

Preparation of $C_{70}H_2$, $C_{70}H_4$, and $C_{70}H_8$: Three Independent Reduction Manifolds in the Zn(Cu) Reduction of C_{70}

H. Peter Spielmann,^{*,†} Guan-Wu Wang, Mark S. Meier,^{*,‡} and Brad R. Weedon

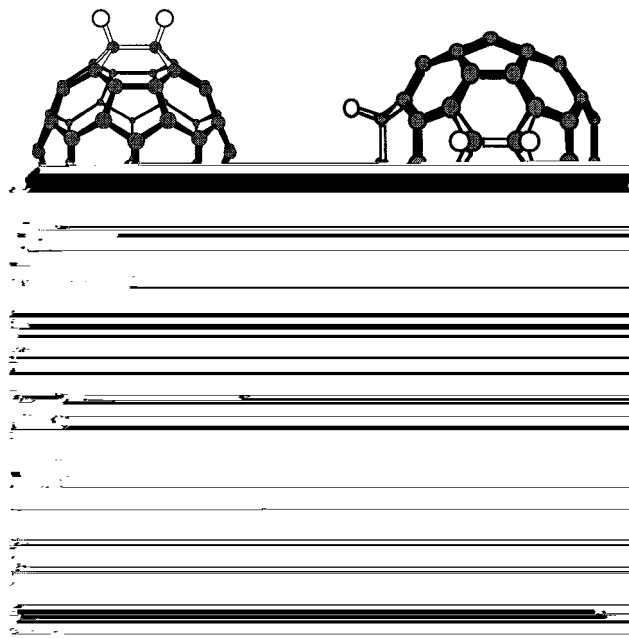
Departments of Chemistry and Biochemistry and Advanced Carbon Materials Center,
University of Kentucky, Lexington, Kentucky 40506-0055

Received August 11, 1998

This article reports the preparation of $C_{70}H_n$ species by Zn(Cu) reduction. The major products were one isomer of $C_{70}H_2$, one major isomer of $C_{70}H_4$, and one major isomer of $C_{70}H_8$. Several minor products were detected by UV–Vis and/or mass spectrometry. The structures of the major products were assigned as 1,2- $C_{70}H_2$, 1,2,56,57- $C_{70}H_4$, and 7,19,23,27,33,37,44,53- $C_{70}H_8$. Interestingly, although the major isomer of $C_{70}H_4$ is generated by reduction of the major isomer of $C_{70}H_2$, the major isomer of $C_{70}H_8$ is *not* generated by reduction of the major isomer of $C_{70}H_2$ or $C_{70}H_4$. The evidence suggests that there are at least three different reduction manifolds operating. One manifold includes 1,2- $C_{70}H_2$ and 1,2,56,57- $C_{70}H_4$, major products in which highly pyramidalized bonds near the poles of C_{70} are reduced. A second manifold includes 5,6- $C_{70}H_2$, a minor product. The third manifold consists of a set of $C_{70}H_2$, $C_{70}H_4$, and $C_{70}H_6$ species that are highly reactive and do not accumulate in solution. This third manifold leads to 7,19,23,27,33,37,44,53- $C_{70}H_8$. This third manifold is unique in that these compounds place hydrogens on nonadjacent carbons, a previously unobserved arrangement.

We report the preparation and structural characterization of a series of $C_{70}H_n$ species resulting from the Zn(Cu) reduction (hydrogenation) of C_{70} .¹ In contrast to the extensive bodies of knowledge concerning the chemistry of hydrocarbons built from tetrahedral sp^3 carbon (alkanes and congeners) and hydrocarbons built from planar sp^2 carbon (alkenes, benzenoid hydrocarbons, and related compounds), relatively little is known about the chemistry of the hydrocarbons built from pyramidal sp^2 carbon. We have developed methods for the preparation and isolation of a number of these new compounds, and we have identified three different reaction pathways (manifolds) that diverge at C_{70} and lead to different sets of isomers of $C_{70}H_2$, $C_{70}H_4$, and $C_{70}H_8$. It is clear that the site of the initial reduction step determines the preferred site of the second reduction step. An understanding of the differences in regiochemical selectivity of different $C_{70}H_2$ or $C_{70}H_4$ isomers will lead to rational synthetic methods for specific addition patterns.

We set out to understand the preferred order of reaction steps in fullerene chemistry, particularly in the regiochemistry of hydrogen addition. We recently reported the preparation of a series of $C_{60}H_n$ compounds by using Zn(Cu) reduction of C_{60} .² This reaction produces 1,2- $C_{60}H_2$, two isomers of $C_{60}H_4$ (1,2,18,36 or "e",³ and 1,2,33,50 or "trans-3"), and two isomers of $C_{60}H_6$ (1,2,33,41,42,50 or "trans-3, trans-3," and 1,2,18,22,23,36 or "e, e").^{3,4}



Although 1,2- $C_{60}H_2$ is the thermodynamic isomer of $C_{60}H_2$,^{5,6} the $C_{60}H_4$ and $C_{60}H_6$ species isolated from the Zn(Cu) reduction are nonthermodynamic isomers of $C_{60}H_4$ and $C_{60}H_6$, respectively.^{7,8} This kinetic selection likely reflects anisotropic charge distribution in dihydro- and tetrahydrofulleride anions formed in the course of the reduction.⁹ The protonation step (irreversible under these conditions)² is expected to have a very early

[†] Department of Biochemistry.

[‡] Advanced Carbon Materials Center.

(1) For an extensive review of reduced fullerenes, see: Gol'dshleger, N. F.; Moravshii, A. P. *Russ. Chem. Rev.* **1997**, *66*, 323–342.

(2) Bergosh, R. G.; Laske Cooke, J. A.; Meier, M. S.; Spielmann, H. P.; Weedon, B. R. *J. Org. Chem.* **1997**, *62*, 7667–7672.

(3) For the "e", "trans-3" bond-labeling system, see: Hirsch, A.; Lamparth, I.; Schick, G. *Liebigs Ann.* **1996**, 1725–1734.

(4) For the IUPAC nomenclature system for fullerenes, see: Godly, E. W.; Taylor, R. *Pure Appl. Chem.* **1997**, *69*, 1411–1434.

(5) Henderson, C. C.; Cahill, P. A. *Chem. Phys. Lett.* **1992**, *198*, 570–576.

(6) Henderson, C. C.; Cahill, P. A. *Science* **1993**, *259*, 1885–1887.

(7) Henderson, C. C.; Rohlfing, C. M.; Assink, R. A.; Cahill, P. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 786–788.

(8) Cahill, P. A. *Chem. Phys. Lett.* **1996**, *254*, 257–262.

transition state, so kinetic isomers dominate. Alternatively, the "e" and "trans-3" bonds may be activated relative to other bonds in the molecule. The nucleophilic bis-addition of bromomalonate anions¹⁰ results in a product mixture that is dominated by these two isomers. This has been rationalized on the basis of LUMO intensities in the corresponding R_2C_{60} species.³ The bis-1,3-dipolar addition of azomethine ylids¹¹ results in a mixture of six products, the major three being the "trans-3," the "cis-3," and the "e" isomers. However, steric effects can mask the underlying reactivity of the fullerene core, leading to the appearance of different selectivity in these two reactions. In the reduction of C_{60} by Zn(Cu) or other methods, $C_{60}H_2$ forms a branch point from which two major reaction pathway manifolds diverge, leading to different $C_{60}H_4$ and $C_{60}H_6$ species.

The chemistry of C_{70} is inherently more complex than the chemistry of C_{60} due to the lower symmetry of the molecule (D_{5h} versus I_h for C_{60}). For example, while there are only two possible isomers of $C_{60}H_2$ in which the hydrogens are on adjacent carbons, there are eight such possible isomers for C_{70} . It appears that for many types of reactions,^{12,13} including cycloadditions,^{14–25} osmylation,²⁶ and cyclopropanations,²⁷ the most reactive bonds in C_{70} are the C1–C2 bond and the C5–C6 bond (Figure 1). The other bonds in C_{70} are significantly less reactive, although there are reports of minor products resulting from addition to the C7–C21 bond,^{18,23} the C7–C8 bond,¹⁸ and the equatorial C20–C21 bond.¹⁵ Hydroboration-protonolysis of C_{70} leads to the formation of two isomers of $C_{70}H_2$ in a 2:1 ratio.²⁸ These were identified²⁸ as the 1,2 isomer (major) and the 5,6 isomer (minor) on the basis of their 1H NMR spectra, an AB pattern for the former and a singlet for the latter. These assignments were supported by ab initio calculations suggesting that the

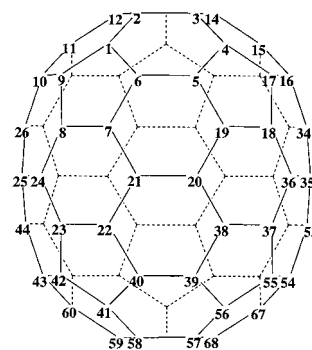


Figure 1. Numbering of C_{70} as recommended by IUPAC.³ For clarity, numbers have been omitted on the back surface of the molecule.

1,2 isomer is the most stable arrangement, followed by the 5,6 isomer.²⁸

Other preparations of $C_{70}H_2$ include reduction of C_{70} with diimide, which results in a 25:1 mixture of the 1,2 and 5,6 isomers.²⁹ In that same study, $C_{70}H_4$ was produced as a mixture of at least four isomers. None of these compounds were characterized as pure samples, and the NMR spectra (1H only) were measured on mixtures of isomers. More highly reduced $C_{70}H_n$ species have also been prepared.^{30–32}

The symmetry of a fullerene derivative is usually deduced by counting carbon resonances in a 1H -decoupled ^{13}C NMR spectrum of a fullerene, but the symmetry alone is insufficient for structural *proof* in many cases. This problem is particularly pronounced in C_{70} chemistry. As shown below, there are cases where isomers which are distinguishable spectroscopically but indistinguishable based on symmetry. For example, the two isomeric compounds **4** and **5** (below) are predicted to have the same symmetry and therefore the same number of ^{13}C resonances. 1H -coupled ^{13}C NMR spectroscopy can be profitably employed to solve structural problems when a simple count of the ^{13}C resonances does not provide a definitive structure.^{2,33} In this current work, we make extensive use of 1H -coupled ^{13}C NMR spectral data in the structural assignment of $C_{70}H_n$ species.

Synthesis of $C_{70}H_n$. Reduction of C_{70} with Zn(Cu) proceeded in a manner similar to that observed in the reduction of C_{60} with Zn(Cu). However, prolonged reaction allows the reduction of C_{70} to proceed farther than that of C_{60} .² After 6 h of heating at 100 °C, HPLC analysis of the reaction mixture revealed a chromatogram that was dominated by three bands (Figure 2). Isolation of the major chromatographic bands by HPLC and subsequent analysis by MALDI mass spectrometry indicated reaction products consistent with $C_{70}H_2$, $C_{70}H_4$, and $C_{70}H_6$, respectively. Several minor products were also formed, some of which were resolved under the chromatographic conditions described in Figure 2. A total of five bands

(9) Boyd, P. D. W.; Bhyrappa, P.; Paul, P.; Stinchcombe, J.; Bolshar, R. D.; Sun, Y.; Reed, C. A. *J. Am. Chem. Soc.* **1995**, *117*, 2907–2914.

(10) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437–438.

(11) Lu, Q.; Schuster, D. I.; Wilson, S. R. *J. Org. Chem.* **1996**, *61*, 4764–4768.

(12) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: Stuttgart, 1994.

(13) Taylor, R. *The Chemistry of Fullerenes*; Taylor, R., Ed.; World Scientific: River Edge, NJ, 1995.

(14) Zhang, X.; Foote, C. S. *J. Am. Chem. Soc.* **1995**, *117*, 4271–4275.

(15) Akasaka, T.; Mitsuhide, E.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 2627–2628.

(16) Seiler, P.; Herrmann, A.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 344–354.

(17) Wang, Y.; Schuster, D. I.; Wilson, S. R.; Welch, C. J. *J. Org. Chem.* **1996**, *61*, 5198–5199.

(18) Meier, M. S.; Wang, G. W.; Haddon, R. C.; Brock, C. P.; Lloyd, M. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1998**, *120*, 2337–2342.

(19) Mestres, J.; Duran, M.; Solá, M. *J. Phys. Chem.* **1996**, *100*, 7449–7454.

(20) Zhang, X.; Fan, A.; Foote, C. S. *J. Org. Chem.* **1996**, *61*, 5456–5461.

(21) Meier, M. S.; Poplawska, M.; Compton, A. L.; Shaw, J.; Selegue, J. P.; Guarr, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 7044–7048.

(22) Meidine, M. F.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Ohashi, O.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1189–1193.

(23) Wilson, S. R.; Lu, Q. *J. Org. Chem.* **1995**, *60*, 6496–6498.

(24) Bellavia-Lund, C.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 943–946.

(25) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2187–2188.

(26) Hawkins, J. M.; Meyer, A.; Solow, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7499–7500.

(27) Bingel, C.; Schiffer, H. *Liebigs Ann.* **1995**, 1551–1553.

(28) Henderson, C. C.; Rohlfing, C. M.; Gillen, K. T.; Cahill, P. A. *Science* **1994**, *264*, 397–399.

(29) Avent, A. G.; Darwish, A. D.; Heimbach, D. K.; Kroto, H. W.; Meidine, M. F.; Parsons, J. P.; Remars, C.; Roers, R.; Ohashi, O.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 15–22.

(30) Darwish, A. D.; Abdul-Sada, A. K.; Langley, J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2359–2365.

(31) Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2497–2498.

(32) Attalla, M. I.; Vassallo, A. M.; Tattam, B. N.; Hanna, J. V. *J. Phys. Chem.* **1993**, *97*, 6329–6331.

(33) Meier, M. S.; Weedon, B. R.; Spielmann, H. P. *J. Am. Chem. Soc.* **1996**, *118*, 11682–11683.

were isolated: one composed of $C_{70}H_2$, two small bands containing $C_{70}H_4$ (composed of a total of five isomers), one large band composed of $C_{70}H_4$, and one band consisting of $C_{70}H_8$. The typical yields of these compounds under these conditions were 15%, 3%, 2%, 25%, and 28%, respectively. Higher yields of $C_{70}H_2$ (27%) could be obtained in reactions that were stopped at shorter times. We were able to isolate sufficient quantities for ^{13}C NMR characterization of one isomer of $C_{70}H_2$, one major and one minor isomer of $C_{70}H_4$, and one isomer of $C_{70}H_8$.

Purification and Characterization of $C_{70}H_2$. Careful analytical HPLC of the $C_{70}H_2$ band revealed two isomers in a 95:5 ratio. Comparison of 1H NMR and UV–Vis spectral data with literature data²⁸ indicated that the major form of $C_{70}H_2$ produced under these conditions is the 1,2 isomer **1**. The minor product, which elutes on the

displayed an absorption spectrum (obtained with a photodiode array HPLC detector) consistent with the 5,6 isomer **2**.

The 1H -decoupled ^{13}C NMR spectrum of the major isomer (**1**) showed 36 resonances with two resonances superimposed at 131.72 ppm, consistent with a structure with a plane of symmetry containing the long axis of the molecule. In the 1H -coupled ^{13}C spectra of fullerenes, we can reliably detect and measure 1H – ^{13}C coupling constants down to 0.1 Hz. All 1-bond 1H – ^{13}C J -couplings in these systems are large (135–145 Hz), whereas multi-bond

leading edge of the $C_{70}H_2$ band shown in Figure 2,

difference becomes even more pronounced in the more highly reduced species discussed below.

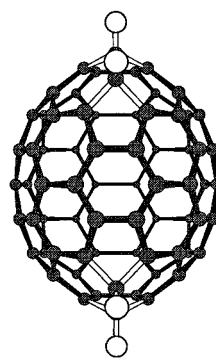
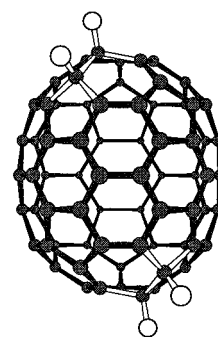
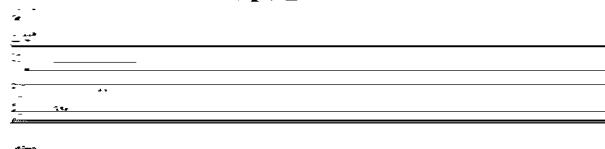
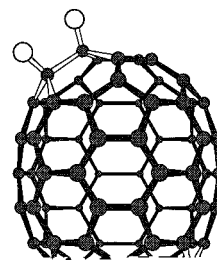
We are able to resolve $^nJ_{\text{HC}}$ couplings to 26 of the 36 observed ^{13}C resonances in **1**. Roughly half of the ^{13}C resonances exhibit J -coupling to *both* of the protons. ^1H – ^{13}C coupling manifests itself out to five bonds from the proton. Given the distance that observable coupling extends away from the protons, the analysis of coupling constants will provide a great deal of structural information for any C_{70} derivative that has hydrogens on the fullerene surface. However, full analysis and utilization of this information awaits the complete assignment of all the ^{13}C resonances.

The chemical shifts of the two proton resonances of **1** were sufficiently far apart to allow selective decoupling of each proton in separate experiments. Some spillover of rf power, resulting in partial decoupling of the second proton, was unavoidable. Most of the ^1H – ^{13}C coupling constants in the spectrum were affected to some extent. When sufficient rf power was applied to fully decouple one proton, coupling constants due to the other proton diminished by 35%. Interestingly, when the *upfield* proton was decoupled, the *downfield* sp^3 carbon resonance simplified, indicating that the upfield proton is directly bonded to the downfield sp^3 ^{13}C resonance. Likewise, when the *downfield* proton resonance was decoupled, the *upfield* carbon resonance simplified. Assuming that the most downfield sp^3 resonance is due to the C2 (polar) carbon (in analogy with the pattern of chemical shifts in C_{70} itself^(29,35)), it is possible to use Table 1 to make assignments of other carbon resonances to specific carbon atoms near the protonated carbons. In addition, the two single-intensity sp^2 resonances must be due to the two sp^2 carbons that lie on the symmetry plane, and these signals can be assigned as well.

Isolation and Characterization of C_{70}H_4 . Addition of a second pair of hydrogens to C_{70}H_2 occurred preferentially at bonds at the opposite pole of the molecule. This has been observed in the addition of metal complexes³⁶ and malonate anions²⁷ to C_{70} . The three isomers shown below are expected in the reduction of **1** to C_{70}H_4 . We observed a total of six C_{70}H_4 isomers by mass spectrometry, although five of the isomers were very minor products (<2% yield). Sufficient quantities for spectral characterization were obtained for the major isomer and one of the minor isomers.

Both of the isomers gave ^{13}C NMR spectra consisting of 35 resonances of equal intensity, consistent with C_2 products but not with products of higher symmetry. On this basis, we exclude isomer **3**. The two remaining C_2 structures are indistinguishable based on a ^1H -decoupled ^{13}C NMR line count alone.

The ^1H -coupled ^{13}C NMR spectrum of the major C_{70}H_4 isomer showed that the sp^3 resonances are split by large 1-bond J -couplings ($J = 138.63, 140.75$ Hz) and then again by smaller 2-bond J -couplings ($J_2 = 4.50, 4.88$ Hz). These coupling constants are consistent with 1,2 arrangements of hydrogens, based on the 2-bond J -couplings observed in **1**, although the 2-bond J -couplings are slightly smaller than those observed in **1**. There is no evidence for additional J -couplings to these sp^3 reso-

1,2,41,58- C_{70}H_4 (**3**)1,2,56,57- C_{70}H_4 (**4**)

nances, indicating that the symmetrically equivalent pairs of protonated carbons are located far from each other. This is consistent with the expectation that the pairs of hydrogens would be located at opposite poles of the C_{70} carbon framework. Similar spectral data were acquired for the minor isomer, leading to the same conclusion that the pairs of hydrogens are located far from each other on the surface of the fullerene.

Analysis of ^1H – ^{13}C J -coupling allowed us to assign the structures of the two isolated C_{70}H_4 isomers **4** and **5**. The ^1H -coupled ^{13}C spectra of these compounds show 35 resonances each, with significant H – C J -coupling to most of the sp^2 resonances. Small H – C J -couplings to many resonances in the ^{13}C spectra of both isomers were manifest as broadening of lines, indicating J -couplings on the order of the line width of these resonances. Observable J -coupling in 1,2- C_{70}H_2 (**1**) extends as far as five bonds from the protons, so it is not surprising that nearly all of the carbon resonances in **4** and **5** show some C – H J -coupling. Systematic analysis of these couplings is difficult, but the presence of observable coupling in a given resonance suggests that the resonance is due to a carbon that is located within six bonds of a proton and that true singlets are due to carbon atoms that are six or more bonds away from protons.

More resonances in the spectrum of the major isomer appear to be true singlets (i.e., single lines with no apparent broadening from small J -coupling) than in the spectrum of the minor isomer. This implies that there are some carbon atoms in the major isomer that are six or more bonds away from the protonated carbons. In **4**, the carbons most distant from the hydrogens are six bonds away from the protonated carbons, whereas in **5**, the most distant carbons are only five bonds from the protonated carbons. On this basis, we assign the struc-

(35) Taylor, R.; Hare, J. P.; Abdul-Sada, A. D.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423–1424.

(36) Balch, A. L.; Lee, J. W.; Olmstead, M. M. *Angew. Chem., Int. Ed.* **1992**, *31*, 1356–1358.

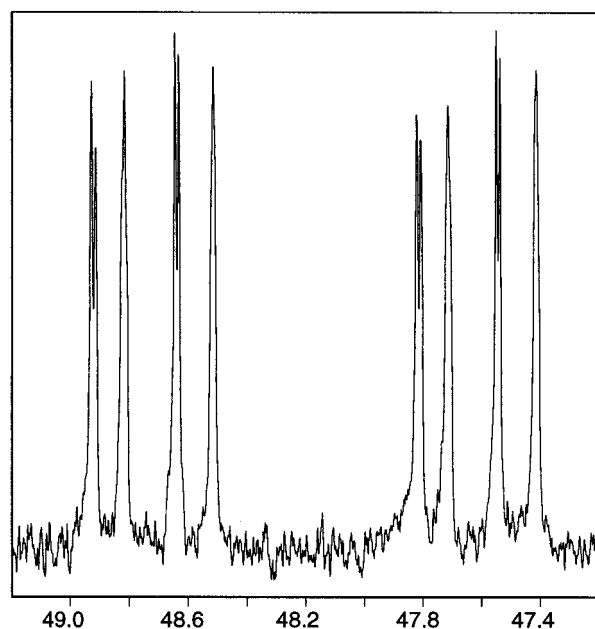


Figure 3. The sp^3 region of the H-C coupled ^{13}C NMR spectrum of $C_{70}H_8$ (**6**).

ture of the major isomer as **4** and the structure of the minor isomer as **5**.

Bingel²⁷ has observed three isomers of biscyclopropanated C_{70} , one having C_{2v} symmetry and two having C_2 symmetry. The two C_2 structures were assigned on the basis of calculated dipole moments and the order of elution from chromatography columns. The conclusion from that study was that the 1,2,56,57 isomer was the major biscyclopropane adduct. Also, the 1,2,56,57 addition pattern is the structure of a bis(iridium) complex isolated by Balch.³⁶ The C56-C57 bond is more reactive than other nearby bonds in 1,2-dihydro C_{70} species.

Isolation and Characterization of $C_{70}H_8$. We obtained one isomer of $C_{70}H_8$ as a major component of the reaction mixture (Figure 2). The 1H -decoupled ^{13}C NMR spectrum shows 37 resonances, composed of 33 double-intensity and four single-intensity lines, consistent with C_s symmetry (a plane of symmetry containing the long axis of the molecule). The sp^3 region of the 1H -coupled ^{13}C NMR spectrum shows four double-intensity resonances, confirming that the eight hydrogens are attached to two symmetry-related sets of four carbons (Figure 3). These resonances are slightly downfield relative to the protonated carbons of **1**, **4**, and **5** and are all located within a very narrow 0.5 ppm chemical shift range.

Analysis of the cross-peak connectivity pattern from a 1H - 1H DQF-COSY spectrum (Figure 4) acquired at high digital resolution indicates a linear ABCD spin system.

The 1H resonances of $C_{70}H_8$ fall in a narrow 0.4 ppm range giving a second-order spectrum which must be analyzed by simulation. The coupling constants J_{ab} (3.9 Hz), J_{bc} (2.9 Hz), J_{cd} (5.3 Hz), and J_{ad} (1.2 Hz) were determined directly from the cross-peak multiplet structure. Successful simulation³⁷ of the 1-D spectrum requires inclusion of couplings between the AA' ($J_{aa'} = 3.8$ Hz) and BB' ($J_{bb'} = 1.1$ Hz) proton resonances (Figure 5), showing that the two symmetry-related ABCD spin systems are connected into a AA'BB'CC'DD' system. There is no

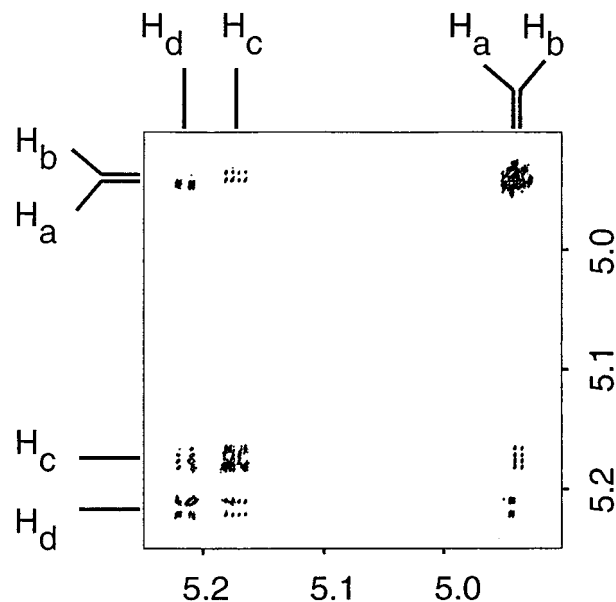


Figure 4. The DQF-COSY spectrum of $C_{70}H_8$.

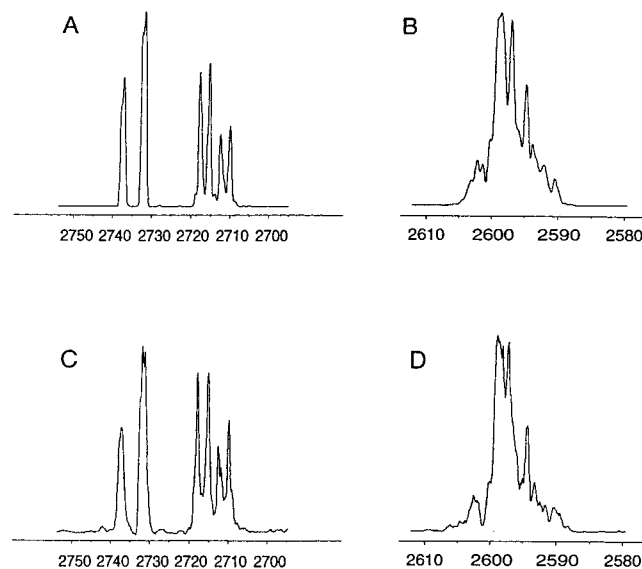


Figure 5. Simulated and experimental spectrum of $C_{70}H_8$. The simulated spectrum is in panels A and B, and the experimental spectrum is in panels C and D. Panels A and C are for the downfield H_c and H_d resonances, and panels B and D are for the upfield H_a and H_b resonances. The downfield and upfield multiplets are displayed on different scales for clarity. The axes are in hertz.

evidence of J_{ac} or J_{bd} couplings greater than 0.5 Hz in the spectra of $C_{70}H_8$.

Unlike the spectra of fullerenes with adjacent protonated carbons, there are no J -coupling constants larger than 6 Hz. The observed 1H - 1H J values are significantly smaller than those found in the $C_{60}H_x$ series, where they were between 10 and 15.5 Hz.^{2,7,33} The apparent 1H - 1H J values for 1,2- $C_{70}H_2$ (**1**) and for the two isomers of $C_{70}H_4$ (**4** and **5**) are also 12 Hz. The evidence suggests that the protons in $C_{70}H_8$ are *not* on adjacent carbons. The topology of the $C_{70}H_8$ spin system is shown in Figure 6.

We find that the 5-bond 1H - 1H J -couplings are between 2.9 and 5.3 Hz and the 7-bond 1H - 1H J -couplings are about 1 Hz. The proposed spin topology is supported by the similarity of the derived $J_{bb'}$ and the measured

(37) Balacco, G. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1235-1241.

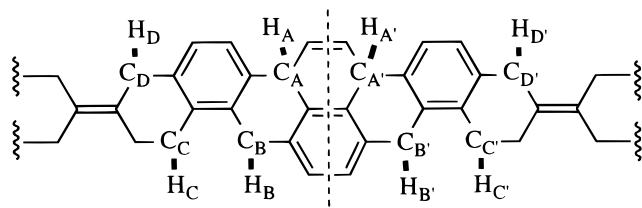
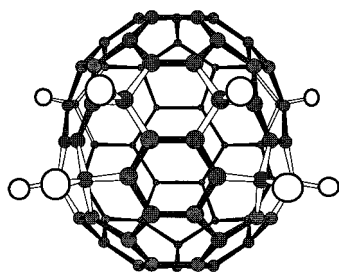


Figure 6. The spin system in $C_{70}H_8$ (**6**). The dashed line represents the mirror plane through the molecule.

J_{ad} coupling constants, both of which are smaller than the 5-bond couplings. Cahill has found a 1.8 Hz 5J coupling in 1,2,3,4- $C_{60}H_4$, lending further support for the observation of small 1H – ^{13}C couplings between protons arranged in a 1,4-fashion (5-bond) on a fullerene. In this same system, the 1,3 J coupling (4-bond) was determined to be 0 Hz.

Consistent with the 1H AA'BB'CC'DD' spin system, the protonated carbons in $C_{70}H_8$ show couplings to several magnetically inequivalent protons. Most of the sp^2 carbons show small couplings to protons. Unlike the pattern observed in **1**, **4**, and **5**, only one of the most downfield sp^2 resonances shows a large multi-bond (>2 Hz) C–H coupling. Instead, there are 6–10 Hz, presumably 2-bond, 1H couplings to some of the most *upfield* sp^2 carbon resonances. There is a distinct trend for the chemical shifts of carbons in C_{70} . The furthest downfield chemical shifts are assigned to the pole carbons, and each of the remaining “belts” of carbons resonate at progressively higher chemical shift as one proceeds toward the equator of the molecule, an assignment³⁵ that seems very reasonable because the equatorial carbons have the most benzene-like geometry of all the carbons in C_{70} .³⁴ In analogy to C_{70} , we assign five of the six most upfield sp^2 resonances in $C_{70}H_8$ to the equatorial carbons.

Taken together, these data indicate that in the structure of this isomer of $C_{70}H_8$ the protonated carbons are neither on the poles nor on the equator and that the protonated carbons are not adjacent to each other. There are relatively few structures that are consistent with this collection of data. We believe that the structure of this isomer is 7,19,23,27,33,37,44,53- $C_{70}H_8$ (**6**).



6

Such a structure would require 12 chemically distinct sp^2 carbons to be within 2 bonds of each protonated carbon, and all of these, save one, would also be within 3 bonds of two other protons. We do find 12 carbons with 5–10 Hz 1H – ^{13}C coupling constants, only one of which exhibits coupling to only one proton.

This structural assignment is supported by a long-range heteronuclear correlation experiment (J -filter set for 7 Hz) where the four 1H -coupled belt carbons correlated with the appropriate protonated carbons. Second,

the observation of no secondary couplings to the sp^3 carbons larger than 1.8 Hz in the presence of 4–10 Hz couplings between the protons and sp^2 carbons is further confirmation that the protonated carbons are not adjacent to each other. A simple appeal to the Karplus relationship for vicinal CH groups indicates that there is no way to organize two adjacent protonated sp^3 carbons on the surface of C_{70} and achieve a 1.8 Hz coupling constant.

This structure (**6**) does *not* result from direct reduction of the major isomers of $C_{70}H_2$ or $C_{70}H_4$, unless significant rearrangement occurs in the process, and we have found no evidence for such rearrangements.² We believe that **4** and **6** are kinetic traps: further reduction of these species is slower than their rates of formation.

The structures suggest that **4** is not a precursor to **6**. To confirm this view, we subjected a purified sample of **4** to Zn(Cu) reduction. It was clear that **4** does react further and leads to a number of different, more highly reduced species, but **6** is not produced. In addition, we subjected 1,2- $C_{70}H_2$ (**1**) to the same conditions; $C_{70}H_4$ forms, but **6** is not produced, even after extended reaction times.

Interestingly, the set of protonated carbons of **6** are among the most favorable sites for radical^{38,39} or hydride⁴⁰ additions to C_{70} . Our experiments confirm that several reaction manifolds are operating, and that **1** and **6** are on different manifolds. In fact, it appears that there are at least three different manifolds: C_{70} initially reduces to produce either the 1,2 or 5,6 isomers of $C_{70}H_2$ (**1** and **2**). These two species can then react further, leading to the $C_{70}H_4$ species we isolate, but *not* to **6**. There must also be a third reduction manifold that leads to **6** through a series of $C_{70}H_n$ species that are relatively reactive and that do not accumulate to significant levels in solution under these conditions. Resubjecting **6** to the reaction conditions *does* produce two of the three $C_{70}H_{10}$ species we have observed before.² The remaining $C_{70}H_{10}$ isomer must be produced from one of the minor $C_{70}H_2$ or $C_{70}H_4$ species that we observe, or it may result from an *additional* reaction manifold. We did not identify any chromatographic bands containing $C_{70}H_6$. Any $C_{70}H_6$ species formed react further at a rate comparable to their rate of formation. As a result, we do not observe the accumulation of any one $C_{70}H_6$ species. The reactivity pathways of C_{70} under Zn(Cu) reduction conditions are summarized in Figure 7.

Compound **6** is the first example of a hydrogenated fullerene with the hydrogens on nonadjacent carbons. In all other cases of isolated, characterized hydrogenated fullerenes, hydrogens are arranged on adjacent carbons.¹ In the few systems where a hydrogen and an alkyl group have been placed on nonadjacent carbons, migration to a 1,2 (adjacent) relationship is very facile.^{41,42} We have performed AM1 calculations on **6** and on a set of other $C_{70}H_8$ isomers with protons on adjacent carbons and have found that, within the set of structures we have inves-

(38) Borghi, R.; Lunazzi, L.; Placucci, G.; Krusic, P. J.; Dixon, D. A.; Matsuzawa, N.; Ata, M. *J. Am. Chem. Soc.* **1996**, *118*, 7608–7617.

(39) Borghi, R.; Guidi, B.; Lunazzi, L.; Placucci, G. *J. Org. Chem.* **1996**, *61*, 5667–5669.

(40) Karfunkel, H. R.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1468–1470.

(41) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697–9699.

(42) Banim, F.; Cardin, D. J.; Heath, P. *J. Chem. Soc., Chem. Commun.* **1997**, 25–26.

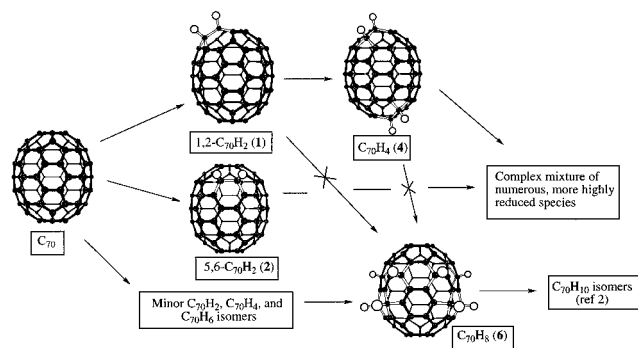


Figure 7. The three reduction manifolds in the Zn(Cu) reduction of C_{70} .

tigated, **6** is the lowest energy isomer. It appears that **6** is a particularly favorable isomer, and migration of hydrogens to adjacent carbons should not be thermodynamically favorable in this system. Cahill's ab initio calculations suggested that 1,4 (nonadjacent) addition of hydrogen to C_{60} becomes competitive with 1,2 (adjacent) addition of hydrogen for highly reduced species.⁴³

The structure of **6** resembles certain halogenated fullerenes,⁴⁴ specifically $C_{70}Cl_{10}$ ⁴⁵ and corresponds to the $C_{70}Ph_8$ derivatives prepared from $C_{70}Cl_{10}$.⁴⁶ The chlorination reaction is most likely to be more reversible than the reduction studied herein and therefore produces only the most thermodynamically favored species. Our current results illuminate several different competing pathways in the reactions of C_{70} with Zn(Cu), one of which is probably common to the halogenation reactions.

Experimental Section

General experimental and chromatographic procedures have been described previously.² All NMR samples were prepared in CS_2 containing 10% acetone- d_6 . These samples were dissolved, transferred to NMR tubes, deoxygenated by at least 3 freeze–pump–thaw cycles, flame-sealed, and stored in a freezer. The samples were protected from light when being handled in the laboratory.

Preparation of Reduced C_{70} Species. C_{70} (101.8 mg, 0.121 mmol) and toluene (300 mL) were combined in a 500 mL, three-neck flask with a magnetic stir bar. The resulting solution was deoxygenated with argon. The Zn/Cu couple was prepared by treating zinc dust (1.636 g, 25.03 mmol) five times with 4 mL portions of 3% HCl, H_2O , 2% $CuSO_4$, H_2O , THF, and toluene. The Zn/Cu couple was rinsed into the reaction flask using toluene (5 mL). Water (2 mL) was added. The mixture was heated at 100 °C for 5 h with vigorous stirring. A second Zn/Cu couple was prepared by treating zinc dust (0.783 g, 12.0 mmol) five times with 2 mL portions of 3% HCl, H_2O , 2% $CuSO_4$, H_2O , THF, and toluene. The Zn/Cu couple was rinsed into the reaction flask using toluene (5 mL). Additional water (0.5 mL) was added. Heating and stirring was continued for an additional hour. The reaction was allowed to cool to room temperature, filtered (0.2 μm), concentrated in vacuo, refiltered (0.2 μm), and purified by HPLC (preparative Buckyclutter column, 1:1 toluene/hexane mobile phase, 15

mL/min flow rate, monitored at 335 nm). Five bands were isolated: C_{70} , $C_{70}H_2$ major (**1**, 18% yield), a band composed of three minor isomers of $C_{70}H_4$ (2.9% total yield), a second band composed of two minor isomers of $C_{70}H_4$ (2.1% yield), $C_{70}H_4$ (**4**, 25% yield), and $C_{70}H_8$ (**6**, 27% yield). The reaction time is highly dependent on the temperature, the efficiency of stirring, and the quality of Zn/Cu, so it is strongly recommended that the reaction be monitored by HPLC. Separation of **5** from the first band of minor $C_{70}H_4$ isomers was accomplished on a Cosmosil Buckyprep column (10 \times 250 mm) eluted with 60:40 toluene/hexane. Compounds **1**, **4**, **5**, and **6** gave satisfactory negative ion MALDI MS spectra and distinctive UV–vis spectra (see Supporting Information).

1,2- $C_{70}H_2$ (1): 1H NMR (200 MHz, CS_2 , acetone- d_6) AB pattern δ 5.46 ($J = 16.1$ Hz), 5.01 ($J = 16.1$ Hz); ^{13}C NMR (125.6 MHz, CS_2 , acetone- d_6) (rel intensity) δ 44.06 (1), 46.37 (1), 131.72 (4), 131.95 (2), 134.5 (2), 135.0 (2), 138.68 (2), 140.85 (2), 141.8 (2), 142.93 (2), 143.4 (2), 143.43 (2), 143.46 (2), 143.7 (2), 146.55 (2), 146.96 (2), 147.34 (2), 147.47 (1), 147.79 (2), 147.95 (2), 148.55 (2), 149.2 (2), 149.57 (2), 149.83 (2), 150.19 (2), 150.358 (2), 150.365 (2), 150.49 (2), 151.18 (2), 151.41 (2), 151.81 (2), 151.86 (2), 151.9 (1), 152.63 (2), 156.34 (2), 157.48 (2).

1,2,56,57- $C_{70}H_4$ (4): 1H NMR (500 MHz, CS_2 , acetone- d_6) AB pattern δ 5.43 ($J = 16.1$ Hz), 5.01 ($J = 16.1$ Hz); ^{13}C NMR (125.6 MHz, CS_2 , acetone- d_6) (all lines are of equal intensity) δ 44.70, 46.86, 132.32, 133.10, 134.60, 135.08, 138.35, 138.86, 139.05, 140.58, 140.63, 141.16, 141.34, 143.10, 143.88, 144.41, 144.55, 144.99, 146.14, 147.85, 148.11, 148.70, 149.23, 150.61, 150.74, 151.02, 152.07, 152.27, 152.69, 153.41, 155.24, 156.83, 156.99, 158.43, 159.50.

1,2,67,68- $C_{70}H_4$ (5): 1H NMR (400 MHz, CS_2 , acetone- d_6) AB pattern δ 5.36 ($J = 16.0$ Hz), 5.87 ($J = 16.4$ Hz); ^{13}C NMR (125.6 MHz, CS_2 , acetone- d_6) (all lines are of equal intensity) δ 44.58, 46.20, 128.82 (imp), 129.55 (imp), 131.78, 134.01, 134.04, 134.71, 135.44, 136.29, 137.48, 140.29, 142.32, 142.84, 143.11, 143.196, 143.203, 143.82, 144.56, 144.88, 147.30, 147.37, 147.51, 147.64, 148.97, 149.20, 150.27, 150.42, 150.49, 151.01, 151.66, 151.68, 152.36, 152.42, 153.13, 158.12, 158.44.

7,19,23,27,33,37,44,53- $C_{70}H_8$ (6): 1H NMR (500 MHz, CS_2 , acetone- d_6) δ 5.23–5.25 (m, 4H), 5.48–5.52 (m, 4H); ^{13}C NMR (125.6 MHz, CS_2 , acetone- d_6) (rel intensity) δ 47.97 (2), 48.10 (2), 48.27 (2), 48.37 (2), 129.60 (2), 130.08 (2), 131.32 (2), 132.88 (2), 136.62 (2), 139.62 (2), 142.68 (1), 142.91 (2), 145.56 (2), 146.28 (2), 146.99 (2), 147.58 (2), 147.66 (2), 147.91 (2), 148.21 (2), 148.59 (2), 149.96 (2), 150.27 (2), 150.83 (2), 151.03 (2), 151.14 (2), 151.19 (2), 151.27 (2), 151.52 (2), 151.53 (2), 151.67 (2), 151.79 (2), 153.03 (1), 153.06 (2), 153.21 (1), 154.40 (1), 155.51 (2), 158.22 (2).

Acknowledgment. Mass spectra (MALDI and FAB/MS) were obtained through the University of Kentucky Mass Spectrometry Facility. The authors also wish to thank the National Science Foundation (grant CHE 9404704) and the Kentucky NSF-EPSCoR program (NSF OSR-9452895) for (partial) financial support of this project. This work was supported in part by the MRSEC Program of the National Science Foundation under award number DMR-9809686. We also thank Professors Robert Haddon and John Selegue for helpful discussions.

Supporting Information Available: Absorption spectra for compounds **1**, **4**, **5**, and **6** are available as Supporting Information (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO981627R

(43) Cahill, P. A.; Rohlfing, C. M. *Tetrahedron* **1996**, 52, 5247–5256.

(44) Fowler, P. W.; Sandall, J. P. B.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1997**, 419–423.

(45) Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1995**, 683–684.

(46) Avent, A. G.; Birkett, P. R.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Tetrahedron* **1996**, 52, 5235–5246.