rivative, 4113-97-7; **12** 1-methyl acetate derivative, 5236-60-2; **13**, 135790-03-3; **14**, 135790-04-4; **15**, 135790-05-5; **15** mesylate derivative, 135790-12-4; **16**, 135790-06-6; **17**, 135790-07-7; **18**, 135790-08-8; **19**, 135790-09-9; **20**, 135822-29-6; **21**, 135790-10-2; **22**, 135790-11-3; DDQ, 84-58-2; allyl iodide, 556-56-9.

Supplementary Material Available: Spectroscopic data for **16**, **19**, and **22** and X-ray structural parameters for **16** (11 pages). Ordering information is given on any current masthead page.

2D Nuclear Magnetic Resonance Analysis of Osmylated C_{60}

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Buckminsterfullerene (C_{60}) presents a novel array of pyramidalized tricoordinate carbons with a spherical closed-shell topology. Derivatives of C_{60} where added atoms make specific carbons tetracoordinate generate new topologies. For example, our 1:1 and 2:1 adducts of OsO_4 with C_{60} correspond to cup- and band-shaped arrays of unsaturated carbons.[1] With our crystal structure of the 1:1 adduct $C_{60}(OsO_4)$(4-*tert*-butylpyridine)$_2$ (**1**) we proved the soccer ball shaped carbon framework of C_{60} and provided structural information for the cup-shaped π-system.[1] Here we report a 2D NMR analysis of **1** whereby we establish regioselective osmylation of C_{60}, assign chemical shifts for the carbons in **1**, determine C–C coupling constants corresponding to the two types of C–C bonds in C_{60}, and provide the first correlation of quaternary–quaternary carbon bond lengths to $^1J_{CC}$.

Carbon-13-enriched C_{60} was prepared from cored natural abundance carbon rods packed with ^{13}C powder[2] and converted to **1**.[1] The 1D ^{13}C NMR spectrum of enriched **1** showed 22 peaks. Five of the peaks were assigned to coordinated 4-*tert*-butylpyridine.[3] 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 1a). Accordingly, the C_{60} 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 1b).

The resolution of multiple cluster carbons indicates that the C–O bonding is not fluxional on the NMR time scale. Signals corresponding to the other possible 1:1 adduct where OsO_4 has added across the junction of a five- and a six-membered ring were not detectable. The isomer observed in the crystal thus represents the whole, and the observed regioselectivity agrees with theory.[1]

The 17 types of carbons were assigned on the basis of the connectivities derived from a 2D NMR INADEQUATE experiment (Figure 2, Table I).[2,4,5] The half-intensity peaks (a, g, n, and p) were assigned to the carbons on the approximate 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.[6,7] Starting from carbon

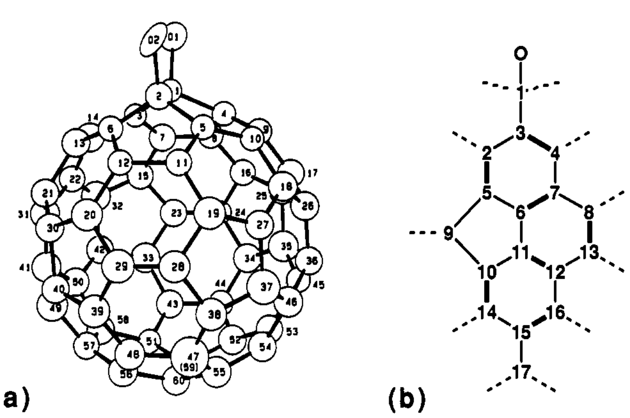

Figure 1. $C_{60}O_2$ unit of crystal structure of $C_{60}(OsO_4)$(4-*tert*-butylpyridine)$_2$ (**1**) showing cluster carbon numbering scheme (a), and fragment showing the connectivities of the 17 types of carbons in the cluster (b). Narrow lines indicate six–five ring fusions, bold lines indicate six–six ring fusions, and dashed lines indicate bonds between symmetry-related carbons or nonindependent couplings.

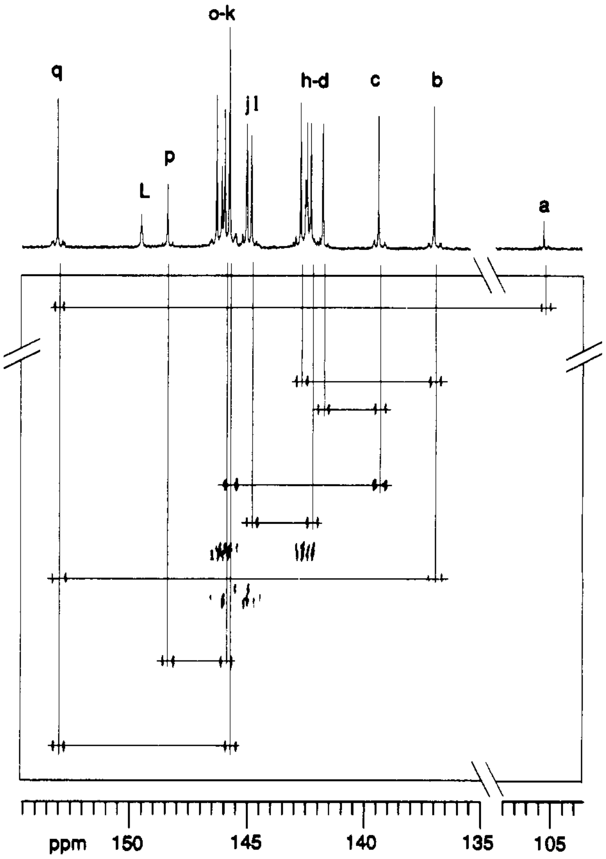

Figure 2. Upper spectrum: 1D ^{13}C NMR spectrum of **1**. Cluster carbons are labeled a–q as assigned in Table I; L indicates 4-*tert*-butylpyridine. Lower spectrum: 2D NMR INADEQUATE spectrum of **1**.[4,5] Vertical and horizontal lines delineate couplings: a–q, b–h, b–q, c–d, c–k, c–l, e–i, k–q, and m–p. Other couplings are not marked for clarity.

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[1] Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312.

[2] Johnson, R. D.; Meijer, G.; Salem, J. R.; Bethune, D. S. *J. Am. Chem. Soc.* **1991**, *113*, 3619.

[3] Coordinated 4-*tert*-butylpyridine carbons: δ 165.95, 149.51, 122.85, 35.16, 30.52 ppm.

[4] A 2D ^{13}C–^{13}C chemical shift correlation spectrum of 40 mg of **1** (C1–C60 5.0% ^{13}C) in 3.3 mL of $CDCl_3$ at 26 °C was acquired at 125.276 MHz on a Bruker AM-500 instrument using a 10-mm probe. The INADEQUATE experiment[5a] was used with a modified phase cycling using 45° phase shifts.[5b] Proton decoupling simplified 4-*tert*-butylpyridine signals. The spectral width was set to 8196 Hz in F_2 and 16 392 Hz in F_1; 8K points were sampled in F_2; 400 increments of 96 scans were acquired in F_1. The refocusing delay was set to 5 ms. The repetition time was set to 5.5 s (T_1 for C(type 2)–C(type 17) < 4 s). The resulting matrix was processed with zero-filling in F_1 for a final size of 4K × 2K points. The F_1 dimension was processed with a real transform; a magnitude calculation was not applied. Coupling constants were measured from individual rows.

[5] (a) Mareci, T. H.; Freeman, R. *J. Magn. Reson.* **1983**, *51*, 531. (b) Bruker INAD2D3.AU pulse program.

[6] Peaks b–p fall within the range observed for C_{70}, 130.28–150.07 ppm, and average 143.8 ppm, close to the resonance of C_{60} at 142.68 ppm. Taylor, R.; Hare, J. P.; Abdul-Sada, K. A.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423. Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983.

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Table I. Chemical Shifts, Peak Assignments, and Carbon–Carbon Coupling Constants for the C_{60} Portion of **1**

peak	chemical shift (ppm)	carbon type	cluster carbons	carbon type, $^1J_{CC}$ (Hz)
a	105.38	1	1, 2	3, 48
b	137.02	4	9, 10, 13, 14	3, 71; 7, 56
c	139.42	5	15, 16, 19, 20	2, 68; 6, 56; 9, 56
d	141.81	9	23, 24, 28, 29	5, 56; 10, not first order
e	142.32	10	33, 34, 38, 39	9, not first order; 11, 56[a]
f	142.48	14	43, 44, 47, 48	15, 56[a]
g	142.55	13	36, 41	8, 67; 12, 56
h	142.75	7	17, 18, 21, 22	4, 56; 6, 67; 8, 55
i	144.85	11	35, 37, 40, 42	6, 54; 10, 56; 12, 68
j	145.04	16	53, 54, 57, 58	12, 56; 15, 65
k	145.76	2[b]	7, 8, 11, 12	3, 57; 5, 68
l	145.77	6[b]	25, 27, 30, 32	5, 56; 7, 67; 11, 54
m	145.99	15	51, 52, 55, 56	14, 56; 16, 65; 17, 56
n	146.10	8	26, 31	7, 55; 13, 67
o	146.32	12	45, 46, 49, 50	11, 68; 13, 56; 16, 56
p	148.41	17	59, 60	15, 56
q	153.03	3	3, 4, 5, 6	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.

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 coupling between carbon types 9 and 10 (peaks d and e) was not first order, and $^1J_{CC}$ could not be measured. Peaks e and f, corresponding to types 10 and 14, are very close, and the associated cross peaks are not visible.[8] Connectivities from carbon type 17 completed the assignments. The up–down pattern aided assignments in complicated regions.

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,[6] and C–C couplings corresponding to the two types of C–C bonds are not discernible. In contrast, derivative **1** shows 17 peaks and the associated couplings (Table I). 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 3).[9] The 48-Hz coupling corresponds to the bond between carbon types 1 and 3 and is comparable with the 47.7-Hz $C(sp^2)–C(sp^3)$ coupling in benzyl alcohol.[10] 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 1b).[11] Considering carbon types 2 and 4–17, which have approximately equivalent geometries and symmetrical bonds,[1] 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: 31.5% s for six–five ring fusions, and 34.0% s for six–six ring fusions.[12] The π-orbital accordingly has 3% s character.[13]

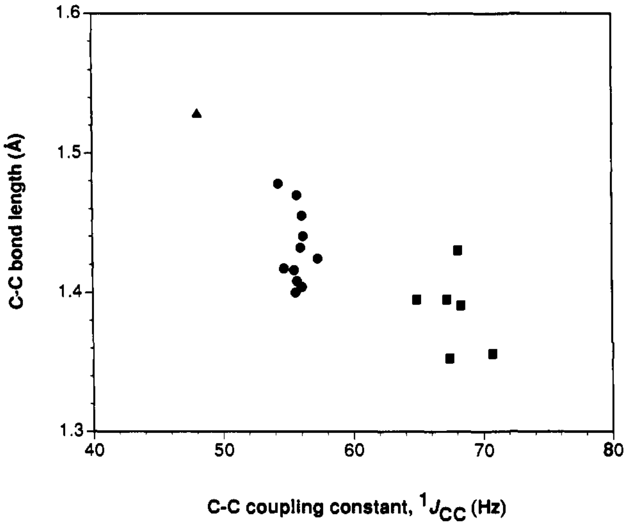

Figure 3. Plot of C–C bond length versus C–C coupling constant in **1** showing three groupings: C(type 1)–C(type 3) (▲), six–five ring fusions (●), and six–six ring fusions (■).

Since the structure of this portion of **1** closely fits the soccer ball structure of buckminsterfullerene,[1] these hybridizations provide a good model for C_{60}.

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(10) Ihrig, A. M.; Marshall, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 1756.

(11) 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.[2] 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}.

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Selective Modification of DNA Controlled by an Ionic Signal

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Oligonucleotide-directed alkylating agents[1] provide an exciting new method for site-specific derivatization of nucleic acids in vitro and in vivo.[2] The ultimate utility of this type of affinity technique is determined in part by the functional groups chosen for modifying the desired target. Selective modification by a compound of innate reactivity requires a slow rate of conversion in order to permit binding recognition to precede target derivatization. Consequently,

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