

- Lett. 17, 1353 (1990); D. A. Senske, *Earth Moon Planets* 50/51, 305 (1990).
39. S. E. Smrekar and R. J. Phillips, *Earth Planet. Sci. Lett.*, in press.
40. R. J. Phillips and M. C. Malin, in *Venus*, D. M. Hunten, L. Colin, T. M. Donahue, V. I. Moroz, Eds. (Univ. of Arizona Press, Tucson, 1983), pp. 159-214.
41. J. W. Head and L. S. Crumpler, *Nature* 346, 525 (1990).
42. P. Janle, D. Jannsen, A. T. Basilevsky, *Earth Moon Planets* 39, 251 (1987).
43. E. R. Stofan and J. W. Head, *Icarus* 83, 216 (1990).
44. A. A. Pronin and E. R. Stofan, *ibid.* 87, 452 (1990).
45. Quetzalpetlatl has been proposed to the IAU as the name of this corona, but as of this writing the name has not been officially approved.
46. A. L. Sukhanov, *Geotectonics* 20, 294 (1986).
47. D. L. Bindschadler and J. W. Head, *Icarus* 77, 3 (1989).
48. ———, *Earth Moon Planets* 42, 133 (1988).
49. D. L. Bindschadler et al., *Geophys. Res. Lett.* 17, 171 (1990).
50. W. L. Sjogren et al., *J. Geophys. Res.* 88, 1119 (1983).
51. R. C. Kozak and G. G. Schaber, *Lunar Planet. Sci.* 17, 44 (1986).
52. J. W. Head, *J. Geophys. Res.* 95, 7119 (1990).
53. R. R. Herrick and R. J. Phillips, *Geophys. Res. Lett.* 17, 2129 (1990).
54. D. L. Bindschadler and J. W. Head, *J. Geophys. Res.*, in press.
55. R. J. Phillips, R. E. Grimm, M. C. Malin, *Science*, in press.
56. R. White and D. McKenzie, *J. Geophys. Res.* 94, 7685 (1989).
57. J. Weertman, *Phys. Earth Planet. Inter.* 19, 197 (1979); D. L. Bindschadler and E. M. Parmentier, *J. Geophys. Res.* 95, 21,329 (1990).
58. S. C. Solomon and J. W. Head, *Science* 252, 252 (1991).
59. We are grateful to the engineering and mission support teams at the Jet Propulsion Laboratory, Martin-Marietta Corporation, and Hughes Aircraft Company whose dedicated efforts ensured the success of the Magellan mission. Important contributions to this work have been made by K. K. Beratan, D. L. Bindschadler, A. de Charon, S. L. Frank, P. G. Ford, D. M. Janes, L. Meinke, S. E. Smrekar, S. W. Squyres, and E. R. Stofan. R. E. Grimm, G. G. Schaber, R. A. Schultz, S. E. Smrekar, S. W. Squyres, and J. Suppe are thanked for helpful comments on earlier drafts. This research has been supported by NASA and by the U.K. Natural Environment Research Council.

14 January 1991; accepted 13 March 1991

Crystal Structure of Osmylated C₆₀: Confirmation of the Soccer Ball Framework

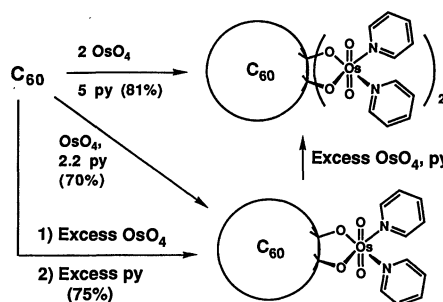
JOEL M. HAWKINS,* AXEL MEYER, TIMOTHY A. LEWIS, STEFAN LOREN, FREDERICK J. HOLLANDER

An x-ray crystal structure that confirms the soccer ball-shaped carbon framework of C₆₀ (buckminsterfullerene) is reported. An osmyl unit was added to C₆₀ in order to break its pseudospherical symmetry and give an ordered crystal. The crystal structure of this derivative, C₆₀(OsO₄)(4-*tert*-butylpyridine)₂, reveals atomic positions within the carbon cluster.

IN 1985, KROTO, SMALLEY, AND CO-workers discovered that 60 carbon atoms form a particularly stable cluster in the gas phase. They proposed a simple and beautiful truncated icosahedral structure for C₆₀ with a novel carbon framework resembling the seams of a soccer ball, and christened the molecule buckminsterfullerene (1). Late last year, Krätschmer, Huffman, and co-workers (2) reported that C₆₀ could be prepared and isolated in macroscopic quantities (3-5). Since then, chemists and physicists have sought to confirm or disprove the soccer ball structure for C₆₀. The infrared (2, 6), Raman (7), ¹³C NMR (3, 8, 9), and photoelectron spectra (10) are each consistent with icosahedral symmetry and are collectively highly supportive of the originally proposed structure, but they do not strictly prove the soccer ball framework or provide atomic positions. For example, the ¹³C NMR spectrum (8) does not rule out the possibility of coincident peaks or a fluxional structure. We (11) and others (2, 12) have attempted to obtain a crystal structure of C₆₀, but could not determine specific atomic positions due to extensive disorder in the crystals. While the ball-like molecules pack in an ordered fashion, their nearly spherical symmetry promotes orientational

disorder (9). We reasoned that if C₆₀ could be derivatized in a way that broke its apparent spherical symmetry, it might crystallize with orientational order. We report here the synthesis of a one-to-one C₆₀-osmium tetroxide adduct and its crystal structure displaying the soccer ball framework of C₆₀.

Our recent report of the osmylation of C₆₀ established that heteroatoms can be added to buckminsterfullerene without disrupting its carbon framework (13). Our conditions favored the addition of two osmyl units to C₆₀, giving the two-to-one adduct in 81% yield as a mixture of regioisomers (Scheme I). Chromatographic anal-



Scheme I

ysis of the crude reaction mixture revealed six peaks: five peaks corresponding to the precipitate which collectively analyzes with two-to-one stoichiometry, and a single

sharp peak corresponding to toluene-soluble material. Use of one equivalent of OsO₄ increased the yield of the toluene-soluble material to 70%. Osmylation in the absence of pyridine, followed by dimer disruption with pyridine (14), gave the same species in 75% yield. The toluene-soluble material was shown to have one-to-one stoichiometry by converting it to the mixture of two-to-one adducts upon further exposure to the osmylation conditions. Solubility and crystal quality were improved by exchanging the pyridine ligands for 4-*tert*-butylpyridine.

The observation of a single sharp chromatographic peak for the one-to-one adduct suggested that it is a single regioisomer, rather than a mixture of the two regioisomers which are possible from the proposed soccer ball structure for C₆₀. This would be

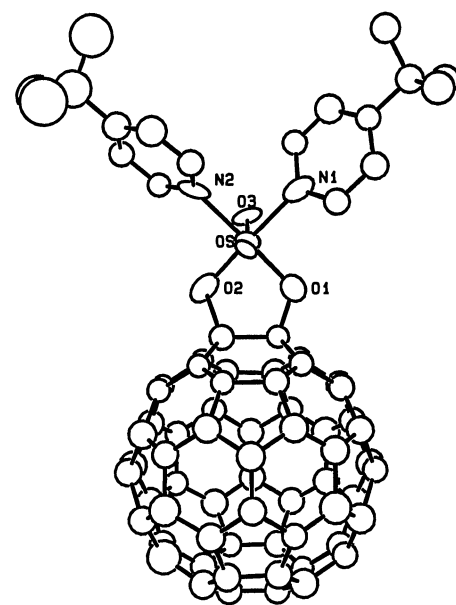


Fig. 1. ORTEP drawing (50% ellipsoids) of the one-to-one C₆₀-osmium tetroxide adduct C₆₀(OsO₄)(4-*tert*-butylpyridine)₂ showing the relationship of the osmyl unit with the carbon cluster.

Department of Chemistry, University of California, Berkeley, CA 94720.

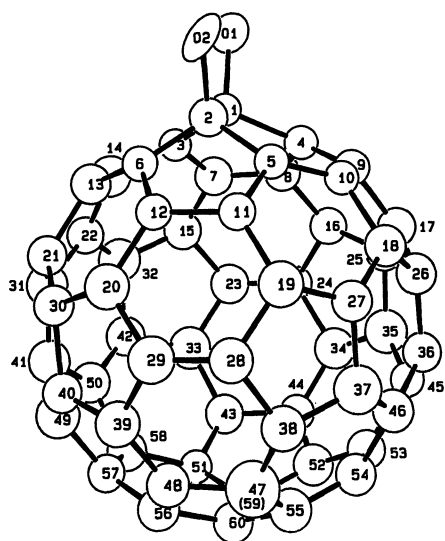


Fig. 2. ORTEP drawing (50% ellipsoids) of the one-to-one C_{60} -osmium tetroxide adduct $C_{60}(OsO_4)(4\text{-}tert\text{-butylpyridine})_2$ showing the geometry of the $C_{60}O_2$ unit and the numbering scheme.

true if the bisoxygenation was strongly favored across one of the two unique bonds in C_{60} , the junction of two 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} as required for an ordered crystal. The one-to-one adduct $C_{60}(OsO_4)(4\text{-}tert\text{-butylpyridine})_2$ indeed gave a sufficiently ordered crystal for the determination of atomic positions by x-ray crystallographic analysis (15).

The crystal structure (Figs. 1 and 2) confirms 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. No two five-membered rings are fused together, and each six-membered ring is fused to alternating six- and five-membered rings. The O-Os-O unit has added across a six-six ring fusion, consistent with the regiochemistry predicted by extended Hückel calculations on C_{60} and the principle of least motion or minimum elec-

tronic reorganization (16).

The tricoordinate carbons C3-C60 all lie within a spherical shell of radius 3.46 to 3.56 Å, with an average distance of 3.512(3) Å from the calculated center of the cluster. 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-C angles equal to 330°, slightly more than 328°, the sum for an ideal tetrahedral 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)°, compared with 360° for a planar atom. 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)°, equals the value for an ideal junction of two regular hexagons and a regular pentagon. All 60 carbons within the cluster are pyramidalized concave inwards.

The five- and six-membered rings not containing C1 and C2 are planar with deviations from least-squares planes less than 0.05(3) Å. In contrast, tetracoordinate carbons C1 and C2 lie 0.22(2) to 0.30(3) Å 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 1.388(9) Å for six-six ring fusions, and 1.432(5) Å for six-five ring fusions. These values are within the range of bond lengths predicted by theory for the two types of bonds in C_{60} (17). The C1-C3, C1-C4, C2-C5, and C2-C6 bond lengths average 1.53(3) Å, comparable with normal $C(sp^3)\text{-}C(sp^2)$ single bonds. The geometry of the OsO_2N_2 (diolate) unit is similar to that observed for conventional arene adducts, although our C1-C2 bond length [1.62(4) Å] is longer than the corresponding bonds in the other structures [1.40(4) to 1.54(2) Å] (18).

The functionalization of C_{60} via the selective osmylation described here and other organic reactions will allow chemists to go beyond buckminsterfullerene in the pursuit of new and unusual types of organic molecules. We are presently studying the novel

cup and band shaped conjugated π -systems of the one-to-one and two-to-one $C_{60}\text{-}OsO_4$ adducts from chemical, spectroscopic, and theoretical perspectives.

REFERENCES AND NOTES

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **318**, 162 (1985).
2. W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *ibid.* **347**, 354 (1990).
3. R. Taylor, J. P. Hare, A. K. Abdul-Sada, H. W. Kroto, *J. Chem. Soc. Chem. Commun.* (1990), p. 1423.
4. R. E. Haufler *et al.*, *J. Phys. Chem.* **94**, 8634 (1990).
5. H. Ajie *et al.*, *ibid.*, p. 8630.
6. W. Krätschmer, K. Fostiropoulos, D. R. Huffman, *Chem. Phys. Lett.* **170**, 167 (1990).
7. D. S. Bethune, G. Meijer, W. C. Tang, H. J. Rosen, *ibid.* **174**, 219 (1990).
8. R. D. Johnson, G. Meijer, D. S. Bethune, *J. Am. Chem. Soc.* **112**, 8983 (1990).
9. R. Tycko *et al.*, *J. Phys. Chem.* **95**, 518 (1991); C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, J. R. Salem, *ibid.*, p. 9.
10. D. L. Lichtenberger *et al.*, *Chem. Phys. Lett.* **176**, 203 (1991).
11. J. M. Hawkins *et al.*, *J. Chem. Soc., Chem. Commun.*, in press.
12. R. M. Fleming *et al.*, *Mater. Res. Soc. Symp. Proc.* (Boston), November 1990.
13. J. M. Hawkins *et al.*, *J. Org. Chem.* **55**, 6250 (1990).
14. R. J. Collin, J. Jones, W. P. Griffith, *J. Chem. Soc. Dalton Trans.* (1974), p. 1094.
15. $[C_{60}(OsO_4)(4\text{-}tert\text{-butylpyridine})_2 \cdot 2.5 \text{ toluene}]$: Tetragonal, space group $I4_1/a$, $a = 30.751(5)$ Å, $c = 24.800(7)$ Å, $V = 23452(14)$ Å³, $Z = 16$. All atoms were located and all positions were refined. Osmium, oxygen, nitrogen anisotropic, all other isotropic thermal parameters. $R = 10.6\%$, $wR = 10.3\%$, $GOF = 1.77$; 442 parameters, 3668 observed data.
16. J. R. Dias, personal communication; *J. Chem. Ed.* **66**, 1012 (1989); D. Amic and N. Trinajstić, *J. Chem. Soc. Perkin Trans. 2* (1990), p. 1595. Extended Hückel calculations on a Tektronix CAChe system qualitatively agree with the HMO calculations described in these papers.
17. W. Weltner, Jr., and R. J. Van Zee, *Chem. Rev.* **89**, 1713 (1989).
18. J. M. Wallis and J. K. Kochi, *J. Am. Chem. Soc.* **110**, 8207 (1988).
19. J.M.H. is grateful to the National Science Foundation (Presidential Young Investigator Award, CHE-8857453), the Camille and Henry Dreyfus Foundation (New Faculty Grant), the Merck Sharp & Dohme Research Laboratories (postdoctoral fellowship for A.M.), the Shell Oil Company Foundation (Shell Faculty Fellowship), the Xerox Corporation, and the Monsanto Company for financial support. We thank J. R. Heath, A. F. Moretto, and R. Apodaca for assistance with the synthesis and purification of C_{60} , R. E. Smalley and co-workers for a generous gift of soot, and W. D. Shrader for assistance with computer graphics.

4 March 1991; accepted 18 March 1991