Fulleroid Addition Regiochemistry Is Driven by π-Orbital Misalignment

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Abstract: This article reports the first investigation into the regiochemistry of addition to the fulleroid $C_{61}H_2$ by Zn(Cu) reduction and hydroboration. Two major isomers of $C_{61}H_4$ are formed by the reduction with Zn-(Cu) while only one major isomer is formed by hydroboration. The structures of the major isomers formed by reduction with Zn(Cu) were identified as $1,2$-$C_{61}H_4$ and $3,4$-$C_{61}H_4$. The $1,2$-$C_{61}H_4$ isomer is the only dominant isomer formed by hydroboration with no indications of the $3,4$-$C_{61}H_4$ isomer being formed. The regiochemistry observed in the formation of $1,2$-$C_{61}H_4$ is the same regiochemistry seen in the further reactivity of azafulleroids ($C_{60}NR$). Strain energies (calculated at the B3LYP-6-31G* level of theory) show that the relief of strain is greater for the hydrogenation of the fulleroid $C_{61}H_2$ than it is for the hydrogenation of C_{60} itself. This indicates that the twisted, anti-Bredt's rule, double bonds of the fulleroid are a source of greater localized strain than the pyramidalization of the carbons in the rest of the molecule. Thus, the regiochemistry observed for the fulleroid is due to π-orbital misalignment and not pyramidalization.

Fulleroids are fullerenes that have been inflated by one (or more) carbon atom as a result of the formal insertion of a carbene into a C−C bond shared by a five-membered ring and a six-membered ring (a "5,6-ring fusion") and are among the most interesting fullerene derivatives.[1−5] This inflation is usually accomplished through 1,3-dipolar addition of a diazoalkane to a fullerene, followed by extrusion of N_2 and closure of the resultant diradical.[1,2,6−11] Closure across a 5,6-ring fusion is immediately followed by a norcaradiene rearrangement, opening the ring fusion and producing a fulleroid. Azafulleroids[12−14] result from the insertion of one (or more) nitrogen atom into a C−C bond shared by a five-membered ring and a six-membered ring through a similar mechanism.

In previous work, we developed a method for the facile synthesis of $C_{60}H_2$, $C_{60}H_4$ (3 isomers), $C_{60}H_6$ (2 isomers),[15,16] as well as $C_{70}H_2$, $C_{70}H_4$, and $C_{70}H_8$[17] using Zn(Cu) dissolving metal reduction. We have identified some characteristic ^1H-^{13}C couplings and ^{13}C chemical shifts for fullerene carbons as far as seven bonds from the proton(s), which allows us to confidently assign structures to derivatized fullerenes. In this paper we report the first investigation of the sites of reactivity in the simplest fulleroid, $C_{61}H_2$ (**1**), by hydrogenation with Zn(Cu) and also by hydroboration.[18,19] In addition to identifying the preferred sites of reduction, we explore the roles of strain due to π-orbital misalignment and the degree of pyramidalization of the fullerene carbons in directing the reduction of **1** and the effects these strains have upon the observed ^{13}C chemical shifts of fullerene carbons. We report herein the identification and characterization of two isomers with formulas $C_{61}H_4$.

Fulleroids, unlike other fullerene derivatives, retain the fullerene's original π-bonding pattern. For C_{60} mono-fulleroids there are 60 π-electrons and 90 conjugated bonds, one of which is now homoconjugated.[5,13] As a result of this retention of the bonding pattern, the spectroscopic[1,2,12,13,20,21] and electrochemical[22] properties of fulleroids are very similar to their parent fullerenes. The presence of a methylene group bridging a 5,6-ring fusion gives rise to 17 chemically different double bonds

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(C_s symmetry). In a fulleroid, unlike in C_{60}, there are varying amounts of strain among the double bonds. This strain could therefore influence, perhaps dominate, the pattern of reactivity.[5] The reactivity of the fulleroid core of azafulleroids has been investigated,[13,14,21,23−26] but to the best of our knowledge, there have been no reports of reactions of the fulleroid core of **1**.
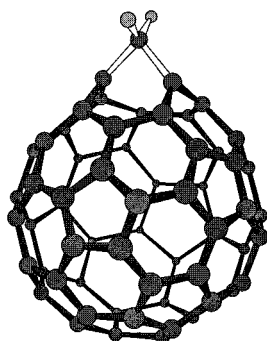
C$_{61}$H$_2$ fulleroid (**1**)

Results and Discussion

Initial Zn(Cu) reduction of the fulleroid proved to be significantly slower than the reduction of C_{60} itself. Reductions done under the conditions used for the reduction of C_{60}[16] proceeded very slowly and to incomplete reduction of **1**. After 24 h of reaction time, less than 50% conversion of **1** was observed. This is in contrast to the complete conversion of C_{60} to reduced products in less than 2 h under the same conditions.

The parent $C_{61}H_2$ fulleroid is less soluble in toluene than is C_{60}. Accordingly, the reduction was carried out in *o*-dichlorobenzene (*o*-DCB), a solvent in which the fulleroid is significantly more soluble. Reduction of **1** with Zn(Cu) in *o*-DCB proceeded quickly and in a similar fashion as the reduction of C_{60} and C_{70}.[27] The lower density of water relative to *o*-DCB resulted in the separation of the water from the metal, stopping the reaction if the mixture was not vigorously stirred.[28] HPLC analysis of the mixture after 1 h of reaction produced the chromatogram shown in Figure 1. Two bands, both identified by mass spectrometry as $C_{61}H_4$ ($M^+ = 736$), are initially formed in a 3:1 ratio. These two bands were each isolated by preparative HPLC (see Experimental Section). Upon further analysis, the larger band was found to be composed of a mixture of one isomer of $C_{61}H_4$, **2**, and at least three other isomers while the minor band was found to be composed of a second single isomer of $C_{61}H_4$ (**3**). The isomers **2** and **3** are formed in a 2:1 ratio, respectively, as determined by HPLC. Significant degradation of concentrated solutions occurs within a few days time under an atmosphere of air, even when stored in the dark at −35 °C. Prolonged exposure of these reduced fulleroids to laboratory light, under air or inert atmosphere, causes precipitation of an unidentified compound(s).

The fulleroid $C_{61}H_2$ has an absorption spectrum that is very similar to that of C_{60}.[2] The absorption spectrum has the same

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(27) Reduction of C_{60} and C_{70} in *o*-dichlorobenzene occurs at a facile pace in the same manner as in toluene.

(28) Complete consumption of C_{60} may range from 45 min to more than 3 h depending on the volume of the solution and efficiency of mixing.
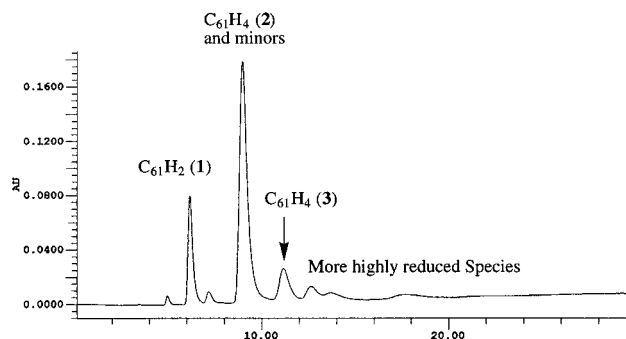
Figure 1. HPLC chromatogram of Zn(Cu) reduction of **1**, showing $C_{61}H_4$ bands, and more highly reduced products. Conditions: Buckyclutcher column (10 mm × 250 mm), 1:1 toluene−hexane mobile phase, 4.5 mL/min flow rate, and monitored at 335 nm.

general shape as C_{60} in the region 290−600 nm, but is blue shifted by several nanometers. The $C_{61}H_4$ isomers **2** and **3** have distinctly different absorption spectra in the 290−600 nm range. $C_{61}H_4$ (**3**) has an absorption curve very similar to $C_{60}H_2$, but red-shifted a few nanometers relative to the spectrum of $C_{60}H_2$. The local λ_{max} for **3** is at 332 nm (325 nm for $C_{60}H_2$) and the characteristic absorption for 1,2-addition to C_{60}, normally around 430 nm,[29] has shifted to 440 nm. The absorption spectrum of **2** has a broader, blue-shifted λ_{max} at 322 nm and the absorptions at longer wavelengths are much weaker compared to $C_{60}H_2$.

The ^{1}H NMR spectrum of **1** consists of an AB pattern ($\delta = 2.89$ and 6.36 with $J = 9.7$ Hz) in which one proton is shielded and the other proton deshielded by fullerene ring currents.[2] The major isomer of $C_{61}H_4$ (**2**) showed four resonances in the ^{1}H NMR spectrum. The most downfield resonance, a one-proton doublet at 7.17 ppm, resembles the downfield resonance for **1** (doublet at 6.36 ppm). Unlike in the ^{1}H NMR spectrum for **1** where the upfield resonance is at 2.9 ppm, the most upfield resonance in **2** is at 4.83 ppm. This large downfield shift implies that a significant reduction of at least one of the ring currents has occurred.

To elucidate the topology of the protons, a set of decoupling experiments were performed. Decoupling of the doublet at 7.17 ppm caused the one-proton multiplet centered at 5.47 ppm to collapse to an apparent triplet (doublet of doublets), while the apparent doublets (one proton each) at 4.84 and 4.83 ppm remained unchanged. When the multiplet centered at 5.35 ppm was selectively decoupled, the downfield resonance collapsed to a singlet (one proton) and the two doublet resonances upfield also collapsed to form a single doublet (two protons). Decoupling of the furthest upfield resonances together collapsed the multiplet at 5.47 ppm to a doublet (one proton) while the downfield doublet (one proton) at 7.17 ppm remained unchanged. These data demonstrate that the most downfield resonance is coupled to only the multiplet centered at 5.47 ppm. The two upfield protons are also coupled to the proton at 5.47 ppm and to each other. The four protons are nonequivalent, with proton A being coupled to protons B and C. Proton B is coupled to protons A and C while proton C is coupled to protons A, B, and D. Proton D is only coupled to proton C. The observed couplings are summarized in Table 1.

Based on the necessity of the protons to be relatively close for significant coupling to occur, only two structures are possible for **2** (Figure 2). In structure **2a** the addition of the hydrogens has occurred across what was originally a 6,6-ring fusion in C_{60}. In the second structure, **2b**, the addition of the hydrogens

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Table 1. Chemical Shifts and $^1H-^1H$ Coupling Data for $C_{61}H_4$ (**2**)

compd	chemical shift (ppm)	proton assign[a]	J_1	J_2	J_3
1	2.89	n.a.	9.7		
	6.36	n.a.	9.7		
2	4.83	A	11.9	2.3	
	4.84	B	11.9	6.3	
	5.35	C	11.2	6.3	2.3
	6.98	D	11.2		
3	4.62	A	−10.4	1.3	
	4.79	B	−10.4		
	7.12	C	1.3		

[a] See Figures 4 and 5 for pictorial labeling of protons of **2** and **3**, respectively. n.a. = not assigned.
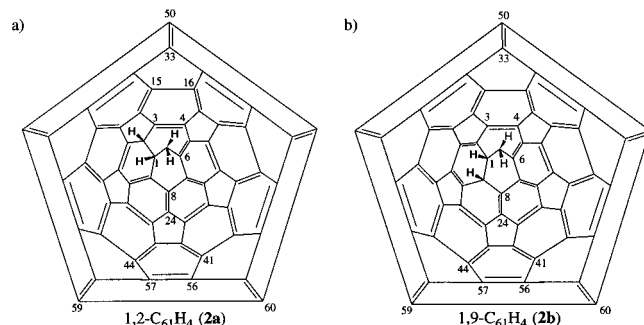

Figure 2. Schlegel diagrams of two possible structures for $C_{61}H_4$ (**2**) with partial numbering.[30] (a) Addition of hydrogens across what was originally a 6,6-ring fusion in C_{60}. (b) Addition of hydrogens across what was originally a 5,6-ring fusion in C_{60}.
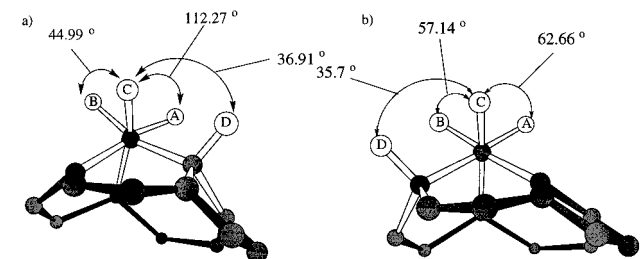

Figure 3. Partial structures of (a) **2a** and (b) **2b**, viewed along the C1−C61 bond showing the dihedral angles between protons.

has occurred across what was a 5,6-ring fusion in C_{60}. The second structure requires the isolation of two double bonds in five-membered rings, an effect that is usually destabilizing.[9]

The magnitudes of the $^1H-^1H$ couplings can be used to further elucidate the structure of **2**. AM1 calculations of isomers **2a** and **2b** (Figure 2) show that there are measurable differences in the dihedral angles of the bridgehead proton to the methylene protons between the two structures. The dihedral angles between the bridging proton and the methylene protons in structure **2a** are 45° and 112° which, based on the Karplus curve, should result in a moderately large and a small coupling, respectively (Figure 3a).[31] The calculated dihedrals for the same protons in structure **2b** are about 57° and 62°, indicating the couplings between protons should be of about the same magnitude (Figure 3b). We observe couplings with significantly different magnitudes (6.3 and 2.3 Hz), suggesting that structure **2a** is the correct structural assignment for isomer **2**.

The ^13C NMR of **2** showed 60 carbon resonances, one of double intensity, consistent with C_1 symmetry. Reduction at any one of 13 of the 17 chemically distinct double bonds of **1**
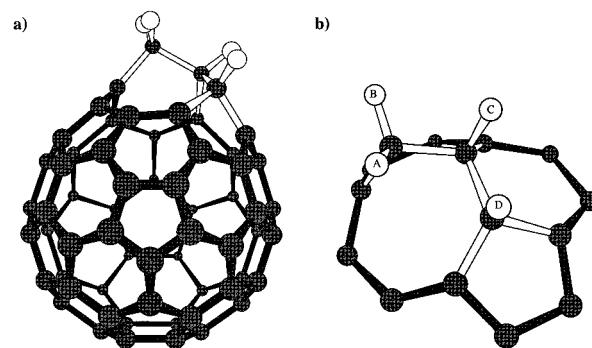
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Figure 4. (a) Structure of $C_{61}H_4$ (**2**). (b) Enlarged partial structure of **2** showing the arrangement of the protons.

produces a $C_{61}H_4$ reduced fulleroid with C_1 symmetry that would show 61 carbon resonances in the ^13C NMR if no lines are superimposed. The fulleroid methylene carbon resonance in **2** (32.7 ppm) is 6 ppm upfield from the methylene resonance of **1** (38.81 ppm), consistent with the conversion of an adjacent carbon from sp^2 to sp^3 hybridization. The assignment of the protonated carbons was confirmed by correlations revealed from an HMQC experiment. Hydrogenation of **1** to **2** increases the dispersion of the remaining sp^2 carbon resonances. In the ^13C spectrum of **1**, there is only one resonance upfield of 144.58 ppm and no resonances downfield of 147.64 ppm. Conversion to **2** causes the appearance of 21 resonances downfield of 145 ppm, including four resonances downfield of 148 ppm. The downfield resonances for the reduced fullerene, $C_{60}H_2$, range from 137 to 153 ppm. In $C_{60}H_2$ the carbon giving the most downfield resonance is bonded to the sp^3 carbon that resonates at 54 ppm.[16] Interestingly, for **1** the two most upfield sp^2 resonances show the greatest couplings to the protons.

$C_{61}H_4$ (**3**) was isolated by HPLC (see Experimental Section). The ^1H NMR of **3** was relatively simple with an apparent doublet of triplets (one proton) centered at 4.62 ppm ($J_1 = −10.4$ Hz, $J_2 = 1.3$ Hz), an apparent doublet (one proton) centered at 4.79 ppm ($J = −10.4$ Hz), and a two-proton doublet centered at 7.12 ppm ($J = 1.3$ Hz). It is apparent that the protons that are on the core of the fullerene in **3** are close enough to the methylene protons for spin communication to occur. Also, the presence of two protons resonating at the same frequency with no observable $^1H-^1H$ *J* coupling between them suggests that they are related to each other by a plane of symmetry.

The ^13C NMR spectrum of **3** proved to be much simpler than the ^13C NMR spectrum of **2**. A total of 33 resonances were observed indicating the molecule contains a plane of symmetry, thus retaining the C_s symmetry of the fulleroid. The presence of only two sp^3 resonances confirms that the protonated carbons on the fullerene core are equivalent by symmetry. There are only two double bonds in **1** that are bisected by a plane of symmetry (C3=C4 and C56=C57, see Figure 5). Reduction of the C3=C4 bond produces a fulleroid where the protons on the ball are five bonds from the methylene protons, close enough for coupling to be observed.[17,19] Reduction of the C56=C57 bond places the protons significantly further away, too far for significant coupling to be observed.

The proximity of the protons on the fullerene to the methylene protons was established by NOE experiments. Irradiation of the downfield protons (7 ppm, 2 H) results in a positive NOE to the low-field fulleroid methylene proton and a negative NOE to the upfield fulleroid methylene proton. Irradiation of the low-field fulleroid methylene proton gives a positive NOE to both sets of protons, and irradiation of the upfield fulleroid methylene proton gives a positive NOE to the fulleroid methylene proton
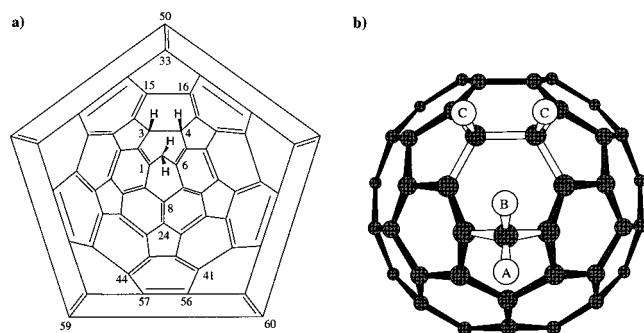
Figure 5. (a) Schlegel diagram of **3** with partial numbering;[30] (b) 3D structure of **3** showing proton arrangement. (Carbons in the back of the ball have been omitted for clarity in the 3D structure.)

Table 2. Partial Assignment of Carbon Resonances for **1** and **3**

carbon assign[a]	$C_{61}H_2$ (**1**) resonance	$C_{61}H_4$ (**3**) resonance
61	38.82	39.44
1 (6)	136.04	132.84
2 (5)	134.31	161.63
3 (4)	n.a.	58.63
7 (9)	152.51	142.72
8	141.29	136.50
14 (17)	n.a.	149.53
24	137.56	137.12
33	143.27	143.99
50	143.91	144.92

[a] Carbon in parentheses is the symmetrically equivalent carbon. n.a. = not assigned.

and a negative NOE to the low-field protons. This is a signature for a roughly linear arrangement of the nuclei with the low-field (4.79 ppm) methylene proton in the middle. As a result, the low-field (7.12 ppm) protons must be further from one of the methylene protons than the other and must be symmetry related.

We observe a 1.3 Hz coupling between the downfield protons and the upfield proton of the fulleroid methylene. Reduction of the C56═C57 double bond would require that a significant $^1H-^1H$ J coupling (1.3 Hz) extend through 10 bonds, while reduction at the C3═C4 double bond would require the observed $^1H-^1H$ J coupling to extend through 5 bonds. The observed coupling constant J = 1.3 Hz is consistent with the $^5J_{h-h}$ and $^7J_{h-h}$ coupling constants observed in $C_{70}H_8$, which consists of a pattern of nonadjacent hydrogens (5.7−1.3 Hz).[17] We assign the structure of **3** (Figure 5) based on the combined J couplings and the measured NOEs. A significant number of the carbon resonances for **3** can be assigned on the basis of their intensity and observed couplings in the $^1H-^{13}C$ coupled NMR. These assignments are summarized in Table 2 with corresponding resonances for **1** when identifiable. We are unable to explain the dramatic downfield shift of the bridgehead resonance and are currently exploring the reasons underlying this shift.

Hydroboration of **1** in o-DCB led to the formation of **2** and the unidentified minor isomers of $C_{61}H_4$ in a 9:1 ratio with no indications of **3**. Cahill has shown that hydroboration of $C_{60}H_2$ (nine chemically different double bonds) leads to a mixture of six $C_{60}H_4$ isomers in which the thermodynamic 1,2,3,4-$C_{60}H_4$ isomer dominates (50% of the mixture).[19] As mentioned before, there are 17 chemically different double bonds in **1**. At the B3LYP/6-31G* level of calculations, $C_{61}H_4$ (**2**) is calculated to be the thermodynamic isomer (see below). Thus, unlike in the Zn/Cu reduction of C_{60} in which the thermodynamic products were not observed,[15,16] the major product produced upon hydroboration and Zn/Cu reduction of **1** is the thermodynamic isomer, **2**.
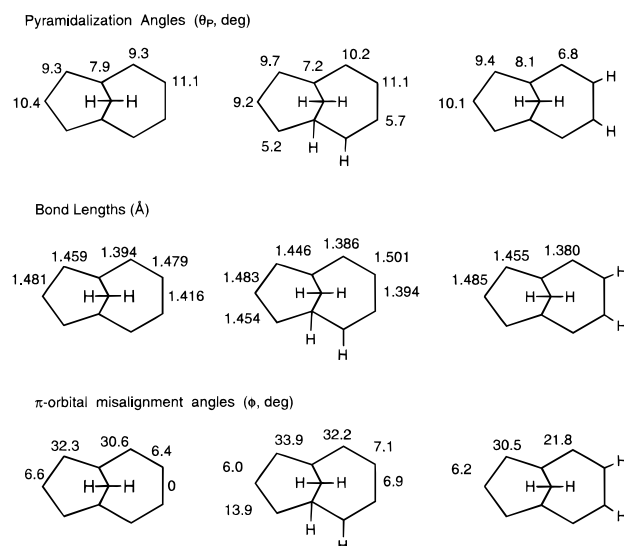

Figure 6. Pyramidalization angles, bond lengths, and π-orbital misalignment angles for the annulene carbons of $C_{61}H_2$ (**1**), $C_{61}H_4$ (**2**), and $C_{61}H_4$ (**3**) (B3LYP/6-31G* optimized structures). C_{60} has bond lengths of 1.395 and 1.453 Å at this theoretical level (by symmetry θ_P = 11.6° and ϕ = 0°).

Although the fullerenes are extremely strained molecules,[32] the π-orbital alignment within this class of molecules remains very high and is perfect in icosohedral C_{60}.[33] This is because the distortions necessary for closure of the fullerene structure involve carbon atom pyramidalization rather than a twisting about the carbon−carbon π-bond. However, as noted previously, this situation changes completely on fulleroid formation.[5] The presence of the methylene group creates a bridged-[9]annulene system on the surface of the fullerene, and the distortions around the ring are quite reminiscent of the free-standing bridged annulenes, with severe π-orbital misalignment in the immediate periphery.[34] The severe π-orbital misalignment in the analogous (5,6)aza-C_{60} fulleroid allowed Wudl and co-workers to obtain opened structures as a result of oxygen addition across the severely twisted bridgehead double bond.[23] In a previous analysis, we predicted similar reactivity for the parent fulleroid.[5] The present work bears out this prediction with the primary product of hydrogenation yielding the bridgehead addition product $C_{61}H_4$ (**2**). Additional analysis has revealed that π-orbital misalignment plays an important role in the formation of **3** as well.

In the previous study,[5] we carried out HF/3-21G geometry optimizations of the structure of **1**. The important fragment of the calculated structure of **1**, together with the geometries of **2** and **3**, optimized at the B3LYP/6-31G* level, are reproduced in Figure 6. The very large bridgehead π-orbital misalignment angles in **1** are apparent. As expected, hydrogenation to give **2** removes one of these twisted π-bonds. Interestingly, the hydrogenation product **3** considerably reduces the twist angle of *both* of the (intact) bridgehead double bonds. Thus in each case, the regioselective hydrogenation products owe their formation to the relief of π-orbital misalignment. The present results emphasize the fact that the chemistry of the fullerenes is driven by strain−pyramidalization in the case of simple fullerenes, but primarily π-orbital misalignment in the case of fulleroids.

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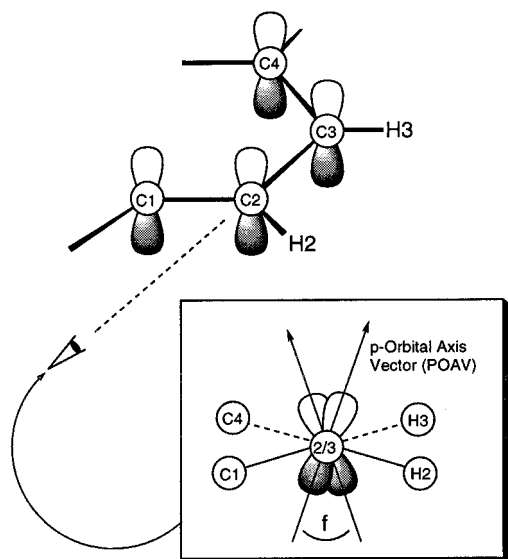(34) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243−249.

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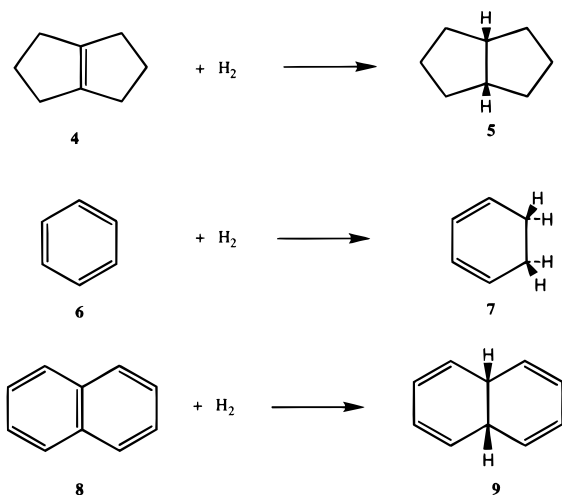
Figure 7. π-orbital axis vector (POAV).

Figure 8. Model hydrogenations.

We assessed the energetic impact of these effects by calculation of the olefin strain energy (OSE).[35] The OSE is defined as the difference between the strain energy of an olefin and that of its parent hydrocarbon. In a further refinement, the energetic effects of strain are measured by comparison of the calculated heat of hydrogenation of a particular alkene with the calculated heat of hydrogenation of some reference (unstrained) olefin.[36] This is a useful approach because it provides a straightforward way of correcting for the errors in calculated heats of hydrogenation. We followed previous work, and adopted the alkene **4** as the reference (unstrained) olefin.[36]

In the present work, the compounds include contributions from both aromatic character and strain, but we collect both effects under the OSE term for convenience. We studied the hydrogenations at the B3LYP/6-31G* level of theory and the results are collected in Table 3. It is interesting to note that the hydrogenation of C_{60} is computed to be 12 kcal/mol less exothermic than that for the reference olefin. Although this comparison is not perfectly balanced (there are differences in adjacent hybridizations), it supports the idea that there is significant resonance stabilization in the fullerenes, particularly when it is considered that hydrogenation relieves a total of 29

kcal/mol of strain in C_{60} (16 kcal/mol of local strain plus 13 kcal/mol of global strain) due to pyramidalization (curvature).[32]

The relief of strain is larger in the hydrogenation of $C_{61}H_2$ (**1**) than in the hydrogenation of C_{60} itself. It is therefore clear that the twisted double bonds are a source of even larger local strain than the pyramidalized carbon atoms in the remainder of the molecule. Thus it is the π-orbital misalignment (and not the pyramidalization) that dictates the regiochemistry in the fulleroid.

The regiochemistry of hydroaddition to the bridgehead double bond of fulleroid **1**, resulting in **2**, is the same regiochemistry that is seen in the addition of azides to the bridgehead double bond of an azafulleroid which results in a mixed triazoline/azafulleroid.[13,24] Extrusion of N_2 from the mixed triazoline/azafulleroid then forms a bisazafulleroid. As mentioned earlier, the photooxygenation of an aza-C_{60} fulleroid results in the initial addition of O_2 across one of the bridgehead double bonds, followed by a ring opening forming a ketolactam.[23] A second photooxygenation of the ketolactam, followed by a ring opening, results in an opening of the fullerene core.[23] The reactivity of the double bond that leads to the formation of **3** has not been similarly reported for azafulleroids.

Conclusions

The Zn(Cu) reduction of **1** appears to proceed in a similar manner as the reduction of C_{60},[16] in which the reaction mixture is initially dominated by products resulting from addition of hydrogens. As the reactions proceed, more highly reduced products at successive levels of hydrogenation are formed. Although there are formally 17 different isomers possible for reduction across a double bond in **1**, a smaller number of isomers of $C_{61}H_4$ (at least five) have been observed, with one isomer (**2**) dominating the reaction mixture. Hydroboration of **1** leads predominantly to the formation of **2**, the thermodynamic product, with no indications of other isomers or higher hydrogenated species.

As in azafulleroids, the preferred site for further reaction of the inflated fullerene is one of the two double bonds containing a bridgehead carbon.[13] The structural assignment of **2** is in accordance to the observed reactivity of azafulleroids. The observed reactivity of the double bonds containing bridgehead carbons can be attributed to the strain imposed by the π-orbital misalignments and not the pyramidalization of the fullerene carbons. This is in accordance with our previous work[5] and the violation of Bredt's rule noted by Diederich.[8] Though the bridgehead double bonds are the most strained in the fulleroid, reduction of the double bond that forms **3** is calculated to relieve more strain than does reduction of one of the bridgehead double bonds. However, **2** is calculated to be thermodynamically lower in energy than **3**. Therefore, unlike in the Zn(Cu) reductions of C_{60} and C_{70},[15-17] the major reduced fulleroid obtained is the thermodynamically, not solely a kinetically, preferred product.

Experimental Section

General. Fullerenes were obtained from MER corp. as a C_{60}/C_{70} mixture and purified by preparative GPC.[37] All reactions were performed in acid-washed glassware. The fulleroid $C_{61}H_2$ was prepared by a literature method[2] and purified by prepartive HPLC (21.1 mm × 250 mm Buckyclutcher column, 1:1 toluene−hexane mobile phase, 15 mL/min flow rate, and monitored at 335 nm). All NMR samples were freeze−pump−thaw deoxygenated solutions in flame-sealed tubes. Spectra were measured on samples in 10 mm tubes unless otherwise noted.

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Table 3. Olefin Strain Energies

compd	calculation method	total energy (hartrees)	reaction	OSE rel **4 → 5**
4	B3LYP/6-31G*	−312.06329		
5	B3LYP/6-31G*	−313.28925	**4 → 5**	−1.22596
6	B3LYP/6-31G*	−232.24866		
7	B3LYP/6-31G*	−233.41588	**6 → 7**	36.9
8	B3LYP/6-31G*	−385.89273		
9	B3LYP/6-31G*	−387.00432	**8 → 9**	71.8
C_{60}	B3LYP/6-31G*	−2286.17383		
$C_{60}H_2$	B3LYP/6-31G*	−2287.38196	$C_{60} \rightarrow C_{60}H_2$	11.8
$C_{61}H_2$ (**1**)	B3LYP/6-31G*	−2325.46544		
$C_{61}H_4$ (**2**)	B3LYP/6-31G*	−2326.68675	**1 → 2**	2.9
$C_{61}H_4$ (**3**)	B3LYP/6-31G*	−2326.67496	**1 → 3**	10.3

$C_{61}H_4$ by Zn(Cu). $C_{61}H_2$ (121.7 mg, 0.166 mmol) and *o*-dichlo-robenzene (35 mL) were combined in a 100 mL, three-neck flask and sparged with argon. Zn−Cu couple (2.72 g, 41.5 mmol of Zn) and water (1 mL) were then added. The resulting mixture was heated in a 50 °C oil bath and stirred vigorously for 1 h. The mixture was then cooled to room temperature, the supernatant was decanted, and the residual solid was washed twice with 1 mL portions of *o*-dichloroben-zene. The combined supernatant and washings were filtered (0.2 μm). The solution was diluted to 130 mL with toluene, re-filtered (0.2 μm), and purified by HPLC with use of a Buckyclutcher column (21.1 mm × 250 mm), 1:1 toluene−hexane mobile phase, 15 mL/min flow rate, and monitored at 335 nm. Isomer **2** and numerous minor isomers coeluted as one band and isomer **3** as a second band. The combined yield of the $C_{61}H_4$ bands (a 2:1 ratio of **2**:**3** by HPLC) was 18.0 mg, 0.0245 mmol (15%). Further purification of isomer **2** was achieved by HPLC with use of a Cosmosil Buckyprep column (10 mm × 250 mm), toluene mobile phase, 5 mL/min flow rate, and monitored at 335 nm. Isomer **3** is further purified (from a small amount of the major band) by HPLC with use of a semipreparative Cosmosil Buckyprep column (10 mm × 250 mm), toluene mobile phase, 5 mL/min flow rate, and monitored at 335 nm.

$C_{61}H_4$ (2). Negative ion FAB (*m*-nitrobenzyl alcohol) *m/z* 736 (M⁻); ^{1}H NMR (500 MHz, CS_2/CDCl₃) δ 4.82−4.89 (m, 2H), 5.47 (ddd, 1H), 7.17 (d, 1H); ^{13}C NMR (125 MHz, CS_2/CDCl₃) (rel intensity) δ 32.72 (1), 36.85 (1), 65.77 (1), 133.27 (1), 135.33 (1), 135.42 (1), 135.55 (1), 135.69 (1), 136.67 (1), 137.50 (1), 137.72 (1), 137.75 (1), 137.90 (1), 138.07 (1), 138.38 (1), 139.69 (1), 140.03 (1), 140.22 (1), 140.43 (1), 141.07 (1), 141.09 (1), 141.16 (1), 142.40 (1), 142.65 (2), 142.66 (1), 142.69 (1), 142.77 (1), 142.80 (1), 142.95 (1), 142.97 (1), 143.14 (1), 143.44 (1), 143.62 (1), 143.96 (1), 144.04 (1), 144.17 (1), 144.48 (1), 144.53 (1), 144.57 (1), 145.27 (1), 145.34 (1), 145.35 (1), 145.40 (1), 145.45 (1), 145.61 (1), 145.78 (1), 145.85 (1), 145.98 (1), 146.03 (1), 146.475 (1), 145.483 (1), 146.64 (1), 146.90 (1), 147.03 (1), 147.13 (1), 147.37 (1), 148.01 (1), 148.74 (1), 151.19 (1), 151.76 (1).

$C_{61}H_4$ (3). Negative ion FAB (*m*-nitrobenzyl alcohol) *m/z* 736 (M⁻); ^{1}H NMR (500 MHz, CS_2/CDCl₃) δ 4.62 (dt, 1H), 4.79 (d, 1H), 7.12 (d, 2H). ^{13}C NMR (125 MHz, CS_2/CD₂Cl₂, 5 mm) (rel intensity) δ 39.44 (1), 58.63 (2), 132.84 (2), 136.43 (2), 136.50 (1), 137.13 (1), 138.16 (2), 138.49 (2), 139.04 (2), 141.05 (2), 141.58 (2), 141.78 (2), 142.66 (2), 142.82 (2), 142.88 (2), 142.99 (1), 143.06 (2), 143.16 (2), 143.34 (2), 143.39 (2), 143.79 (2), 144.89 (2), 144.92 (1), 145.34 (2), 145.44 (2), 145.88 (2), 146.23 (2), 146.36 (2), 146.59 (2), 149.06 (2), 149.52 (2), 152.51 (2), 161.02 (2).

$C_{61}H_4$ by Hydroboration. $C_{61}H_2$ (96.3 mg, 0.131 mmol) and *o*-dichlorobenzene (96 mL) were combined in a 250 mL, three-neck flask and sparged with argon for 1.5 h. The solution was cooled to 0 °C and BH_3 (1 M in THF, 200 μL, 0.200 mmol) was added slowly. The reaction was stirred for 45 min at 0 °C, then stirred at room temperature for 45 min. Water (1 mL) was added. The solution was filtered through a 0.2 μm nylon filter, concentrated in vacuo to 40 mL, then diluted with toluene to 90 mL. The solution was filtered (0.2 μm), and the $C_{61}H_4$ band (**2** and minors) was isolated by HPLC with use of a Buckyclutcher column (21.1 mm × 250 mm), 1:1 toluene−hexane mobile phase, 15 mL/min flow rate, and monitored at 335 nm. Isomer **2** was further isolated from the minors by HPLC with use of a Cosmosil Buckyprep column (10 mm × 250 mm), toluene mobile phase, 5 mL/min flow rate, and monitored at 335 nm. The isolated yield of **2** was 17.8 mg, 0.0242 mmol (19%).

Supporting Information Available: The ^{1}H, ^{13}C, and [1]H−^{13}C coupled NMR spectra of **1**, **2**, and **3**, the proton decoupling series for **2**, and the UV−vis absorption spectra for **2** and **3** (14 pages). See any current masthead page for Web access instructions.

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