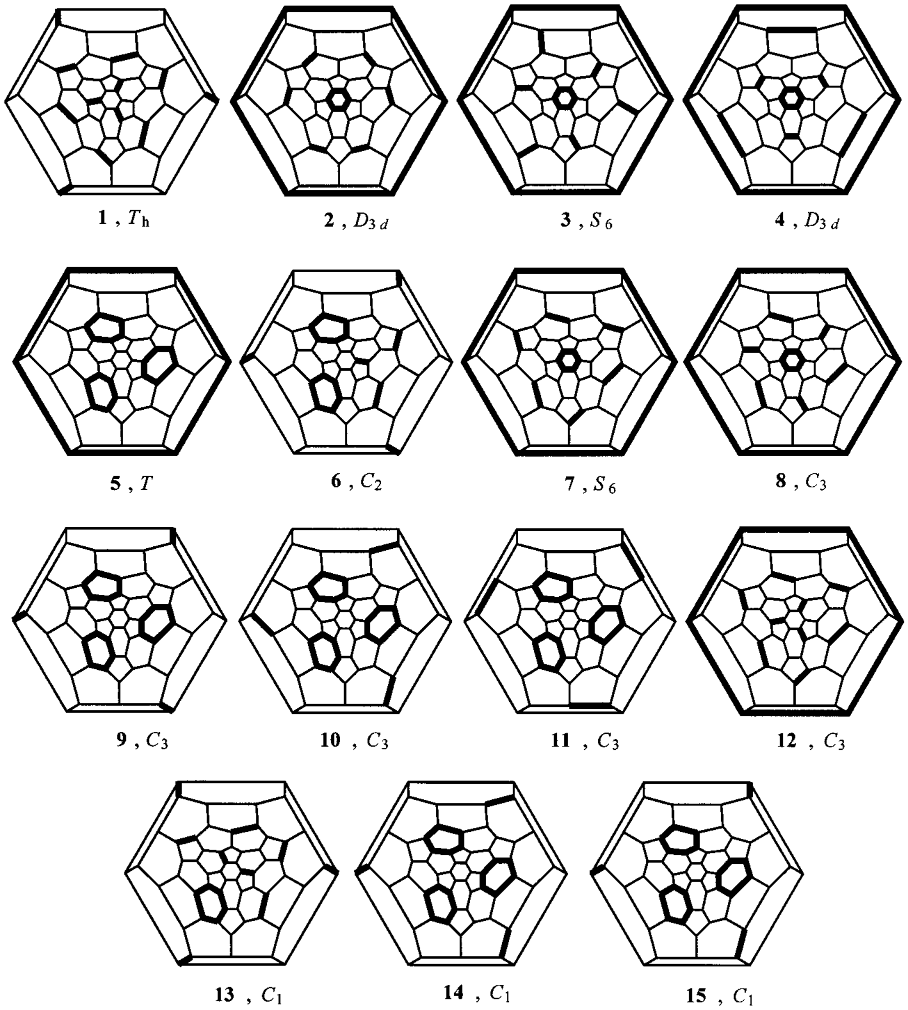
1, T_h **2**, D_{3d} **3**, S_6 **4**, D_{3d}

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

9, C_3 **10**, C_3 **11**, C_3 **12**, C_3

13, C_1 **14**, C_1 **15**, C_1

Figure 1. Schlegel diagrams of 15 isomers of $C_{60}H_{36}$. Isolated heavy lines indicate C═C bonds. A hexagon outlined in heavy lines indicates a benzene ring. The intersection of three light lines represents a methine carbon with three C—C bonds.

discharged with the concomitant formation of C_{60}. Mass spectral analysis confirmed that the product was C_{60} and that the Birch reduction did not involve alteration of the fullerene skeleton.

The addition of 36 hydrogens was not considered surprising, because the Birch reduction is known not to hydrogenate unconjugated double bonds,[15] and 36 is the minimum number of hydrogens required to leave unconjugated double bonds within each of the 12 pentagons. This arrangement leads to $C_{60}H_{36}$ isomer **1** (Figure 1) with 12 unconjugated double bonds. This isomer is now known from semiempirical and ab initio computations to be a high-energy one relative to some of the other possible structures illustrated in the text.[6-8,11,14,16] It was eventually 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 $n = 36$.[17] Balasubramanian estimated that there are 6.0×10^{14} isomers of $C_{60}H_{36}$.[18] Clare and Kepert, who have catalogued about one hundred isomers,[8-10,14] have found that the 10 most stable isomers all lie energetically within less than 15 kcal mol^{-1} at the semiempirical AM1 level of theory.[14] However, our higher level B3LYP/6-31G* computations reported here give an energy range of 49 kcal mol^{-1} for the same set of isomers.

Characterization of the highly reduced fullerenes is difficult, because these materials are unstable toward light and air,[4,16,19-23] especially in solution.[12,13,21,22] Identification of the molecular ions under electron impact conditions requires[3,24,25] that the spectra be obtained using carefully prepared samples immediately after workup.[4,12,13,20-22] Field desorption mass spectroscopy has been reported to give spectra with minimal fragmentation of the molecular ion relative to other techniques.[25]

Difficulties with product stability led to some initial debate as to whether $C_{60}H_{36}$ was the primary product of the Birch reaction,[2,3] but later work confirmed that $C_{60}H_{36}$ was the major product when APCI, CI, and EI mass spectra of the products were recorded immediately after workup.[4,5] The ^{1}H NMR spectrum of the crude product appears as a broad,[12,21,26-28]

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sometimes[21,28] almost featureless, signal between δ 2.5 and δ 4.2. The nearly featureless NMR spectrum of the crude product has been attributed variously to the presence of several isomers, the presence of hydrides other than $C_{60}H_{36}$ or a rapid isomerization or decomposition of the products.[1,3,12,21,26,27]

Rüchardt and co-workers have shown that it is possible to selectively synthesize either $C_{60}H_{18}$ or $C_{60}H_{36}$ by transfer hydrogenation of C_{60}.[25,29] 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 reduction are a mixture of D_{3d} **2** and S_6 **3** isomers (Figure 1).[30,31] It is interesting that D_{3d} isomer **2** is among the most stable $C_{60}H_{36}$ isomers known.[8,10,14] A recent comparison of Raman spectra of $C_{60}H_{36}$ samples prepared by high-pressure hydrogenation with the results of molecular dynamics calculations led Meletov and co-workers to conclude that the three most abundant isomers have D_{3d}, S_6, and T symmetry.[32]

Attalla and co-workers treated fullerite (ca. 85% C_{60}, remainder C_{70} and higher fullerenes) with iodoethane and hydrogen at high pressure and temperature.[24] The FAB-MS spectrum showed strong signals at *m*/*e* 757 and 877 that 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** having D_{3d} symmetry (Figure 1) was proposed. Other work including electron and X-ray diffraction studies also supports the assignment of the D_{3d} **4** structure.[33]

Darwish and co-workers reported that zinc and hydrochloric acid in aromatic solvents can be used to reduce C_{60}.[21,22] Although the T structure **5** (Figure 1) had previously been proposed as the major product,[2,34] analysis of the infrared spectrum led Rüchardt and co-workers to conclude that isomer **3** was the best candidate for $C_{60}H_{36}$ prepared by Zn reduction of C_{60} in aromatic solvents.[31] Nevertheless, the T structure **5** with four benzenoid rings located at the tetrahedral corners of the cage is one of the most stable $C_{60}H_{36}$ isomers.[6−14,16,35,36]

A major advance in the identification of fullerene derivatives was achieved when it was reported[37] that ^{3}He can be introduced into C_{60} and C_{70} by heating the fullerenes at 620 °C under high helium pressure. Because ^{3}He is an excellent NMR nucleus with a spin of 1/2 and a high gyromagnetic ratio,[38] the ^{3}He NMR spectrum of each product will yield a single sharp peak, and no nonfullerene products or impurities will give signals.[37] Bühl, Thiel, and Schneider[35] have suggested that ^{3}He labeling and NMR, assisted by computation of the ^{3}He chemical shifts, might provide new information concerning the nature of highly reduced C_{60} formed either by dissolving metal reductions or by transfer hydrogenation.

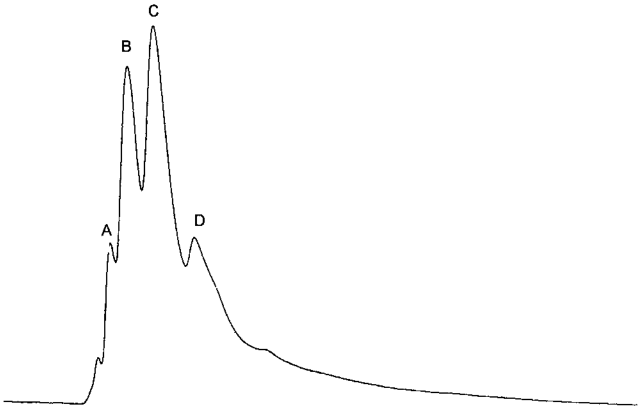

Figure 2. HPLC chromatogram of the products from the Birch reduction of C_{60}.

^{3}He NMR spectra of the crude product from the lithium Birch reduction have been reported.[4] Signals were observed at δ_{He} = −7.7 and −7.8 ppm. A comparison with the endohedral NMR shifts computed by Bühl and co-workers[35] at the GIAO-SCF/tzp(He),dz(C,H)//SCF/3-21G level for five isomers of $^3He@C_{60}H_{36}$ suggested that the major product was D_{3d} $C_{60}H_{36}$ isomer **2** that was predicted to exhibit a signal at −7.7 ppm. The less intense signal at −7.8 ppm most closely matched S_6 $C_{60}H_{36}$ isomer **3** that was calculated to appear at −6.1 ppm, although Billups and co-workers[4] noted that the less intense signal at −7.8 ppm might result from a structure not previously considered. However, subsequent results have shown that the major isomers decompose in the solvent (carbon disulfide) that was used to secure these spectra. In this paper, we present an account of our recent work in this area.

Results and Discussion

Birch Reduction. The mixture of hydrogenated fullerenes obtained from the Birch reduction of C_{60} has been separated and purified by high-pressure liquid chromatography in quantities suitable for spectral investigation (Figure 2). Mass spectra of the purified fractions showed that $C_{60}H_{36}$ is the only component in the major B and C bands. The small A band is a mixture of $C_{60}H_{38}$ and $C_{60}H_{40}$. The broad D band contained a small amount of $C_{60}H_{32}$ along with $C_{60}H_{36}$. The distribution of products did not change when the reaction time was extended to 24 h.

The ^{1}H NMR spectra of bands B and C are presented in Figures 3 and 4, respectively. These broad, nearly featureless spectra could be reproduced over the course of several syntheses and purifications. No rearrangement or isomerization could be detected at −100 °C, because the ^{1}H NMR spectra retained the same features that were observed at room temperature. These results are consistent with our calculations at the B3LYP/6-31G* level of theory (see Technical Methods section) that estimate a barrier of ~100 kcal mol^{-1} for each of two [1,2]-H

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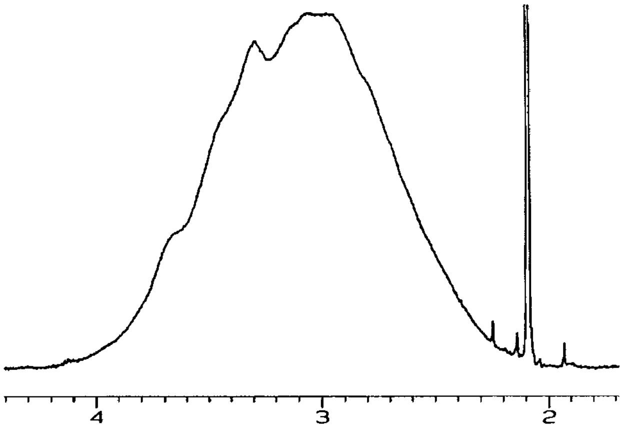

Figure 3. ^{1}H NMR spectrum (400 MHz, *o*-$C_6D_4Cl_2$) of $C_{60}H_{36}$, band B. The signal at 2.09 ppm arises from residual toluene.

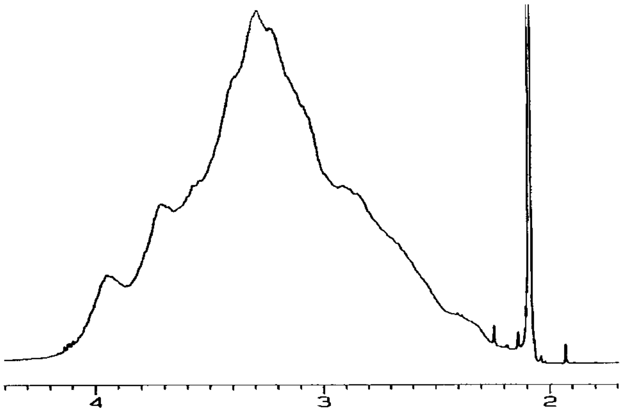

Figure 4. ^{1}H NMR spectrum (400 MHz, *o*-$C_6D_4Cl_2$) of $C_{60}H_{36}$, band C. The signal at 2.09 ppm arises from residual toluene.

shifts for isomerizing a double bond via a diradical intermediate to an adjacent position in a typical $C_{60}H_{36}$ isomer.

The ^{13}C NMR and DEPT-135 ^{13}C NMR spectra of band B could not be obtained in solution because of decomposition of the sample during the long acquisition time. Band C exhibited a broad signal at 20−40 ppm in both experiments. Broad signals for the sp^2- and sp^3-hybridized carbons have been previously observed in a ^{13}C spectrum of $C_{60}H_{36}$ prepared by the Birch reduction of C_{60}.[28]

Because the hydrides are moderately stable in the solid state, it was possible to obtain solid state ^{13}C NMR spectra of bands B and C. These are presented in Figures 5 and 6, respectively. Although the broad signal observed in the sp^3 region of each sample offered little information, the sp^2 region of each sample shows at least three overlapping signals whose relative intensities clearly differ in samples B and C. The spectrum of band C is somewhat similar to the one published previously by Attalla and co-workers that was found to be consistent with D_{3d} symmetry.[24,33]

^{3}He NMR spectra of samples obtained from Birch reduction of He@C_{60} and isolated by preparative HPLC were obtained for bands A−D (Figure 2). *o*-Dichlorobenzene-d_4 proved to be a superior solvent for this work, since extensive decomposition that was observed in our earlier[4] work using carbon disulfide can be avoided when *o*-dichlorobenzene-d_4 is used. In addition, fullerene hydrides exhibit greater solubility in this solvent than in other common solvents.

The ^{3}He NMR spectra of the purified fractions gave slightly broadened, but distinctly different, signals for each band (Figure 7a−d). Band A (^{3}He@$C_{60}H_{38}$/^{3}He@$C_{60}H_{40}$) gave a weak signal at $\delta_{He} = -3.2$ to -4.0. Bands B (^{3}He@$C_{60}H_{36}$) and C (^{3}He@$C_{60}H_{36}$) gave broad signals at $\delta_{He} = -4.6$ to -5.8 and $\delta_{He} = -6.0$ to -6.8, respectively, and the spectrum of band D (^{3}He@$C_{60}H_{32}$/^{3}He@$C_{60}H_{36}$) was observed at $\delta_{He} = -7.6$ to -8.4.

The broad signals observed are most probably due to the presence of several isomers that elute under each band. The broad signals for bands B and C are consistent with the broad, nearly featureless ^{1}H spectra (Figures 3 and 4). Alternatively, decomposition of the sample during acquisition could lead to new compounds, which might broaden the signals. Broadening of the NMR signals might also be observed if the decomposition should result in the formation of paramagnetic products.[39]

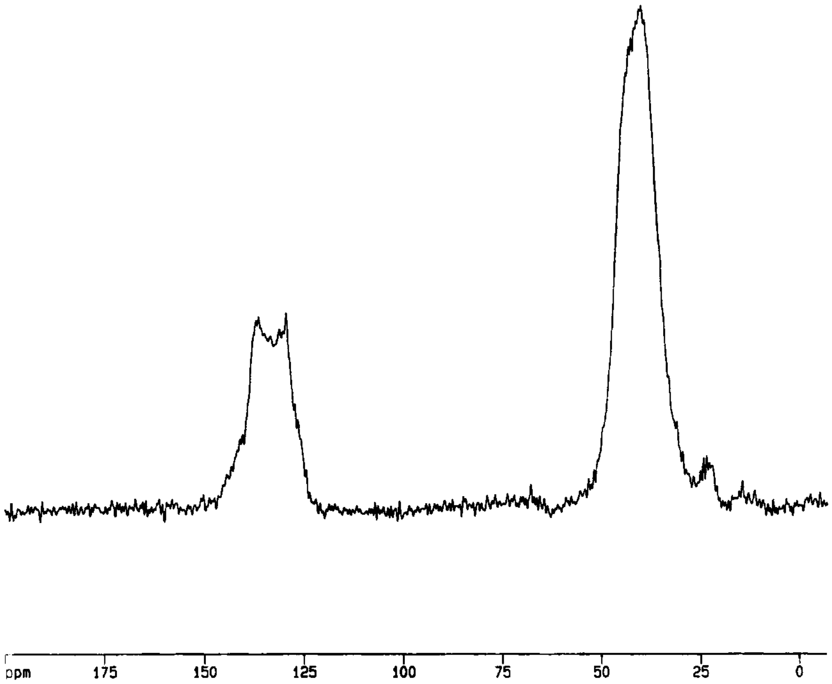

Figure 5. Solid state ^{13}C NMR (50 MHz) spectrum of Birch reduction band B.

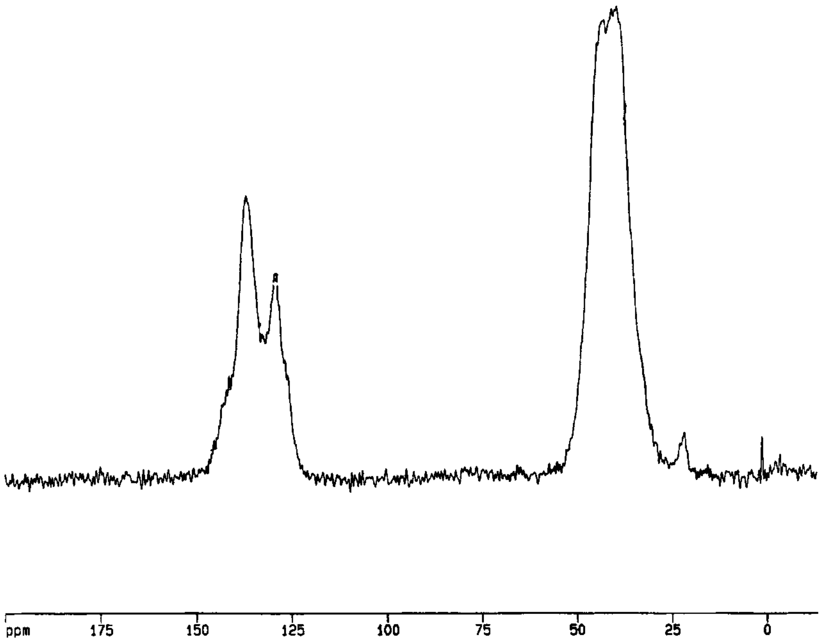

Figure 6. Solid state ^{13}C NMR (50 MHz) spectrum of Birch reduction band C.

Table 1. Relative Energies (in kcal mol^{-1}) of $C_{60}H_{36}$ and He@$C_{60}H_{36}$ Isomers at Various Levels of Theory

isomer[a]	AM1[14]	HF/3-21G	B3LYP/3-21G	B3LYP/6-31G*	B3LYP/tzp(He),DZP(C,H)[b]
	$C_{60}H_{36}$	$C_{60}H_{36}$	$C_{60}H_{36}$	$C_{60}H_{36}$	He@$C_{60}H_{36}$
2 (1), D_{3d}	11.6	21.1	17.5	16.7	16.4
3 (91), S_6	13.2	28.7	21.9	19.6	17.5
5 (2), T	12.4	−0.8	−9.5	−14.9	−12.5
6 (74), C_2	5.4	7.4	6.8	6.1	6.0
7 (88), S_6	0	0	0	0	0
8 (90), C_3	8.3	20.6	16.3	14.4	13.8
9 (64), C_3	4.6	−2.8	−7.3	−9.7	−8.1
10 (3), C_3	not listed	49.0	36.4	30.7	29.4
11 (65), C_3	14.8	18.9	9.6	5.5	5.3
12 (75), C_3	13.5	28.3	29.8	30.2	28.7
13 (78), C_1	14.7	35.0	34.8	34.1	32.1
14, C_1	not listed	22.7	13.8	10.0	not yet available
15, C_1	not listed	7.3	0.8	−2.3	not yet available

[a] Clare-Kepert isomer numbers (ref 14) are given in parentheses. Molecular point group symmetries are also given. [b] Using the optimized B3LYP/6-31G* geometry.

Lobach has reported that $C_{60}H_{36}$ obtained by reduction of C_{60} with dihydroanthracene is ferromagnetic.[13]

To facilitate the experimental identification, we computed the structure, energies, and ^3He chemical shifts of 13 $C_{60}H_{36}$ and He@$C_{60}H_{36}$ isomers (see Theoretical Methods section for technical details). A similar approach, albeit with a smaller set of $C_{60}H_{36}$ isomers and at a lower level of theory, was reported previously by Bühl et al.[35] and by Boltalina et al.[40] We studied those 10 $C_{60}H_{36}$ forms found to be most stable by Clare and Kepert at the AM1 level of theory. In addition, we also included the C_3 symmetry isomer previously studied by Boltalina and co-workers[40] and two additional isomers with C_1 symmetry. In agreement with earlier ab initio computations,[7,16,35] but at variance with the AM1 results of Clare and Kepert,[14] we find that the T isomer **5** is the lowest energy $C_{60}H_{36}$ species considered here (Table 1). Whereas the 10 most stable isomers lie within 15 kcal mol^{-1} at the AM1 level, the difference between the T form and the least stable $C_{60}H_{36}$ considered here is 49 kcal mol^{-1} at the B3LYP/6-31G* level of theory.

The geometry obtained for the T isomer at B3LYP/6-31G* is similar to those reported earlier.[35] In particular, the elongated C—C bonds (1.638 Å) are a characteristic of this isomer. The energetic penalty for stretching these bonds is compensated by the aromatic stabilization energy of the four aromatic rings making this isomer very energetically competitive.

Comparison of the ^3He NMR shifts of the different bands with computationally determined values (Table 2) proved to be particularly informative. Isomers with computed (B3LYP/tzp-(He),DZP(C,H))//B3LYP/6-31G*) ^3He NMR shifts that fall into the range observed for band B (−4.6 to −5.8 ppm) are S_6 **3**, C_2 **6**, S_6 **7**, and C_3 **8** (Figure 1). The calculated shifts for these four isomers are $\delta_{He} = -4.7, -5.1, -5.0$, and -4.9, respectively (Table 2).

Two benzene rings are a common feature of isomers **3**, **6**, **7**, and **8**. Both **7** and **3** 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 perpendicular, as in isomer **3**. The S_6 $C_{60}H_{36}$ **3** has been reported to be one of the $C_{60}H_{36}$ isomers formed by the dihydroanthracene reduction of C_{60}.[30,31] Isomer **6** is structur-

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(39) Brown, D. W.; Floyd, A. J.; Sainsbury, M. *Organic Spectroscopy*; John Wiley and Sons: New York, 1988, p 87.

(40) Boltalina, O. V.; Bühl, M.; Khong, A.; Saunders, M.; Street, J. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1475.

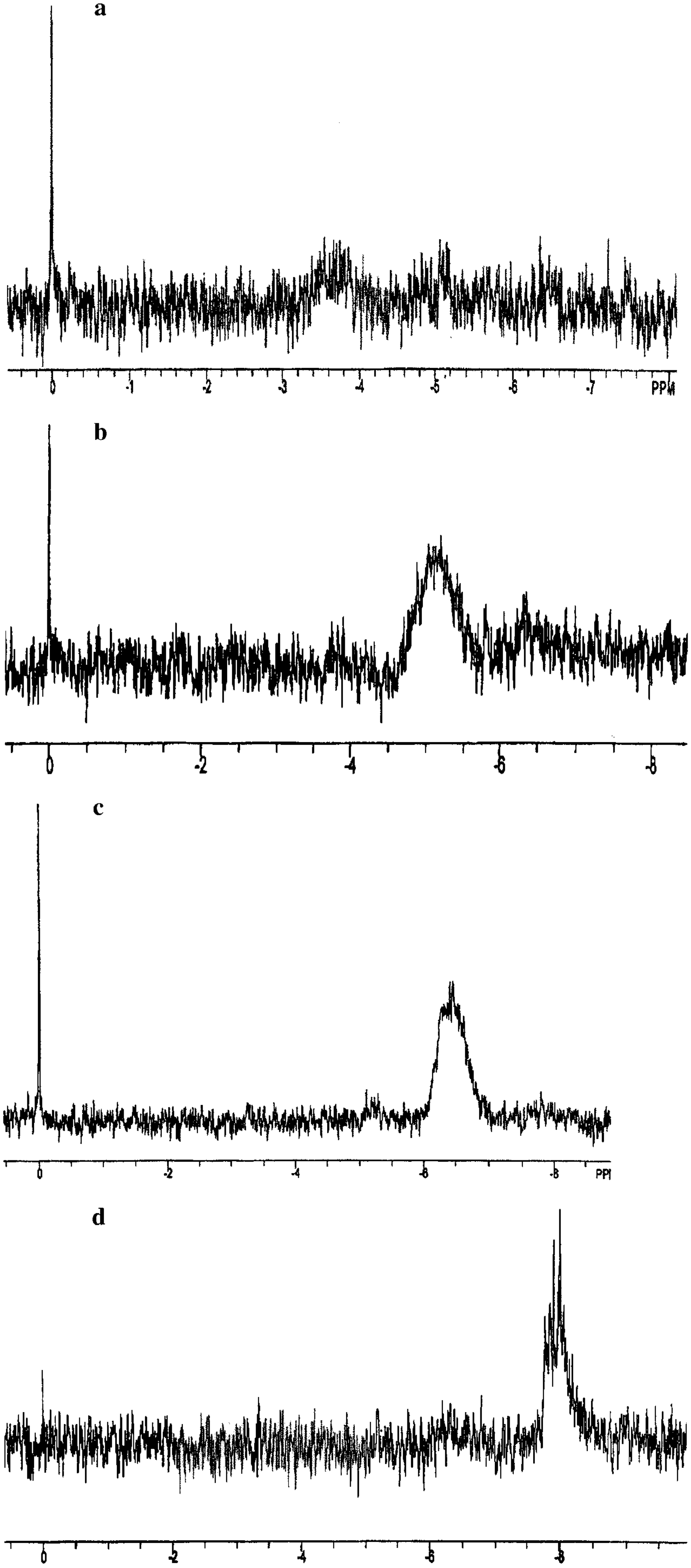

Figure 7. (a) ^{3}He NMR spectrum of band A. (b) ^{3}He NMR spectrum of band B. (c) ^{3}He NMR spectrum of band C. (d) ^{3}He NMR spectrum of band D.

Table 2. ^{3}He NMR Chemical Shifts (ppm Relative to Free ^{3}He) for ^{3}He@$C_{60}H_{36}$ Isomers Calculated at Various Levels of Theory

isomer	GIAO-SCF/tzp(He) DZ(C,H)//3-21G[35]	GIAO-BPW91/tzp(He) DZP(C,H)//3-21G[40]	GIAO-B3LYP/tzp(He) DZP(C,H)[a]
1	−3.4	n/a	n/a
2	−7.7	−6.1	−6.1
3	−6.1	n/a	−4.7
4	−5.6	n/a	n/a
5	−10.8	−8.8	−8.8
6	n/a	n/a	−5.1
7	n/a	n/a	−5.0
8	n/a	n/a	−4.9
9	−9.0[40]	−7.4	−6.8
10	−8.5[40]	−7.0	−6.9
11	n/a	n/a	−6.3
12	n/a	n/a	−3.4
13	n/a	n/a	−3.6

[a] Current work using the optimized B3LYP/6-31G* geometry.

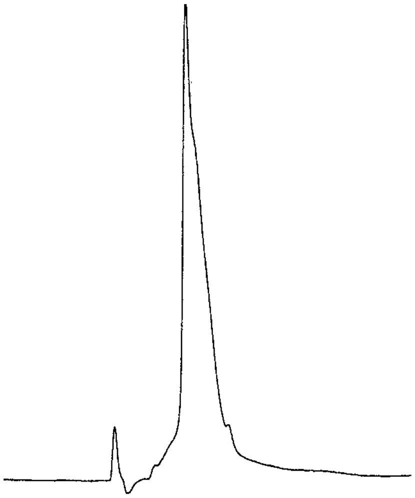

Figure 8. HPLC chromatogram of purified band C showing a trailing shoulder. The small band to the left of the main band is a solvent peak.

ally similar to the celebrated *T* $C_{60}H_{36}$ **5** isomer in which two of the four benzenoid moieties present in **5** have been converted to 1,3,5-C_6H_3 rings.

The ^{3}He NMR shift of band C (−6.0 to −6.8 ppm) is in agreement with the values calculated for D_{3d} $C_{60}H_{36}$ **2** ($\delta_{He} = -6.1$), for C_3 $C_{60}H_{36}$ **9** ($\delta_{He} = -6.8$), and for C_3 $C_{60}H_{36}$ **11** ($\delta_{He} = -6.3$) (Figure 1). After purification, the HPLC chromatogram of band C (Figure 8) showed a trailing shoulder, which indicates that at least two isomers elute under this band.

Although $C_{60}H_{36}$ appeared to be the major component of band D, the mass spectrum shows the presence of hydrides other than $C_{60}H_{36}$. The observed $\delta_{He} = -8.1$ shift of band D most closely matches the $\delta_{He} = -8.8$ shift predicted at two levels of theory for *T* $C_{60}H_{36}$ **5**. If this assignment is correct, it would confirm the prediction that hydrogenation and fluorination of C_{60} favor isostructural products, because *T* $C_{60}F_{36}$ **5** has been identified as a minor $C_{60}F_{36}$ isomer.[40] *T* $C_{60}H_{36}$ **5** has also been proposed for $C_{60}H_{36}$ obtained by the Zn/HCl reduction of C_{60}.[21,22] 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 Birch band D. Its calculated ^{3}He NMR shift (Table 2) is $\delta_{He} = -6.9$. Note that **10** is significantly less stable than **5** (46 kcal mol^{-1}), according to our B3LYP/6-31G* computations.

The tentative assignments have been summarized in Table 3. The breadth of the ^{3}He signals suggests that many compounds are actually present in each band. For band D, several sharp signals are also clearly evident above the broad hump. In contrast, previously published ^{3}He NMR spectra of ^{3}He@$C_{60}H_{36}$ obtained using the crude product from both the Birch reduction and dihydroanthracene reduction of ^{3}He@C_{60} produced two sharp signals at $\delta_{He} = -7.7$ and −7.8.[4] These are approximately the same shifts as observed for the relatively broad Birch reduction band D, with any difference in chemical shift attributable to the use of a 1:1 C_6D_6:CS_2 solution in the earlier work. An attempt to obtain ^{3}He NMR spectra of Birch reduction band B with a C_6D_6:CS_2 NMR solvent produced no signal at all, a phenomenon that was attributed to decomposition of the sample during the 10-h acquisition time.

Table 3. Predicted and Experimentally Observed ^{3}He NMR Chemical Shifts (ppm Relative to Free ^{3}He) for C_{60} Birch Reduction Products

band	obs ^{3}He chem shift	tent. assignment	predicted ^{3}He chem shift
A	-3.6, $\Delta\delta = 0.8$	$C_{60}H_{38}$, $C_{60}H_{40}$	n/a
B	-5.2, $\Delta\delta = 1.2$	**6**, **7**, **8**, **3**	−5.1, −5.0, −4.9, −4.7
C	-6.4, $\Delta\delta = 0.8$	**2**, **9**, **11**	−6.1, −6.8, −6.3
D	-8.0, $\Delta\delta = 0.8$	**5**, **10**	−8.8, −6.9

Dihydroanthracene Reduction. We also reduced C_{60} by the Rüchardt procedure[25] (9,10-dihydroanthracene, DHA) and compared the products with those from the Birch reduction. The HPLC chromatogram of the product mixture is shown in Figure 9.

The bands labeled 1−3 were isolated by HPLC and identified as isomers of $C_{60}H_{36}$ by mass spectroscopy. The major component (band 2) was found to coelute with band D from the Birch reduction (Figure 2). Thus, the major product from the dihydroanthracene reduction can be only a minor constituent of the Birch reduction. Similarly, Rüchardt and co-workers had previously concluded that their work clearly demonstrated that different methods of synthesis prepare quantitatively different mixtures of isomers of $C_{60}H_{36}$.[30,31] In addition, when Mittal and co-workers[41] compared the spectroscopic properties of $C_{60}H_{36}$ prepared by Zn/HCl reduction against the spectroscopic properties of $C_{60}H_{36}$ that Rüchardt and co-workers[30] had prepared by transfer hydrogenation, many differences were apparent that could reasonably be attributed to isomers having different symmetries forming via the two procedures.

The ^{3}He NMR spectrum of band 2 (contaminated with 2% band 3) isolated by preparative HPLC is shown in Figure 10. In marked contrast to the broad signals in the ^{3}He NMR spectra of the Birch reduction products (Figure 7), two sharp signals are observed at δ_{He} −8.014 and −8.139 (ratio 3:1) in the ^{3}He NMR spectrum of band 2 of the dihydroanthracene reduction products. Accordingly, just two $C_{60}H_{36}$ isomers in a 3:1 ratio

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[41] Palit, D. K.; Mohan, H.; Mittal, J. P. *J. Phys. Chem. A* **1998**, *102*, 4456.

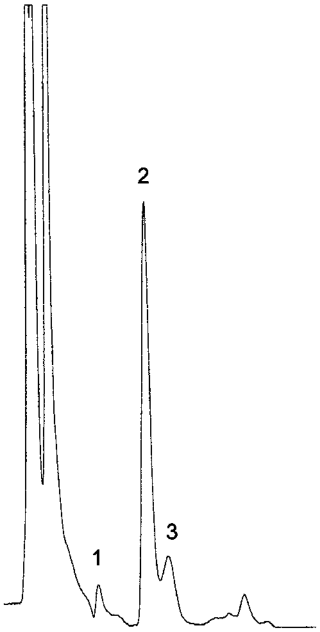

Figure 9. HPLC chromatogram of crude C_{60} dihydroanthracene reduction product mixture. The two large leading bands are due to solvent and residual dihydroanthracene and anthracene.

appear to be present. The similarity of these two ^{3}He signals to the two signals reported earlier[4] suggests that the same two isomers are responsible for the signals in each case.

The ^{13}C NMR spectrum of band 2 of the dihydroanthracene reduction products reveals 32 sp^2-hybridized carbon signals and 48 sp^3-hybridized carbon signals for the solute, with all 80 solute signals having a similar intensity (Figure 11).

This spectrum was obtained in 5.9 h after 1800 scans with a 30° ^{13}C pulse, a 6.76-s FID, and a 5-s relaxation delay with decoupling to maximize NOE and S/N (rather than with a substantially longer relaxation delay without decoupling to attenuate NOE for more accurate relative signal intensities, provided that enough scans are taken for adequate S/N). *The observation of 80 solute signals of similar intensity severely limits the types of isomers that might be present.* (Highly expanded plots showing most of the 80 solute signals and their chemical shifts are provided in the Supporting Information.)

Prior work has clearly shown the need to approach the interpretation of spectra of derivatized fullerenes with an open mind (i.e., not with the expectation that a particular isomer will be present) and to be sure that the number of signals observed is consistent with the symmetry point group of the proposed isomer(s) in order to avoid drawing conclusions[42] that later have to be revised.[43]

The possibility of a D_{3d} or T_h isomer being present can be immediately excluded, because a D_{3d} isomer would give six signals in a 12:12:12:12:6:6 ratio for the two sp^2-hybridized and four sp^3-hybridized carbons, but a T_h isomer would give three signals in a 24:24:12 ratio for the sp^2-hybridized and two sp^3-hybridized carbons.[35] Although a T isomer would give 5 signals of equal intensity and a S_6 isomer would give 10 signals of equal intensity,[35] neither isomer seems to be present, because it is not then possible to reasonably account for the remaining signals. Specifically, the presence of the T isomer **5** would require assigning the remaining 30 sp^2-hybridized and 45 sp^3-hybridized carbon signals for the solute, with all 75 signals having a similar intensity, but no set of $C_{60}H_{36}$ isomers appears to satisfy this constraint; the ^{3}He NMR spectrum imposes the further constraint that just two isomers appear to be present in a 3:1 ratio. Similarly, the presence of the S_6 isomer either **3** or **7** would require assigning the remaining 28 sp^2-hybridized and 42 sp^3-hybridized carbon signals for the solute, with all 70 signals having a similar intensity, but again, no set of $C_{60}H_{36}$ isomers appears to satisfy this constraint, let alone the constraint imposed by the ^{3}He NMR spectrum.

Four different isomers of C_3 symmetry could account for the ^{13}C NMR spectrum (4 × 8 sp^2-hybridized carbon signals and 4 × 12 sp^3-hybridized carbon signals), but this would require that all four isomers be essentially equally abundant and that three of the four isomers have the same ^{3}He chemical shift. The well-known extraordinary sensitivity of ^{3}He chemical shifts to the structure of the fullerene in which the ^{3}He atom is trapped[4,37f,40] makes it extremely unlikely that three isomers will all exhibit the same ^{3}He chemical shift. Furthermore, all four isomers would have to be essentially equally abundant to satisfy the ^{13}C spectrum. (Also note that in interpreting the ^{19}F spectrum of $C_{60}F_{36}$, others had similarly concluded that there was an exceedingly low probability that four components would be present in amounts that would give equal intensities for each line in the ^{19}F NMR spectrum).[43]

In contrast, one isomer with C_1 symmetry (24 sp^2-hybridized carbon atoms and 36 sp^3-hybridized carbon atoms) and one isomer with C_3 symmetry (8 sp^2-hybridized carbon atoms and 12 sp^3-hybridized carbon atoms) present in a 3:1 ratio would account for both the ^{3}He and ^{13}C spectra.

Highly congested regions are evident in the ^{13}C spectrum. Indeed, three pairs of ^{13}C signals differ by no more than 5 ppb (digital resolution of FID = 1.2 ppb, digital resolution = 0.6 ppb after zero-filling once). Very high field homogeneity and very high digital resolution are required to detect such small differences.[44] Of the 32 solute signals for sp^2-hybridized carbons, four are rather shielded (at δ 122.40, δ 123.03, δ 124.52, and δ 125.35) when compared to the other 28 signals at δ 133.60 and further downfield. Perhaps the four rather upfield signals result from four isolated double bonds (one C=C in the C_3 symmetry isomer and three C=C in the isomer with C_1 symmetry).

The 500 MHz ^{1}H spectrum of the $C_{60}H_{36}$ sample (band 2) prepared by DHA reduction is shown in Figure 12. This spectrum exhibits a level of spectral detail considerably greater than that previously reported at an unspecified field strength for a sample of $C_{60}H_{36}$ that was prepared by catalytic hydrogenation of C_{60} over Pd/C in toluene;[45] however, the overall similarity of the spectra obtained by the two groups is obvious. While Sui and co-workers[45] did not propose any structures, the spectral similarity suggests that catalytic hydrogenation[45] and dihydroanthracene reduction yielded very similar products. The level of spectral detail shown in the 500 MHz spectrum (Figure 12) is far greater than that previously shown[12,21,26−28] or indicated[1,22,25,46] in ^{1}H spectra of other samples of $C_{60}H_{36}$. The instability of solutions of $C_{60}H_{36}$ isomers, even under an inert atmosphere, has frequently been noted. For example, previous work[21] has noted that solutions of $C_{60}H_{36}$ in CS_2 produced a

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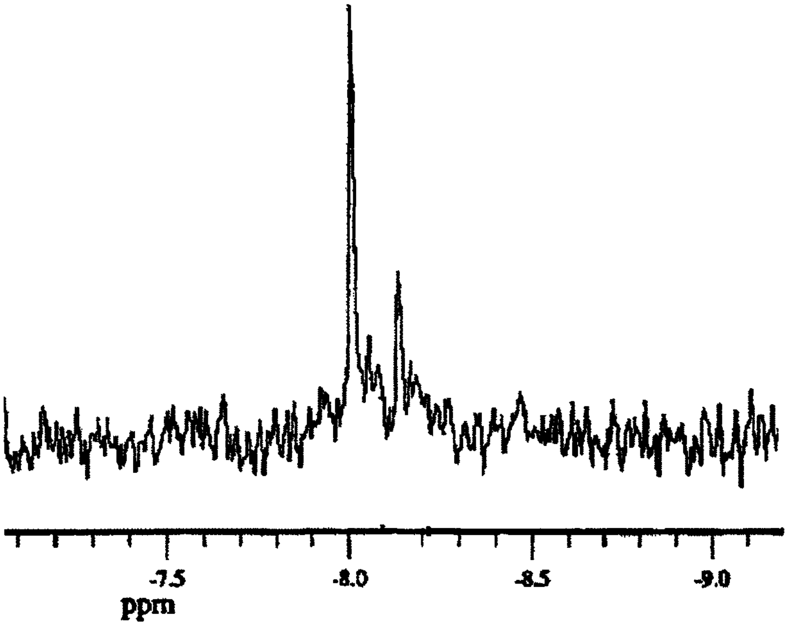

Figure 10. ^{3}He NMR spectrum of band 2 (contaminated with 2% band 3) of the dihydroanthracene reduction of C_{60}.

black precipitate within 5−10 min in air and within 30 min under nitrogen; even if the sample is sealed under nitrogen, the authors noted that the spectra have to be obtained immediately. In contrast, the $C_{60}H_{36}$ isomers from the DHA reduction, as well as the minor products from the Birch reduction, exhibit much greater stability with regard to decomposition in solution. A spectrum identical to that in Figure 12 was obtained several weeks later; this sample of $C_{60}H_{36}$ appears to be stable, unlike many previous samples.

Even a cursory examination of Figure 12, of ^{1}H spectra of other samples containing predominantly $C_{60}H_{36}$,[12,21,26−28] and of the ^{1}H chemical shifts for $C_{60}H_{18}$[47] indicates that the protons in $C_{60}H_{36}$ and $C_{60}H_{18}$ are significantly deshielded, as compared to their counterparts in "ordinary" organic molecules. For example, the benzhydrylic protons in $C_{60}H_{18}$ give a signal at δ 4.49, which is at least 0.5 ppm downfield of benzhydrylic protons in typical organic molecules. Even more noteworthy is the observation that the $C_{60}H_{18}$ protons beta to three benzene rings give a signal at δ 3.95, just 0.20 ppm upfield of the signal from the benzylic (acenaphthene-like) protons and 0.50 ppm *downfield* of other benzylic protons. Subsequent calculations by Taylor and co-workers[48] indicated that three relatively long C—C bonds averaging 1.588 Å are associated with the β proton in $C_{60}H_{18}$. (In contrast, the calculated average C—C bond lengths for the benzhydrylic and two benzylic sites are 1.531, 1.568, and 1.551 Å.) This difference in calculated average C—C bond lengths associated with the β and non−β protons has also been noted by Taylor and co-workers[48] and by us for C_3 $C_{60}H_{36}$ **10** and C_3 $C_{60}H_{36}$ **9** (Table 4). Invariably, the β protons have a considerably longer calculated average C—C bond length.

We believe that the exceptionally deshielded β proton signal in $C_{60}H_{18}$ (δ 3.95) results from the relatively long C—C bonds associated with it in a molecule with substantial conformational rigidity. The observed (isotropic) chemical shift δ_{iso} is the average of the three principal values of the chemical shift tensor: $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. The three principal values lie along three mutually perpendicular directions in space. Thus, if one or more of the principal values are unusually deshielded, this will be reflected in the observed chemical shift. The chemical shift tensor is well-known to be sensitive to local structure; modest changes in bond distances and bond angles can lead to variations in the calculated principal values of the chemical shift tensor and, therefore, in the isotropic chemical shift.[49] Thus, lengthening the C—C bonds associated with the β proton would change the electronic environment around this proton, thereby changing its chemical shift. Indeed, a calculated structure for $C_{60}H_{18}$ is not at all spherical.[48] Rather, the calculated structure is nearly flat around the central benzene ring surrounded by the "crown" of CH units.[48]

Preliminary calculations of ^{1}H chemical shifts in $C_{60}H_{36}$ **9** and $C_{60}H_{36}$ **10** also indicate that exceptionally deshielded β proton signals are associated with sites having relatively long C—C bonds. These preliminary calculations indicate that the four sites with calculated average C—C bond lengths of 1.596−1.604 Å (Table 4) should have chemical shifts from 3.8 to 4.0 ppm, and the three sites with calculated average C—C bond lengths of 1.581−1.589 Å should have chemical shifts from 3.1 to 3.4 ppm. Substantial intensity is observed in each of these regions (Figure 12). Additional calculations of C—C bond lengths and ^{1}H chemical shifts in other $C_{60}H_{36}$ isomers are planned to determine if any other isomers of $C_{60}H_{36}$ can be expected to exhibit unusually deshielded proton signals.

The unusually deshielded benzhydrylic and acenaphthene-like benzylic proton signals in $C_{60}H_{18}$ (δ 4.49 and δ 4.15), the exceptionally deshielded β proton signal in $C_{60}H_{18}$ (δ 3.95), and our preliminary chemical shift calculations for some isomers of $C_{60}H_{36}$ clearly indicate that the spectrum of $C_{60}H_{36}$ (Figure 12) cannot be interpreted by considering the proton chemical shifts exhibited by "ordinary" organic compounds. Of course, that our sample apparently contains a mixture of an isomer with C_1 symmetry and an isomer with C_3 symmetry in a 3:1 ratio enormously complicates any attempt at interpreting the ^{1}H spectrum. A recent compilation of chemical shift tensors does not include any chemical shift tensor information for aliphatic

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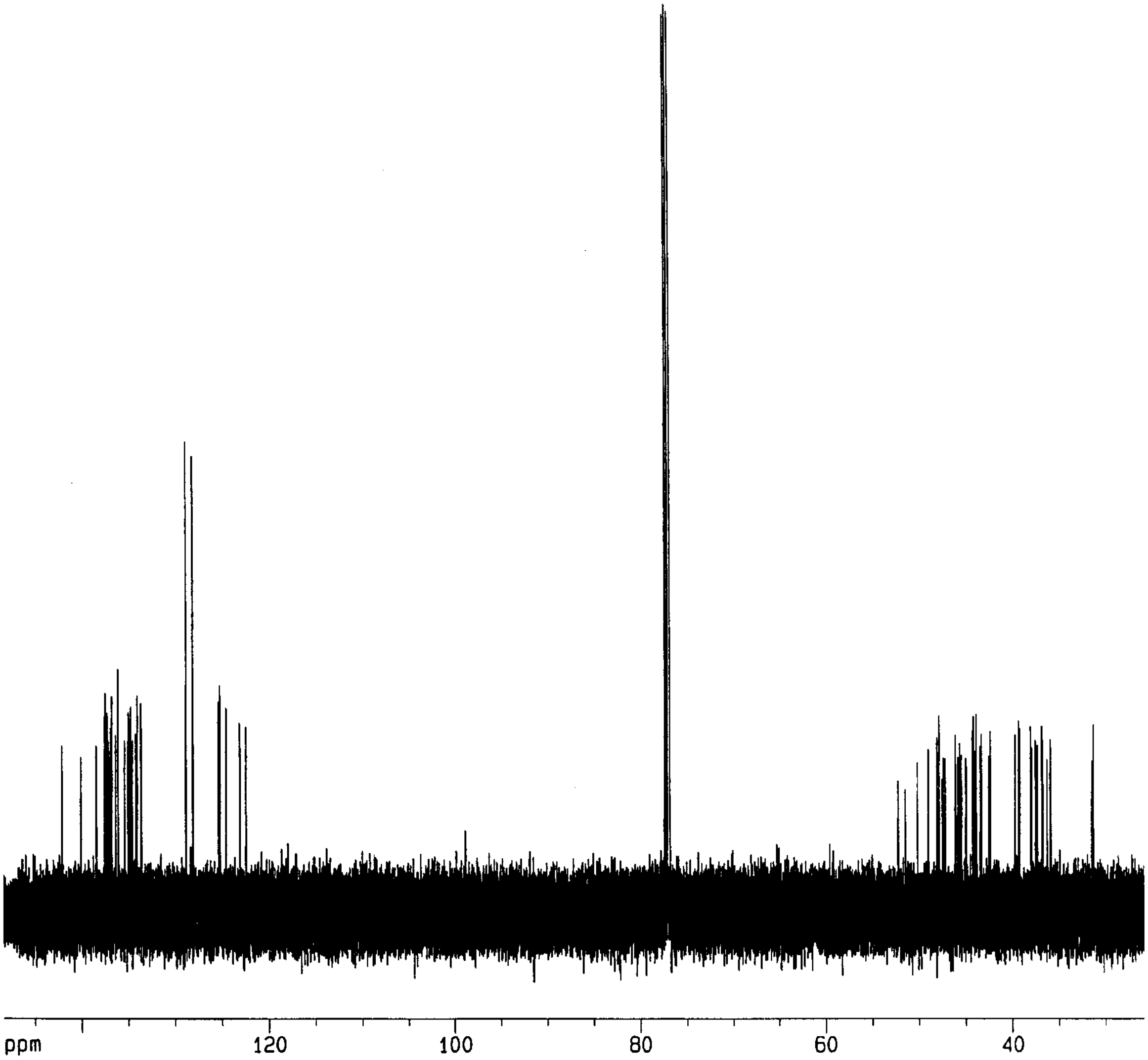

Figure 11. Expanded plot of the 126 MHz ^{13}C NMR spectrum of band 2 of the dihydroanthracene reduction of C_{60}. The sample was dissolved in 3:1 CS_2:$CDCl_3$ containing TMS, repeatedly degassed (freeze−pump−thaw cycles) on a vacuum line, sealed, and then kept in the dark prior to NMR analysis. The three most intense sp^2-hybridized carbon signals result from residual toluene (as does as the quaternary signal at δ 137.483) used in the HPLC purification.

methine protons.[50] In this context, it is interesting to note that significantly deshielded proton signals have been observed not only for $C_{60}H_{18}$ and $C_{60}H_{36}$, but also for dodecahedrane (δ 3.38[51]), methyldodecahedrane (a broad singlet also at δ 3.38 for the 16 protons not adjacent to the methyl group[52]), and the closely related secododecahedrane (a series of multiplets from δ 3.5 to δ 2.9 for the methine protons[51]). The dodecahedranes, $C_{60}H_{18}$, and $C_{60}H_{36}$ all have substantial conformational rigidity, but dodecahedrane does not have unusual C—C bond lengths and bond angles.[53] Thus, a different explanation is needed for its exceptionally deshielded proton signal. The range of ^1H chemical shifts for the methine protons in secododecahedrane[51] clearly demonstrates the great sensitivity of ^1H chemical shifts to small structural perturbations in a compound with substantial conformational rigidity.

Extensive calculations of the relative energies, C—C bond lengths, and chemical shifts of different isomers of $C_{60}H_{36}$ with C_3 symmetry and with C_1 symmetry (presumably differing in the position of one or two of the isolated double bonds, as in the series C_3 **10**, C_1 **14**, C_1 **15**, C_3 **9**) will be required to try to find isomers that could reasonably be expected to give the observed ^1H spectrum. For example, preliminary calculations indicate that

- the ^3He chemical shifts differ by only 0.2 ppm (cf. the observed 0.1-ppm difference, Figure 10) for the C_3 and C_1 symmetry isomers **9** and **15**;
- these two calculated ^3He shifts are only 1 ppm more deshielded than the observed signals; and
- only the *T* isomer **5** has a lower energy than isomers **9** and **15** (Table 1).

However, although C_3 and C_1 symmetry isomers **9** and **15** may be promising candidates, such calculations need to be performed on many more isomers. In addition, the calculated ^1H chemical shifts and potential coupling patterns need to be compared against those actually observed (see below). As Jameson has noted, nuclear magnetic shielding, a second-order molecular electronic property, provides a severe test of the accuracy of molecular quantum mechanical predictions.[54]

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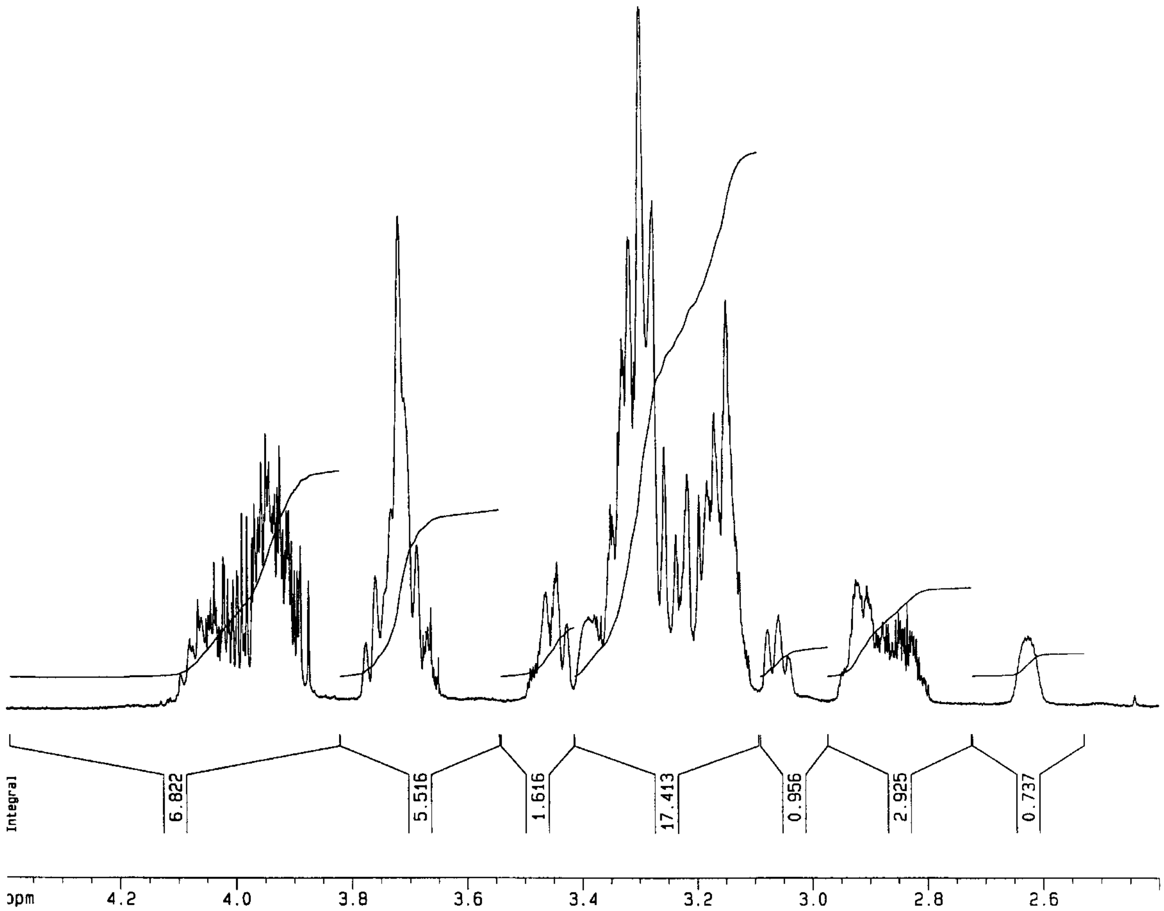

Figure 12. Expanded plot of the 500 MHz ^{1}H NMR spectrum of band 2 of the dihydroanthracene reduction of C_{60}. The same sample was used to obtain Figure 11.

Table 4. Calculated Average C—C Bond Lengths in C_3 $C_{60}H_{18}$, C_3 $C_{60}H_{36}$ **10**, and C_3 $C_{60}H_{36}$ **9**

type of proton	no. of such protons	calcd ave C—C bond length Å
	$C_{60}H_{18}$	
beta to 3 benzene rings	1	1.588[a]
benzylic	3	1.531−1.568[a]
	$C_{60}H_{36}$ **10**	
beta to 2 benzene rings beta to 1 isolated C=C	1	1.586[a]
beta to 2 benzene rings	1	1.590[a]
beta to 1 benzene ring beta to 2 isolated C=C	1	1.580[a]
beta to 2 isolated C=C	1	1.574[a]
benzylic and/or allylic	8	1.521−1.558[a]
	$C_{60}H_{36}$ **10**	
beta to 2 benzene rings beta to 1 isolated C=C	1	1.596[b]
beta to 2 benzene rings	1	1.597[b]
beta to 1 benzene ring beta to 2 isolated C=C	1	1.589[b]
beta to 2 isolated C=C	1	1.581[b]
benzylic and/or allylic	8	1.530−1.567[b]
	$C_{60}H_{36}$ **9**	
beta to 2 benzene rings	2	1.604, 1.599[b]
beta to 1 benzene ring beta to 1 isolated C=C	1	1.589[b]
benzylic or allylic	9	1.525−1.567[b]

[a] Local spin density approximation with pseudopotentials, ref 48. [b] B3LYP/6-31G*, present work.

With the ^{3}He NMR signals for the two isomers differing by only 0.125 ppm, one can reasonably conclude that the two isomers are similar, and thus, extensive overlap of ^{1}H signals can certainly be expected. Indeed, for just a single isomer, particularly the isomer with C_1 symmetry, extensive overlap of ^{1}H signals could occur. Unfortunately, a method to separate the two isomers is not readily apparent. As a first step toward resolving signals and determining the identity of the two isomers that are present, we have obtained a 900 MHz ^{1}H spectrum (Figure 13) and 800 MHz COSY and TOCSY spectra (Supporting Information).

The 900 MHz spectrum differs significantly from that obtained at 500 MHz in the region upfield of 3.1 ppm; five signals in a very nearly 1:2:1:1:1 ratio become evident at 900 (or 800) MHz. Even at 500 MHz, the rather broad, upfield, symmetrical signal at δ 2.63 stands out because of its shape and its chemical shift; its intensity is consistent with either (1) 3 equivalent protons in the 25% abundant isomer with C_3 symmetry or (2) 1 of 36 protons in the 75% abundant isomer with C_1 symmetry. The correlations that are observed in the 800 MHz COSY spectrum, particularly those involving the well-resolved proton signals upfield of 3.1 ppm, will serve as a critical test of the chemical shifts calculated for the different protons in various isomers. The connectivity patterns for coupled spin systems observed in the 800 MHz TOCSY spectrum will serve as an additional test; obtaining TOCSY spectra with different spin lock times to follow the magnetization transfer pathway should allow the connectivity patterns to be more easily recognized.

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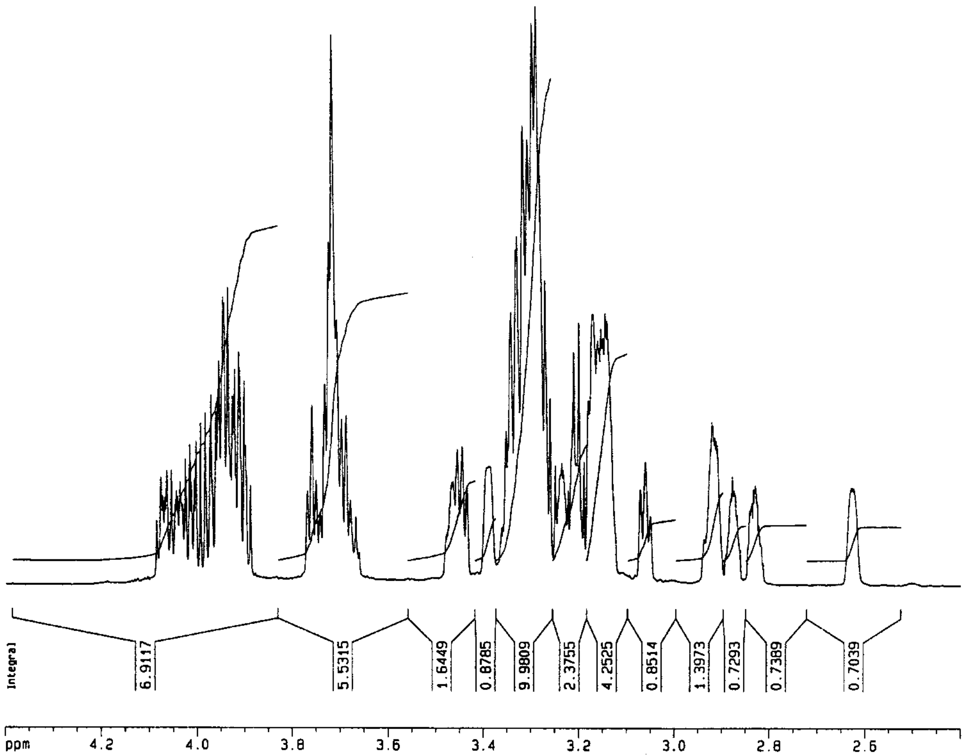

Figure 13. Expanded plot of the 900 MHz ^1H NMR spectrum of band 2 of the dihydroanthracene reduction of C_{60}. (The same sample was used to obtain the 11.7 T ^{13}C and ^1H spectra shown in Figures 11 and 12.)

Other preliminary attempts at obtaining a detailed understanding of the ^1H and ^{13}C spectra have been made by obtaining $^1H-^{13}C$ HSQC and HMBC spectra. The HSQC spectrum (optimized for $^1J_{CH} = 145$ Hz) clearly shows correlations between many of the most deshielded protons and many of the most deshielded aliphatic carbons. The HMBC spectrum (optimized for $^nJ_{CH} = 7.6$ Hz, i.e., a 65-ms delay for evolution of long-range couplings) clearly shows much stronger contours between sp^2-hybridized carbons and the most deshielded protons than between sp^2-hybridized carbons and the more upfield protons. Clearly, the relative intensities of the contours in the HSQC and HMBC spectra are sensitive to the time allowed for couplings to evolve, and thus, these preliminary HSQC and HMBC experiments should not be overinterpreted. At this point, the 1D ^{13}C and ^3He spectra are far more significant.

Numerous calculations,[6-11,14,16,35,36] particularly at higher levels of theory (e.g., Table 1), 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.[32] These calculations, the observation that a $C_{60}H_{36}$ isomer with C_1 symmetry is 75% abundant, and the absence of the long-expected[2,34,40] T $C_{60}H_{36}$ **5** all suggest that a significant energy barrier exists in the dihydroanthracene reduction of C_{60} 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%) for $C_{60}F_{36}$.[40] Calculations indicate that T $C_{60}F_{36}$ **5** is among the most stable $C_{60}F_{36}$ isomers.[11,14] (The remaining 75% of the $C_{60}F_{36}$ sample was assigned to the C_3 isomer **10**.)

Changing the position of one or two isolated double bonds in an isomer of $C_{60}H_{36}$ with a symmetry axis so as to generate a structure with C_1 symmetry does not necessarily raise the energy. The calculations by Clare and Kepert[14] indicate that the 9th- and 11th-lowest-energy isomers of $C_{60}H_{36}$ have C_1 symmetry. The ninth-lowest-energy isomer is **13**, which is the least stable isomer considered in this work (Table 1). Other calculations by Clare and Kepert[10] indicate that moving two of the isolated double bonds in two relatively high energy C_3 $C_{60}H_{36}$ isomers results in lower-energy isomers with C_1 symmetry. Note, though, that moving all three of the isolated double bonds in the C_3 $C_{60}H_{36}$ isomers considered by Clare and Kepert[10] would give still more stable structures **2** and **5**. For $C_{60}F_{36}$, the calculations by Clare and Kepert[14] have shown a case where the energy also decreases upon rearrangement (specifically, $C_{60}F_{36}$ isomers **76** and **79**, where the isomer **79** generated by an unsymmetrical shift of double bonds in T $C_{60}F_{36}$ **5** is calculated to be 10 kcal mol^{-1} more stable than the isomer **76** generated by a symmetrical shift of double bonds).

The major product from the dihydroanthracene reduction can be only a minor constituent of the Birch reduction. In light of the observations noted above by the Rüchardt[30,31] and Mittal[41] groups on different synthetic procedures yielding different mixtures of isomers of $C_{60}H_{36}$, one clearly can no longer assume that C_3 $C_{60}H_{36}$ **10** and T $C_{60}H_{36}$ **5** form in analogy to the C_3 $C_{60}F_{36}$ **10** and T $C_{60}F_{36}$ **5** generated upon fluorination with MnF_3.[40] We also note that Lobach[12] reached the conclusion that T $C_{60}H_{36}$ **5** is the major isomer produced in the dihydroanthracene reduction of C_{60}. Rüchardt and co-workers, however, have shown[30,31] that the composition of the mixture of products is dependent on the conditions employed during purification by sublimation. This indicates that prolonged heating of the product might lead to unreliable analysis.

Clearly, a combination of energy, bond length, and chemical shift calculations; 2D COSY and TOCSY ultrahigh-field ^1H spectra; and heteronuclear chemical shift correlation experiments to be done with unusually high digital resolution in the ^{13}C dimension are required for a more detailed interpretation. A 2D $^{13}C-^{13}C$ INADEQUATE experiment to determine the $^{13}C-^{13}C$ connectivity pattern for each isomer would be enormously helpful—provided that all the coupled nuclei are AX (rather than AB) pairs.[55] Obtaining such a spectrum with the very high digital

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[55] Hawkins, J. M.; Loren, S.; Meyer, A.; Nunlist, R. *J. Am. Chem. Soc.* **1991**, *113*, 7770.

resolution required in each dimension on just a few milligrams of this mixture would clearly present a formidable sensitivity challenge, even with the recent developments in cryogenic probe and preamplifier technology.[56]

Clearly, we cannot rule out the presence of any minor isomers for which signals are not readily detectable above the noise level in the ^{3}He and ^{13}C NMR spectra. Any such isomers would give detectable ^{1}H signals, but at this point, we have no way of recognizing them. The best way to pursue this matter would be to obtain ^{3}He and ^{13}C NMR spectra with much higher S/N.

Conclusion

We have shown that the Birch reduction gives a complex mixture of $C_{60}H_{36}$ isomers. The transfer hydrogenation method of Rüchardt gives mainly two in a 3:1 ratio. The isomers from the transfer hydrogenation route are found to constitute only a small part of the Birch product. Further work will be required to assign definitive structures to the products from the various methods that have been used to synthesize these hydrides. The synthesis of derivatives that will allow structural characterization by X-ray analysis probably has the greatest promise.

Experimental Section

NMR Spectroscopy. Solution state ^{1}H and ^{13}C NMR spectra were recorded at Rice University using Bruker 400 and 500 MHz spectrometers and at Bruker (Rheinstetten) using Bruker 800 and 900 MHz spectrometers. Standard broadband observe probes were used to obtain the ^{1}H and ^{13}C spectra on the 400 and 500 MHz spectrometers; an inverse probe with a z-axis gradient coil was used to obtain gradient-enhanced COSY, HSQC, and HMBC spectra on the 500 MHz spectrometer; and a triple resonance, inverse probe with a z-axis gradient coil was used to obtain spectra on the 800 and 900 MHz spectrometers. High-precision Wilmad 535-PP NMR tubes were employed. The spectroscopic parameters were particularly optimized for the ^{1}H and ^{13}C NMR experiments on the dihydroanthracene reduction products. For example, a relatively narrow ^{13}C spectral width (covering from δ 170 to δ -10), a digital filter to suppress the intense CS_2 signal at δ 192, and 256 K data points were used so as to achieve a digital resolution of 0.15 Hz (1.2 ppb) over the spectral region of interest. No line-broadening was used. The FID was zero-filled once. Solid state ^{13}C NMR spectra were recorded at Rice University using a Bruker 200 MHz spectrometer with magic angle spinning at 7 kHz, ^{1}H$-$^{13}C cross polarization for 1 ms, and a 5-s relaxation delay, following FID acquisition. Glycine was used as an external chemical shift reference. The ^{3}He NMR spectra were recorded at Yale University in o-dichlorobenzene-d_4 using a Bruker 500 MHz spectrometer (^{3}He at 381 MHz).

Other Spectroscopy and Chromatography. Mass spectra were obtained using a Finnigan MAT 95 spectrometer. FT-IR spectra were acquired using a Nicolet Magna-IR 760 spectrophotometer. UV$-$vis spectra were generated using a Hewlett-Packard 8452A Diode Array Photometer. 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 10 mm × 25 cm Buckyclutcher I stationary phase column using a toluene/hexanes (70/30) isocratic mobile phase. A flow rate of 4.0 mL/min and a wavelength (λ) of 280 nm were employed. HPLC-grade solvents purchased from Fisher Scientific were used for all of the chromatography. All other chemicals were of reagent quality and were used as received from the manufacturer. Reactions were carried out under inert atmospheres.

Birch Reduction of C_{60}. C_{60} (100 mg, 0.139 mmol) was placed in a dry 100-mL three-neck round-bottom flask equipped with a dry ice condenser and a magnetic stirrer bar. One neck of the flask was sealed, and the other was equipped with an adapter for introducing ammonia. The flask was placed into a dry ice$-$acetone bath, and the apparatus was flushed with argon for 40 min. The condenser was then filled with dry ice$-$acetone, and ~70 mL of ammonia was condensed in the flask. Small pieces of clean lithium (400 mg, 57.6 mmol) were then added to the flask. The dissolution of the lithium metal produced a deep blue-purple color upon slow stirring of the suspension. The dry ice$-$acetone bath was removed from the three-neck flask, and 5 mL of distilled and dry *tert*-butyl alcohol was added to the reaction mixture. The solution was refluxed for 8$-$10 h at -33 °C, refilling the dry ice condenser as needed. After the reaction, the ammonia was allowed to evaporate completely, leaving behind a blue-gray residue. The flask was then cooled in an ice bath and equipped with a 100-mL dropping funnel filled with distilled water while maintaining the flow of argon gas. Excess lithium metal was destroyed by slow addition of water. The water layer was extracted with freshly distilled benzene (2 × 100 mL) and dried over sodium sulfate to obtain a clear yellow solution. The solvent was stripped under vacuum and without the use of heat to obtain a white-yellow amorphous powder. The product was then analyzed by HPLC, and four bands were isolated by preparative HPLC using the Buckyclutcher I preparative column.

Band A. (4.9 min, retention time) was 6% of the mixture by HPLC analysis. ^{1}H NMR (400 MHz, o-$C_6D_4Cl_2$): broad signal centered at 3.2 ppm ($\Delta\delta = 0.9$ ppm). ^{3}He NMR (381 MHz, o-$C_6D_4Cl_2$): δ_{He} -3.2 to -4.0 (broad singlet). FD-MS for $C_{60}H_{38}$: calculated, 758.3; found, 758.4. FD-MS for $C_{60}H_{40}$: calcd, 760.3; found, 760.5.

Band B. (5.6 min, retention time) was 21% of the mixture by HPLC analysis. ^{1}H NMR (400 MHz, o-$C_6D_4Cl_2$): broad signal centered at 3.3 ppm ($\Delta\delta = 0.9$ ppm). Solid state ^{13}C NMR (50 MHz): broad signals centered at ~133 and 40 ppm. ^{3}He NMR (381 MHz, o-$C_6D_4Cl_2$): δ_{He} -4.6 to -5.8 (broad singlet). UV$-$vis (acetonitrile): 206, 218, 274 nm. IR (KBr): 2914, 2843 (sh), 1737, 1598, 1496, 1465, 1350, 1260, 1081, 1030, 899, 805, 728, 689 cm^{-1}. FD-MS: calcd, 756.3; found, 756.3.

Band C. (6.7 min, retention time) was 44% of the mixture by HPLC analysis. ^{1}H NMR (400 MHz, o-$C_6D_4Cl_2$): broad signal centered at 3.25 ppm ($\Delta\delta = 0.95$ ppm). Solid state ^{13}C NMR (50 MHz): broad signals centered at ~133 and 40 ppm. ^{3}He NMR (381 MHz, o-$C_6D_4Cl_2$): δ_{He} -6.0 to -6.8 (broad singlet). UV$-$vis (acetonitrile): 204, 208, 212, 244, 250, 254, 260, 284 nm. IR (KBr): 2920, 2858, 1742, 1603, 1495, 1460, 1265, 1102, 1030, 880, 805, 733, 702 cm^{-1}. FD-MS: calcd, 756.3; found, 756.1.

Band D. (8.3 min, retention time) was 23% of the mixture by HPLC analysis. ^{1}H NMR (400 MHz, o-$C_6D_4Cl_2$): broad signal centered at 3.4 ppm ($\Delta\delta = 1.0$ ppm). ^{3}He NMR (381 MHz, o-$C_6D_4Cl_2$): δ_{He} -7.6 to -8.4 (broad singlet). FD-MS calcd, 756.3; found, 756.3; FD-MS for $C_{60}H_{32}$: calcd, 752.3; found, 752.4.

Reduction of C_{60} by 9,10-Dihydroanthracene. C_{60} (100 mg, 0.139 mmol) was mixed with freshly crystallized and dried dihydroanthracene (3 g, 16.67 mmol) and sealed under vacuum in a Pyrex tube (1/4 filled). The contents of the tube were heated at 350 °C for 45 min. The color of the melt changed from dark violet to brown, ruby-red, orange, yellow, and finally, colorless white. The tube was allowed to cool with the melt on one end. The tube was opened and the contents scratched out with a spatula. The contents were dissolved in ether (50 mL) and filtered on a PTFE filter paper (0.1 μ). Only dihydroanthracene was dissolved in ether, leaving $C_{60}H_{36}$ lumps on the filter paper. The contents were again suspended from filter paper in ether (50 mL) and filtered, affording a mixture of isomers of $C_{60}H_{36}$ (70 mg). Finally, the light yellow-colored product was purified by preparative HPLC on a Buckyclutcher I column with toluene/hexane (70:30) as eluent. This workup has the advantage over previous methods that employ sublima-

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tion to get rid of dihydroanthracene, because they destroy most of the $C_{60}H_{36}$ isomers, change the relative abundance of isomers, and probably result in isomerization, as well.

Band 2 (Major Isomer). 7.0-min retention time by HPLC analysis. ^{1}H NMR (500 MHz, $CS_2/CDCl_3$, 3:1): 2.58−2.67 (m), 2.78−2.96 (m), 3.03−3.11 (m), 3.12−3.41 (m), 3.41−3.51 (m), 3.64−3.79 (m), 3.88−4.13 (m); ^{13}C NMR (126 MHz): 142.047, 140.054, 138.470, 137.489, 137.416, 137.245, 137.231, 137.126, 137.006, 136.884, 136.737, 136.341, 136.063, 135.365, 135.037, 134.973, 134.935, 134.827, 134.728, 134.716, 134.699, 134.515, 134.184, 134.161, 134.057, 134.045, 134.044, 133.597, 125.351, 124.522, 123.034, 122.395, 52.203, 51.423, 50.142, 48.990, 48.941, 48.061, 48.039, 47.822, 47.498, 47.351, 47.166, 46.092, 45.791, 45.630, 45.434, 44.966, 44.913, 44.280, 44.156, 44.151, 44.004, 43.938, 43.850, 43.846, 43.417, 43.345, 42.523, 42.343, 39.720, 39.296, 39.203, 38.031, 37.937, 37.551, 37.485, 37.305, 36.810, 36.794, 36.773, 36.718, 36.268, 35.968, 35.944, 35.887, 31.459, 31.292, 31.277, 31.243. ^{3}He NMR (381 MHz, *o*-$C_6D_4Cl_2$): δ_{He} −8.014 and −8.139 (ratio 3:1). IR (KBr): 2909, 2844, 1491, 1340, 1316, 1261, 1236, 1178, 742, 698 cm^{-1}. FD-MS for $C_{60}H_{36}$: calcd, 756.3; found, 756.5.

Band 3 (Minor Isomer). 7.5-min retention time by HPLC analysis. ^{1}H NMR (500 MHz, $CS_2/CDCl_3$, 3:1): δ 2.6−4.1 (complex multiplet). ^{3}He NMR (381 MHz, *o*-$C_6D_4Cl_2$): δ_{He} −8.149.

Theoretical Methods. The geometries of $C_{60}H_{36}$ and He@$C_{60}H_{36}$ isomers were optimized using Becke's[57] three parameter hybrid exchange functional as implemented in the Gaussian[58] program and the correlation functional of Lee et al.[59] in conjunction with a 6-31G* basis set (B3LYP/6-31G*). The He atom was put at the center of mass of the B3LYP/6-31G* optimized $C_{60}H_{36}$ in order to preserve the molecular point group symmetry of the hydrofullerene. The obtained He@$C_{60}H_{36}$ was reoptimized at the B3LYP/6-31G* level of theory. The magnetic shielding was computed at the B3LYP level of theory using the gauge-invariant atomic orbitals (GIAO) approach as implemented by Wolinski et al.[60] The magnetic shielding computations were performed at the optimized B3LYP/6-31G* geometries using Dunning's[61] double-ζ basis set with one set of polarization functions (DZP) on carbon ($\alpha_d = 0.75$) and hydrogen ($\alpha_p = 0.75$), and the polarized ($\alpha_p = 1.00$) valence triple-ζ quality [5s]/(3s) basis set (tzp) of Schäfer et al.[62] for He. All computations were performed by using a development version of Gaussian[58] on Intel Pentium III 733 MHz computers.

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Supporting Information Available: Highly expanded plots of the 126 MHz ^{13}C spectrum of the dihydroanthracene reduction products (4 figures) and the 800 MHz COSY and TOCSY spectra of these products. The figures are available on the Internet at http://pubs.acs.org.

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