

Osmylation of C₆₀: Proof and Characterization of the Soccer-Ball Framework

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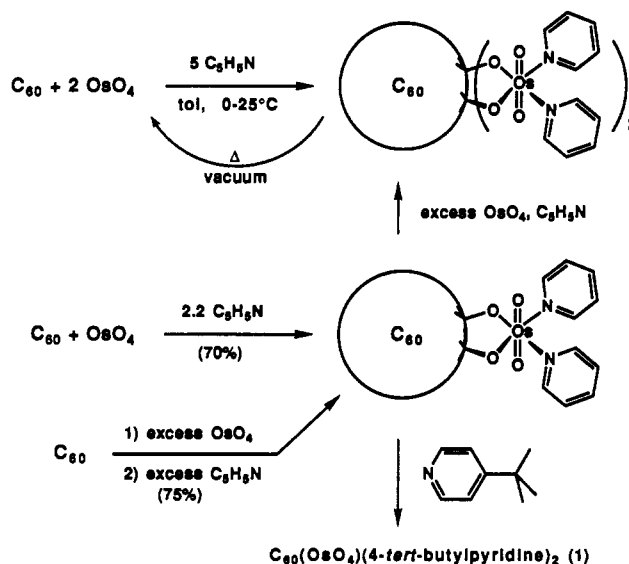
When C₆₀¹ was isolated in macroscopic quantities in 1990,² it transcended the realm of gas-phase physical chemistry and availed itself to the characterizations and utilizations of condensed matter. On one hand, it became a new material, a new allotrope of carbon. On the other hand, it became a new organic compound, one that did not contain elements other than carbon, and one that could serve as the parent and precursor to a whole class of novel organic compounds. When first available in macroscopic quantities, C₆₀ was probed spectroscopically in a number of laboratories. We probed the structure of C₆₀ *chemically* and found that the characterization of pure derivatives of C₆₀ could yield information about C₆₀ which could not be obtained directly. We prepared the first pure fullerene derivative, C₆₀(OsO₄)(4-*tert*-butylpyridine)₂ (1). Our characterization of this species yielded the first atomic-resolution X-ray crystallographic analysis of the carbon framework of C₆₀, thereby providing the first definitive proof of the buckminsterfullerene structure.³ Further analysis of 1 yielded the first measurement of coupling constants and hybridizations corresponding to the two types of bonds in C₆₀⁴ and the first quantitative labeling study probing the mechanism of C₆₀ formation.⁵

Osmylation of C₆₀

Traditional polycyclic aromatic hydrocarbons can be converted to a limitless array of derivatives through *substitution* reactions. As an unsaturated organic compound containing only carbon, C₆₀ lends itself to *addition* reactions. Initially, it was not clear whether the proposed soccer-ball-shaped carbon framework of C₆₀ would tolerate the addition of substituents; once the unsaturated spherical array was disrupted, the carbon framework might lose its kinetic and thermodynamic stability. While the early gas-phase chemistry of C₆₀ suggested that it might be unreactive,⁶ its solution chemistry turned out to be quite rich. Chemists at Rice demonstrated the first solution-state chemistry of C₆₀ with a Birch reduction.⁷ They isolated C₆₀H₃₆ of unknown isomeric composition or purity. Probing the reactivity of C₆₀, we found that it was easy to make the starting material go away, but difficult to generate pure distinct products. We explored various reactions known to add functionality to polycyclic aromatic hydrocarbons, including charge-transfer complexation with electron-deficient or polarized arenes, Diels-Alder reactions, complexation with transition metals, and os-

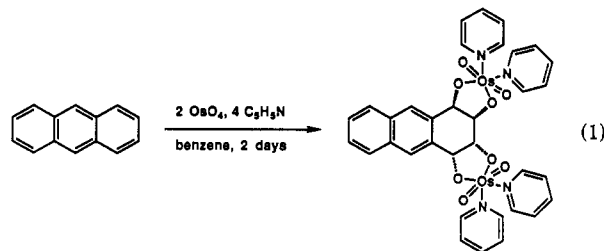
Joel M. Hawkins was born in 1959 in Hinsdale, IL, and received his B.S. in chemistry from the University of Illinois at Urbana. He received his Ph.D. in organic chemistry from the Massachusetts Institute of Technology with K. Barry Sharpless and conducted postdoctoral studies at the California Institute of Technology with Robert H. Grubbs. In 1987, he joined the faculty at the University of California at Berkeley, where he is an Assistant Professor of Chemistry. His research interests include asymmetric catalysis and the organic chemistry of C₆₀.

Scheme I
Osmylation of C₆₀ Giving 1:1 and 2:1 Adducts



mylation. Osmylation was the first reaction to give discrete stable products, and we pursued it in detail.

Osmium tetroxide is a powerful yet selective oxidant, and the osmylation of polycyclic aromatic hydrocarbons has been known for many years. Anthracene adds 2 equiv of osmium tetroxide in the presence of pyridine (eq 1).⁸ Our initial osmylations of C₆₀ also gave 2:1



stoichiometry (Scheme I). Formation of the (diolato)dioxobis(pyridine)osmium(VI) ester moiety in these

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reactions was established spectroscopically. The presence of the intact C_{60} skeleton in the osmate esters was established by thermal reversion to C_{60} under vacuum, a type of reaction known for rhenium(V).⁹ This was observed in the electron-impact mass chromatogram and then repeated preparatively by heating the osmate esters under vacuum. *These experiments established that non-hydrogen functionality can be added to C_{60} without disrupting its carbon framework.*¹⁰

Control of Stoichiometry. The initial osmylation conditions were developed to optimize the yield of osmate ester which precipitates from toluene. This precipitate has 2:1 stoichiometry, so these conditions favored the addition of two osmyl units to C_{60} . The 1:1 adduct was more desirable from the point of view of preparing a pure derivative of C_{60} ; it has only two possible regioisomers, in contrast to bisosmylated material, which has 54 possible regioisomers. Chromatographic analysis of the crude reaction mixture revealed six peaks: five peaks corresponded to the precipitate, and a single sharp peak corresponded to toluene-soluble material. Use of 1 equiv of OsO_4 increased the yield of the toluene-soluble material to 70% (Scheme I). Use of excess OsO_4 in the absence of pyridine, followed by treatment with pyridine, gave the same species in 75% yield. The toluene-soluble material was shown to have the desired 1:1 stoichiometry by converting it to the mixture of 2:1 adducts upon further exposure to the osmylation conditions.³

Thus, the stoichiometry of osmylation can be controlled by the ligands on osmium. The ligand (L) can be chosen to cause the adduct with the desired stoichiometry (n) to precipitate and protect it from further reaction (Figure 1). In the absence of an added ligand, the osmate esters dimerize,¹¹ inducing precipitation for $n = 1$. For L = pyridine, the 1:1 species is soluble and reactive, but the 2:1 species precipitate ($n = 2$). For L = 4-*tert*-butylpyridine, 3:1 and possibly higher adducts are soluble. Adding 4-*tert*-butylpyridine to the $n = 1$ dimer, or exchanging pyridine for 4-*tert*-butylpyridine when $n = 2$, brings the precipitated clusters back into solution for spectroscopic studies or further chemistry. Varying the ligands on osmium also provides an opportunity to optimize crystal quality.

Crystal Structure of $C_{60}(OsO_4)(4\text{-}tert\text{-butylpyridine})_2$ (1)

The spectroscopic analyses of C_{60} in late 1990 and early 1991 were each consistent with icosahedral symmetry and collectively highly supportive of the originally proposed buckminsterfullerene structure, but they did not strictly prove the soccer-ball framework or provide atomic positions. For example, the single-peak ^{13}C NMR spectrum¹² did not rule out the possibility of coincident peaks or of a fluxional structure. Furthermore, while the truncated icosahedral structure was favored,¹³ a truncated dodecahedral structure (which

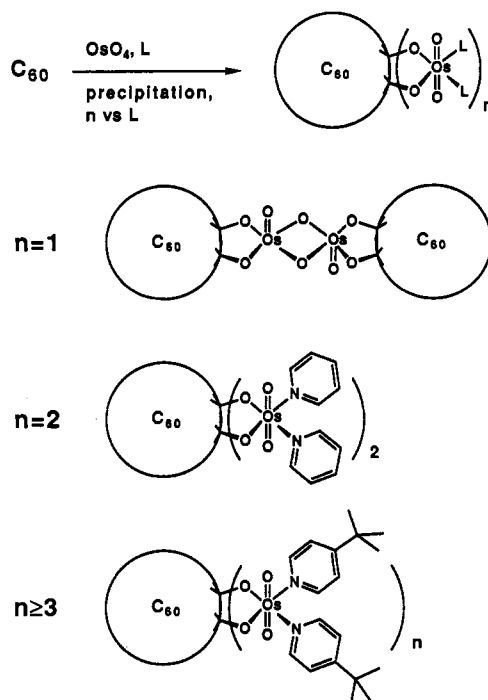


Figure 1. Control of osmylation stoichiometry (n) through choice of ligand (L).

also has icosahedral symmetry) could not be ruled out.¹⁴ In a review published in January 1991, J. Fraser Stoddart wrote, "The chemical world awaits a detailed single crystal X-ray diffraction analysis of the structure of C_{60} or C_{70} , or more likely perhaps, of a derivative in the first instance."¹⁵ We obtained a detailed single-crystal X-ray diffraction analysis of a C_{60} derivative, and this was the first instance.³

Early attempts to obtain an X-ray crystal structure of underivatized C_{60} were daunted by disorder and did not yield atomic positions.^{2,16} While the ball-like molecules readily pack in an ordered fashion, their nearly spherical symmetry promotes orientational disorder. At ambient temperature, they rotate rapidly in the solid state.¹⁷ We reasoned that if C_{60} could be derivatized in a way that broke its apparent spherical symmetry, it might crystallize with orientational order and allow a detailed crystallographic analysis. *Specifically, we needed to regioselectively functionalize C_{60} so that the carbon framework would be organized relative to the attached functional group, with this group serving as a handle to keep the carbon clusters uniformly oriented.* The observation of a single sharp chromatographic peak for $C_{60}(OsO_4)(pyridine)_2$ suggested that it forms as a single regioisomer, rather than a mixture of the two regioisomers which are possible from the soccer-ball structure for C_{60} . This would be true if the bisoxygenation was strongly favored across one of the two unique bonds in C_{60} , the junction of two

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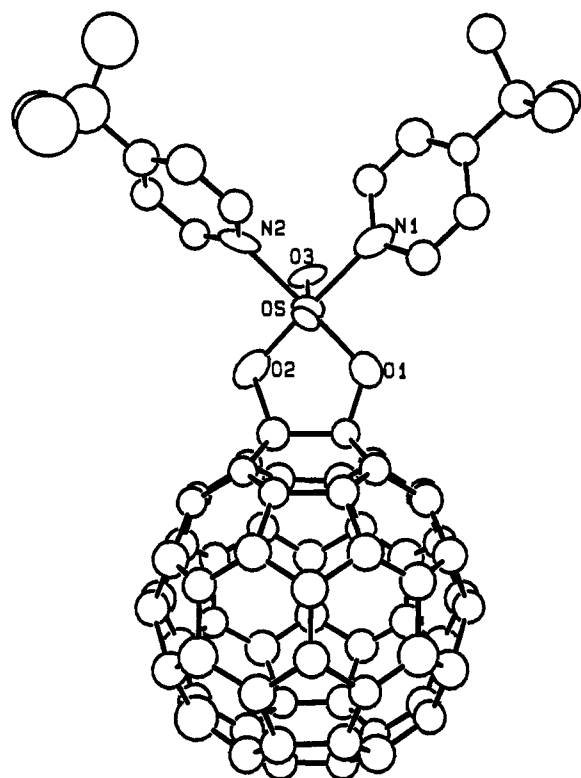


Figure 2. ORTEP drawing (50% ellipsoids) of the 1:1 C_{60} -osmium tetraoxide adduct $C_{60}(OsO_4)(4\text{-}tert\text{-butylpyridine})_2$ (1) showing the relationship of the osmyl unit with the carbon cluster. Reprinted with permission from ref 3. Copyright 1991 AAAS.

six-membered rings, or the junction of a six- and a five-membered ring. Regioselective osmylation would fix the position of the C_{60} carbon framework relative to the osmyl unit, with the osmyl unit breaking the pseudospherical symmetry of C_{60} , promoting an ordered crystal. Adduct $C_{60}(OsO_4)(4\text{-}tert\text{-butylpyridine})_2$ (1) indeed gave a sufficiently ordered crystal for the determination of atomic positions by X-ray crystallographic analysis.

Structural Analysis. The crystal structure (Figures 2 and 3) proved the soccer-ball-like arrangement of carbon atoms in C_{60} by clearly showing the 32 faces of the carbon cluster composed of 20 six-membered rings fused with 12 five-membered rings for the first time.³ No two five-membered rings are fused together, and each six-membered ring is fused to alternating six- and five-membered rings. Sixteen equivalent molecules of 1 occur in the unit cell, which also contains 2.5 toluenes of crystallization per osmate ester. Intermolecular contacts between C_{60} moieties include carbon-carbon distances as small as 3.29 (4) Å.

The crystal structure shows that the O-Os-O unit has added across the fusion of two six-membered rings. As described below, the ^{13}C NMR spectrum of 1 recorded before crystallization indicates that the isomer in the crystal is the only one present within the limits of detection. The osmylation appears to be quite regioselective, and the favored approach of osmium tetraoxide agrees with the regiochemistry predicted by Hückel calculations on C_{60} and the principle of least motion or minimum electronic reorganization.¹⁸ Extended Hückel calculations on a Tektronix CACHE system

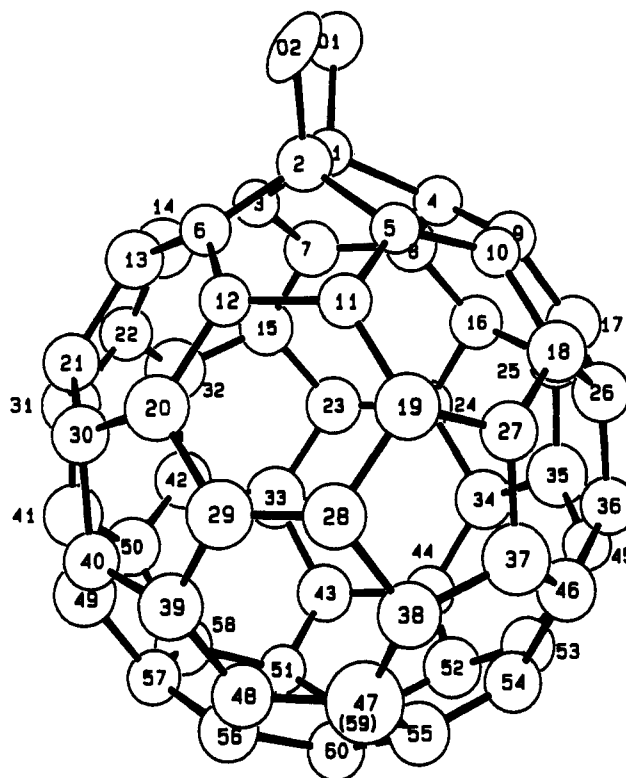


Figure 3. ORTEP drawing (50% ellipsoids) of 1 showing the geometry of the $C_{60}O_2$ unit and the numbering scheme. Reprinted with permission from ref 3. Copyright 1991 AAAS.

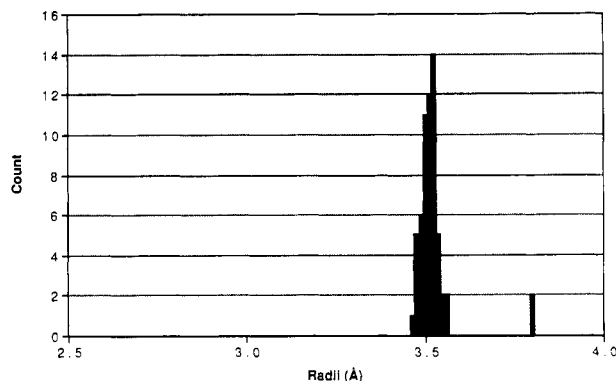


Figure 4. Histogram of distances from the calculated center of the C_{60} moiety to C1-C60 in 1.

qualitatively agree with these HMO calculations. *Chemical reactivity, especially regioselectivity, can thus serve as a probe of fullerene structure and bonding in a way that complements theoretical and spectroscopic techniques.*

Analysis of the structure of the carbon cluster was aided by its apparent symmetry. A histogram of distances from the calculated center of the cluster to each of the carbon atoms in the cluster shows two groupings (Figure 4). The tricoordinate carbons C3-C60 all lie within a spherical shell of radius 3.46-3.56 Å, with an average distance of 3.512 (3) Å from the center of the cluster. (Averages are reported with the standard error of the mean in parentheses.) The tetracoordinate oxygen-bonded carbons C1 and C2 lie significantly outside of this shell at distances of 3.80 (2) and 3.81 (3) Å from the center. They have approximately tetrahedral geometry with sums of C-C angles equal to 330°, slightly more than 328° (the sum for an ideal tetrahe-

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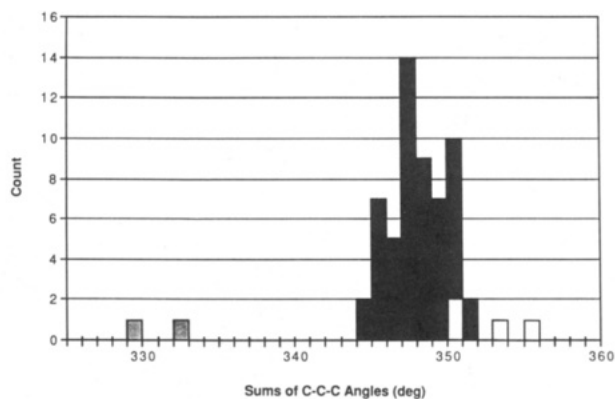


Figure 5. Histogram of sums of C-C-C angles in 1: C1-C2 (shaded), C3-C6 (white), and C7-C60 (black).

dral atom). The proximate carbons, C3-C6, are the least distorted from planarity within the cluster, with sums of C-C-C angles averaging $353(1)^\circ$, compared with 360° for a planar atom (Figure 5). The remaining carbons, C7-C60, have approximately equivalent geometries with sums of C-C-C angles ranging from 344° to 351° . The average sum, $348.0(3)^\circ$, equals the value for an ideal junction of two regular hexagons and a regular pentagon.

The C1-C3, C1-C4, C2-C5, and C2-C6 bond lengths average $1.53(3) \text{ \AA}$, comparable with normal $C(sp^3)$ - $C(sp^2)$ single bonds. The five- and six-membered carbocyclic rings not containing C1 and C2 are planar with deviations from least-squares planes less than $0.05(3) \text{ \AA}$. In contrast, tetracoordinate carbons C1 and C2 lie $0.22(2)$ - $0.30(3) \text{ \AA}$ outside of the planes defined by the other carbons in the rings which contain them. Excluding bonds to C1 and C2, the average C-C bond lengths are $1.386(9) \text{ \AA}$ for six-six ring fusions and $1.434(5) \text{ \AA}$ for six-five ring fusions. Histograms for these two types of bond lengths show overlap between the two sets, but the two averages are statistically different (Figure 6). (Carbon-carbon coupling constants reveal a more distinct division between the six-six and six-five ring fusions in 1 as described below.) These two average bond lengths are within the range of values predicted by theory for the two types of bonds in C_{60} (1.36 - 1.42 \AA for six-six ring fusions, and 0.02 - 0.08 \AA longer for six-five ring fusions)¹⁹ and within experimental error of the two (unassigned) bond lengths in C_{60} determined from ^{13}C - ^{13}C magnetic dipolar coupling (1.40 ± 0.015 and $1.45 \pm 0.015 \text{ \AA}$).¹³

Following our report of the crystal structure of 1, the crystal structures of two other 1:1 adducts with C_{60} ,²⁰ a 6:1 adduct with C_{60} ,²¹ and a 1:1 adduct with C_{70} ²² have been reported. These species also involve metals, this time directly bound to the fullerene through metal-carbon bonds. Like 1, these species show reaction across six-six ring fusions. The average bond lengths for the six-six and six-five ring fusions in $(\eta^2-C_{60})Pt(PPh_3)_2$ are $1.388(30)$ and $1.445(30) \text{ \AA}$, respectively (standard deviations in parentheses).^{20a} In $(\eta^2-C_{60})Ir-$

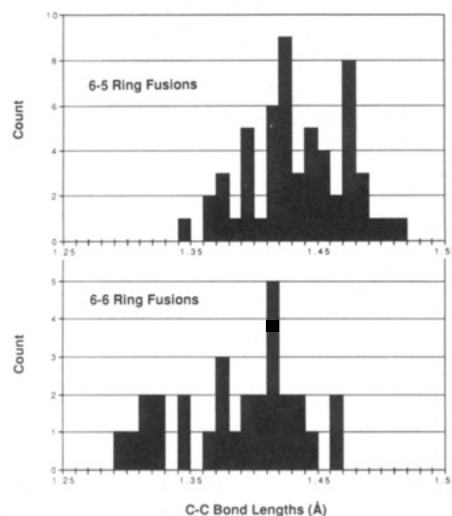


Figure 6. Histograms of carbon-carbon bond lengths for C3-C60 in 1 showing six-five ring fusions (top) and six-six ring fusions (bottom).

$(CO)Cl(PPh_3)_2$, cluster C-C bond lengths range from $1.35(3)$ to $1.53(3) \text{ \AA}$.^{20b} The C_{70} adduct $(\eta^2-C_{70})Ir(CO)Cl(PPh_3)_2$ is particularly interesting from the point of view of regiochemistry. The metal is selectively positioned across one of the four types of six-six ring fusions in C_{70} , presumably due to thermodynamic control. The addition of $Ir(CO)Cl(PPh_3)_2$ to C_{60} is reversible;^{20b} reversible addition to C_{70} could promote regioselectivity through preferential addition²² or selective crystallization. In contrast, osmylation appears to give a kinetically controlled mixture with C_{70} .²³ A similar dichotomy is possible with C_{60} ; kinetically and thermodynamically controlled additions to C_{60} give different sets of 2:1 regioisomers.²³

Quite recently, two atomic-resolution crystal structures²⁴ and a gas-phase electron diffraction study²⁵ of C_{60} have been reported. The average bond lengths for the six-six and six-five ring fusions of C_{60} were determined to be $1.355(9)$ and $1.467(21) \text{ \AA}$, respectively, from the X-ray crystal structure of a twinned crystal of C_{60} at 110 K ,^{24a} $1.391(18)$ and $1.455(12) \text{ \AA}$, respectively, from the neutron powder diffraction of C_{60} at 5 K ,^{24b} and $1.401(10)$ and $1.458(6) \text{ \AA}$, respectively, for thermal average values obtained from the electron diffraction study of gaseous C_{60} volatilized at 730°C .²⁵

The carbon cluster in 1 is fairly undistorted from an ideal soccer-ball shape for C7-C60 and perturbed in the local environment around the added oxygens. The undistorted region of 1 behaves like and provides a model for C_{60} , as described below.

2D NMR Analysis of Osmylated C_{60}

Buckminsterfullerene contains one type of carbon and two types of carbon-carbon bonds. The ^{13}C NMR spectrum of C_{60} thus shows a single peak,¹² and C-C couplings corresponding to the two types of C-C bonds are not discernible. In contrast, 1 contains 17 types of cluster carbons with 20 potentially measurable one-bond C-C couplings. We sought to assign chemical

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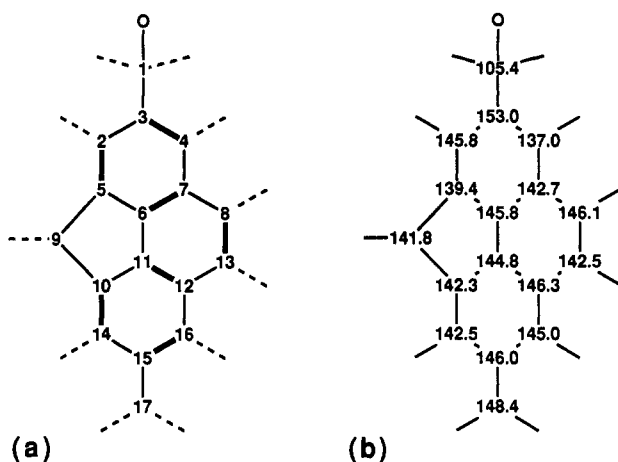


Figure 7. (a) Fragment showing the connectivities of the 17 types of cluster carbons in 1. Narrow lines indicate six-five ring fusions, bold lines indicate six-six ring fusions, and dashed lines indicate bonds between symmetry-related carbons or nonindependent couplings. (b) Pattern of chemical shifts for the 17 types of cluster carbons in 1 (four digits shown for clarity).

shifts and measure coupling constants in 1 in order to learn about bonding in C₆₀.

To improve sensitivity, we prepared ¹³C-enriched C₆₀ from cored natural-abundance carbon rods packed with ¹³C powder²⁶ and converted it to 1 as described above. The 1D ¹³C NMR spectrum of enriched 1 showed 22 peaks. Five of the peaks were assigned to coordinated 4-*tert*-butylpyridine. Of the 17 remaining peaks, four displayed approximately half the intensity of the other 13 peaks. This pattern agrees with the structure of 1 considering that it has two approximate mirror planes, one containing carbons 1, 2, 59, and 60, and one containing carbons 26, 36, 31, and 41 (Figure 3). Accordingly, the C₆₀ segment of 1 has 17 types of carbons, 13 represented four times and four that lie on a mirror plane and are represented two times (Figure 7a). Signals corresponding to the other possible 1:1 adduct where OsO₄ has added across the junction of a five- and a six-membered ring were not detectable. The resolution of multiple cluster carbons indicates that C-O bonding is not fluxional on the NMR time scale for 1:1 adduct 1. (The purification of regioisomeric 2:1 adducts establishes that C-O bonding is not fluxional at room temperature for these species.²³)

Assignment of Chemical Shifts. The 17 types of carbons were assigned on the basis of the connectivities derived from a 2D NMR INADEQUATE experiment (Figure 8 and Table I).⁴ The half-intensity peaks (a, g, n, and p) were assigned to the carbons on the mirror planes (types 1, 8, 13, and 17). Peaks a and p were assigned to types 1 and 17 because they each couple with only one carbon. Of the pair, the remote upfield peak, a, was assigned to the tetracoordinate O-bonded carbon (type 1) on the basis of the spectra of classical arene adducts.⁸ Starting from carbon type 1, C-C connectivities provided assignments for carbon types 2-13 and 16. Types 5 and 7 were readily differentiated in that type 5 (peak c) couples with three full-intensity peaks (d, k, and l), while type 7 (peak h) couples with two full-intensity peaks (b and l) and a half-intensity peak (n). The up-down pattern aided assignments in

Table I
Chemical Shifts, Peak Assignments, and Carbon-Carbon Coupling Constants for the C₆₀ Portion of 1

peak	chemical shift (ppm)	carbon type	carbon type, J_{CC} (Hz)
a	105.38	1	3, 48
b	137.02	4	3, 71; 7, 56
c	139.42	5	2, 68; 6, 56; 9, 56
d	141.81	9	5, 56; 10, not first order
e	142.32	10	9, not first order; 11, 56 ^a
f	142.48	14	15, 56 ^a
g	142.55	13	8, 67; 12, 56
h	142.75	7	4, 56; 6, 67; 8, 55
i	144.85	11	6, 54; 10, 56; 12, 68
j	145.04	16	12, 56; 15, 65
k	145.76	2 ^b	3, 57; 5, 68
l	145.77	6 ^b	5, 56; 7, 67; 11, 54
m	145.99	15	14, 56; 16, 65; 17, 56
n	146.10	8	7, 55; 13, 67
o	146.32	12	11, 68; 13, 56; 16, 56
p	148.41	17	15, 56
q	153.03	3	1, 48; 2, 57; 4, 71

^a No coupling was observed between peaks e and f, presumably due to small δ/J . ^b Peaks k and l are extremely close and may have the reversed assignment.

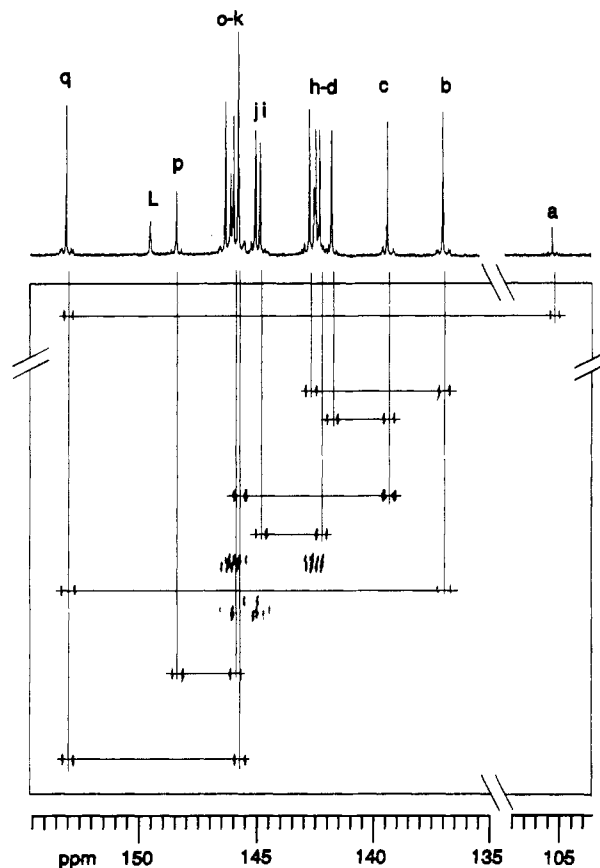


Figure 8. Upper spectrum: 1D ¹³C NMR spectrum of 1. Cluster carbons are labeled a-q as assigned in Table I; L indicates 4-*tert*-butylpyridine. Lower spectrum: 2D NMR INADEQUATE spectrum of 1. Vertical and horizontal lines delineate couplings: a-q, b-h, b-q, c-d, c-k, c-l, e-i, k-q, and m-p. Other couplings are not marked for clarity.

complicated regions. Connectivities from carbon type 17 completed the assignments.

Cluster carbons greater than two bonds away from oxygen (carbon types 2 and 4-17) range from 137.02 to 148.41 ppm (peaks b-p). These peaks fall within the range observed for C₇₀ (130.28-150.07 ppm),^{12a,26} and average 143.8 ppm, close to the resonance of C₆₀ at

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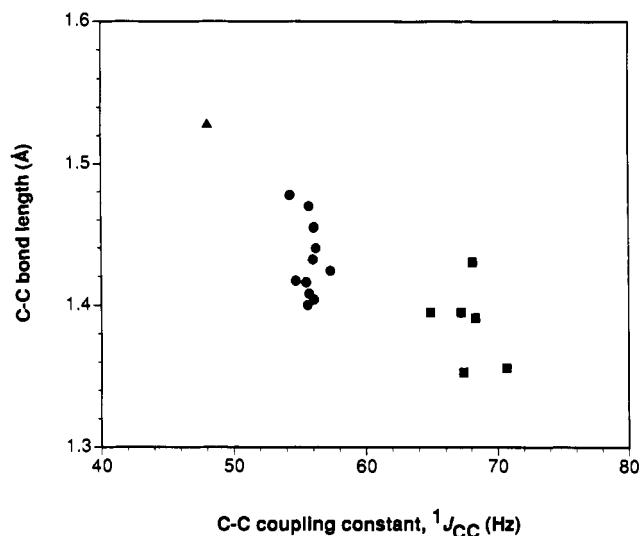


Figure 9. Plot of C-C bond length versus C-C coupling constant in 1 showing three groupings: C(type 1)-C(type 3) (▲), six-five ring fusions (●), and six-six ring fusions (■).

142.68 ppm.¹² While the range of peaks observed for C_{70} can be related to variable degrees of strain within this oblong molecule,^{12a} the 11.4 ppm range observed for this segment of 1 is somewhat surprising considering that these carbons have a fairly even degree of pyramidalization as discussed above. No obvious pattern is followed for the chemical shifts in this region, and even adjacent carbons well separated from the osmyl unit show significant variations (Figure 7b). For example, carbon types 14 and 15 differ by 3.51 ppm. Carbon type 3, two bonds away from oxygen, is the furthest downfield of the cluster carbons (153.03 ppm), even though it is the least distorted from planarity and presumably the least strained. In analogy to C_{70} , the decreased strain should make this carbon relatively upfield. Proximity to the osmyl group may move it downfield, although the quaternary carbons of bisosmylated anthracene (eq 1) differ by only 1.5 ppm.⁸ The factors controlling chemical shifts in these compounds are clearly complicated. Spectra of the regioisomers of bisosmylated C_{60} will provide more insight.²³

Coupling Constants and Hybridizations. With structural and NMR data for 1, we were in a unique position to compare fullerene bond lengths and coupling constants and obtain the first correlation of quaternary-quaternary carbon bond lengths to $^1J_{CC}$.⁴ The C-C coupling constants for the C_{60} portion of 1 fall into three groups, 48 Hz, 54–57 Hz, and 65–71 Hz. A plot of bond length versus $^1J_{CC}$ shows three distinct types of bonds (Figure 9).²⁷ The 48-Hz coupling corresponds to the bond between carbon types 1 and 3 and is comparable with the 47.7-Hz C(sp²)-C(sp³) coupling in benzyl alcohol. The 54–57-Hz couplings correspond to fusions between five- and six-membered rings, and the 65–71-Hz couplings correspond to fusions between two six-membered rings (Figure 7a):²⁸ the two types of

(27) A linear relationship between $^1J_{CC}$ and C-C bond lengths has been observed for benzo[a]pyrenes. Unkefer, C. J.; London, R. E.; Whaley, T. W.; Daub, G. H. *J. Am. Chem. Soc.* 1983, 105, 733.

(28) In C_{70} , $^1J_{b,c} = ^1J_{c,d} = 55$ Hz (six-five ring fusions), $^1J_{d,e} = 62$ Hz (six-six ring fusion), and $^1J_{a,b} = 68$ Hz (six-six ring fusion). Johnson has related the size of $^1J_{a,b}$ and $^1J_{d,e}$ to whether one or both of the bonded carbons belong to five-membered rings.²⁶ In C_{60} and in the C7-C60 portion of 1, each of the carbons belongs to a five-membered ring, so six-six ring fusions in 1 and C_{60} are similar to bond a-b in C_{70} .

Table II
Experimental and Calculated Ratios of Satellite Integration to Central Peak Integration in ^{13}C -Enriched 1

carbon type	experimental ratio	statistical ratio
3	0.22	0.24
4	0.18	0.16
5	0.22	0.24
17	0.14	0.16

bonds in C_{60} resolve in the plot of bond lengths versus coupling constants for 1. Considering carbon types 2 and 4–17 which have approximately equivalent geometries and symmetrical bonds, the average coupling constants for these two ranges, 55.6 (2) and 67.2 (6) Hz, can be used to calculate the s character in the two types of bonds in C_{60} . Bond symmetry allows substitution of (% s)² for (% s_x)(% s_y) in the equation $^1J_{C_xC_y} = [0.073(\% s_x)(\% s_y) - 17]$ Hz,²⁹ yielding 31.5% s character for six-five ring fusions and 34.0% s character for six-six ring fusions. Subtraction of the s character for the two six-five fusions and one six-six fusion per cluster carbon from the total s character at carbon (100%) leaves 3% s character and 97% p character for the π -orbital.³⁰ Since the structure of this portion of 1 closely fits the soccer-ball structure of buckminsterfullerene, these hybridizations provide a good model for C_{60} .

Statistical Incorporation of ^{13}C into C_{60}

Partially ^{13}C enriched C_{60} can be prepared by the laser³¹ or contact-arc¹³ vaporization of heterogeneous mixtures of solid ^{12}C and ^{13}C . Mass spectral analysis of the partially enriched C_{60} suggests that the ^{13}C is statistically distributed among the clusters.^{31,32} Rather than $^{12}C_{60}$ and $^{13}C_{60}$ forming predominately, $^{13}C_n^{12}C_{60-n}$ mixtures form with a distribution consistent with isotopic scrambling via C_m units where m is small. While the mass spectrum indicates the isotope distribution between the carbon clusters, it does not address the isotope distribution within the carbon clusters. ^{13}C NMR can potentially indicate the distribution of ^{13}C atoms within a carbon cluster by the degree of ^{13}C - ^{13}C coupling.^{33,34} The 1D ^{13}C NMR spectrum of enriched C_{70} qualitatively implies carbon atom mixing on an atomic scale during fullerene formation in that the spectrum consists of "predominantly singlets", rather than "predominantly multiplets due to coupling of adjacent ^{13}C atoms."³⁴ We used 1 to quantitatively examine the ^{13}C distribution within enriched C_{60} . Buckminsterfullerene could not be analyzed directly, because $^{13}C_n^{12}C_{60-n}$ shows a single ^{13}C NMR peak¹² and therefore provides no coupling information. Conversion of C_{60} to 1 expands its spectrum into the 17 peaks and asso-

(29) (a) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* 1972, 94, 6021. (b) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden: Philadelphia, 1978; p 57.

(30) POAV1 analysis of bond-equalized icosahedral C_{60} gives s^{0.083}p hybridization for the π -orbital (8% s character). Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* 1986, 131, 165.

(31) Meijer, G.; Bethune, D. S. *J. Chem. Phys.* 1990, 93, 7800.

(32) Heath, J. R. In *Large Carbon Clusters*; Hammond, G. S.; Kuck, V. J., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, in press.

(33) Isolated pairs of ^{13}C spins appear to dominate the ^{13}C - ^{13}C dipolar coupling in the solid-state ^{13}C NMR spectrum of enriched C_{60} .¹³

(34) Johnson, R. D.; Yannoni, C. S.; Salem, J.; Meijer, G.; Bethune, D. S. *Mater. Res. Soc. Symp. Proc.* 1991, 206, 715.

ciated couplings described above. We measured the degree of ^{13}C - ^{13}C coupling for four types of carbons in 1; calculated the expected degrees of ^{13}C - ^{13}C coupling for these carbons, given a random distribution of ^{13}C atoms within the clusters; and found that the two sets of numbers agree within experimental error.⁵

Partially ^{13}C enriched C_{60} was prepared by the contact-arc vaporization of a heterogeneous mixture of ^{12}C and ^{13}C as described above and was converted to 1. Carbon types 3, 4, 5, and 17 (peaks q, b, c, and p) in 1 are well separated from the other peaks, and the ^{13}C satellites could be integrated relative to the central peaks (Table II). Since there is no NOE and the acquisition parameters were optimized for the approximately 4 s T_1 of carbon types 2-17, the integration is quite reliable. For example, the ratios of the integrals of carbon types 3, 4, 5, and 17 (including the ^{13}C satellites) are within 3% of the expected ratios, 4:4:4:2.

The satellite peaks are composed of doublets, quartets, and one-half of the triplet pattern, while the central peaks correspond to singlets plus one-half of the triplet pattern. If the ^{13}C atoms are randomly distributed in C_{60} , the ratio of the satellite integration to the central peak integration is described by eq 2, where s_n , d_n , t_n , and q_n correspond to the singlet, doublet, triplet, and quartet signals per $^{13}\text{C}_n^{12}\text{C}_{60-n}$ molecule, and I_n corresponds to the intensity of the m/z 720 + n peak in the mass spectrum. Carbon types 3 and 5 each

$$\frac{\text{satellite integration}}{\text{central peak integration}} = \frac{\sum_n \left(d_n + \frac{t_n}{2} + q_n \right) I_n}{\sum_n \left(s_n + \frac{t_n}{2} \right) I_n} \quad (2)$$

couple with three adjacent nonequivalent carbons, and carbon types 4 and 17 each couple with two adjacent nonequivalent carbons (Figure 7a). Assuming random ^{13}C distributions, s_n , d_n , t_n , and q_n are given by eqs 3-6 for carbon types 3 and 5 and by eqs 7-10 for carbon types 4 and 17 ($x = 2$ for type 17, and $x = 4$ for type 4). The satellite to central peak ratios calculated for random ^{13}C distribution within the carbon clusters using eqs 2-10 and the mass spectrum agree very well with the experimental values (Table II). In contrast, if the ^{13}C atoms were incorporated into C_{60} as intact C_m units with $m \geq 2$, these ratios would be much larger, approximately 4 for carbon types 3 and 5, and approximately 1.5 for carbon types 4 and 17. Thus, ^{13}C is statistically distributed within the C_{60} portion of 1 and, therefore, within the contact-arc-generated C_{60} used to prepare 1.

From the examination of mass spectral data, Heath concluded, "The chemical species initially ejected from the graphite rods in the carbon arc are ... atoms and possibly dimers."³² From this study, we conclude that if the initially ejected species are dimers, the carbon atoms of the C_2 units must scramble either before or

$$s_n(3,5) = \frac{4n}{60} - d_n(3,5) - t_n(3,5) - q_n(3,5) \quad (3)$$

$$d_n(3,5) = \frac{12n}{60} \left(\frac{n-1}{59} \right) \left(1 - \frac{n-2}{58} \right) \left(1 - \frac{n-2}{57} \right) \quad (4)$$

$$t_n(3,5) = \frac{12n}{60} \left(\frac{n-1}{59} \right) \left(\frac{n-2}{58} \right) \left(1 - \frac{n-3}{57} \right) \quad (5)$$

$$q_n(3,5) = \frac{4n}{60} \left(\frac{n-1}{59} \right) \left(\frac{n-2}{58} \right) \left(\frac{n-3}{57} \right) \quad (6)$$

$$s_n(4,17) = \frac{xn}{60} - d_n(4,17) - t_n(4,17) \quad (7)$$

$$d_n(4,17) = \frac{2xn}{60} \left(\frac{n-1}{59} \right) \left(1 - \frac{n-2}{58} \right) \quad (8)$$

$$t_n(4,17) = \frac{xn}{60} \left(\frac{n-1}{59} \right) \left(\frac{n-2}{58} \right) \quad (9)$$

$$q_n(4,17) = 0 \quad (10)$$

after condensation into the C_{60} cluster, as they do not remain connected in the isolated C_{60} .⁵

Conclusion

Much of C_{60} 's beauty and utility undoubtedly lies in its high symmetry. While this high symmetry makes some methods of characterization simpler, it makes others more difficult or impossible. Selective functionalization by monoosmylation lowered the symmetry of C_{60} , allowing characterization of the carbon framework in unique ways. Osmylation circumvented orientational disorder in solid C_{60} , allowing the formation of an ordered crystal and structural analysis of the carbon framework for the first time. Osmylation expanded the solution-state ^{13}C NMR spectrum of C_{60} into multiple peaks, allowing the measurement of coupling constants (to probe bonding) and degrees of coupling (to probe mechanisms) for the first time. Osmylation offered the advantages of rapid but selective addition to C_{60} , variable ligands on osmium for tuning solubility and crystal quality, and the addition of a symmetrical O-Os-O species to minimize the number of possible isomers. Selective reactions are key because complicated mixtures yield little information about C_{60} . The selective addition of multiple functional groups to C_{60} will allow tailoring properties in order to go beyond buckminsterfullerene in the pursuit of new and unusual molecules and materials with novel π -system topologies.

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