Zum Vergleich wurde auch die chemische Synthese eines Proteins mit sich wiederholenden Nonapeptideinheiten in relativ aufwendiger Weise gemäß Schema 1 durchgeführt[6]. Die Gesamtausbeute nach 18 Stufen betrug bei dem konventionellen Verfahren lediglich 11%. Durch Gelpermeationschromatographie wurde das Vorliegen einer polydispersen Mischung mit nur relativ geringer mittlerer Molekülmasse von ca. 10000 ermittelt.

Nach den neuesten Befunden[1] scheint der Zugang zu Proteinen mit repetierenden Aminosäuresequenzen durch biotechnologische Methoden besonders aussichtsreich zu sein. Die großen Anstrengungen, solche relativ einfach aufgebauten Materialen bereitzustellen, rechtfertigen sich besonders dadurch, daß Anwendungen im Bereich der Medizin schon jetzt erkennbar sind. So könnten z. B. Blockcokondensate aus repetierenden Aminosäuresequenzen als Seide-Analoga und Sequenzen, die eine hohe Bindungsfähigkeit zu Zelloberflächen aufweisen, zur „Verklebung" von einzelnen Zellen zu größeren Aggregaten, wie es z. B. bei Brandverletzungen notwendig ist, genutzt werden. Die Verknüpfung von Hart- und Weichsegmenten von entsprechend repetierend aufgebauten Aminosäuresequenzen wird als Ursache für die hohe Elastizität von Spinnweben angesehen. Die nun biotechnologisch zugänglichen Materialien sollten bei blockartiger Verknüpfung ähnliche Eigenschaften aufweisen und in Form von Folien zur Wundabdeckung oder als Beschichtungsmaterial von Implantaten besonders interessant sein[7].

Der von *Tirrell* et al. gewiesene Weg zum Aufbau von Proteinen, die wenige, immer wiederkehrende Aminosäure-Einheiten enthalten und die eine exakt festgelegte Molekülmasse haben, hat sich gegenüber klassischen Methoden bezüglich Aufwand und Ergebnis als überlegen erwiesen. Damit werden dem Polymer- und Proteinchemiker neue Materialien in die Hand gegeben, die sich durch chemische und enzymatische Prozesse weiter umwandeln lassen sollten, z. B. in Block- oder Pfropfcokondensate. Schließlich bleibt abzuwarten, inwieweit die Strukturvielfalt der monodispersen Proteine, z. B. durch fluorierte Aminosäuren im Nährmedium, noch zu vergrößern ist.

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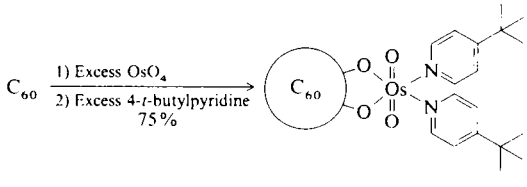
C_{60}: From Soot to Superconductors

By *François Diederich** and *Robert L. Whetten*

In 1990, a team of astronomers led by *Krätschmer* and *Huffman*[1] reported that the new allotrope of carbon C_{60} (buckminsterfullerene, so named after Buckminster Fuller, an architect renowned for his geodesic domes)[2] can be produced in macroscopic quantities through resistive heating of graphite under inert atmosphere. In an *Angewandte Chemie* Highlight article in January 1991, *Fraser Stoddart* summarized the early results in the vigorous worldwide research efforts that were triggered by this surprising development.[3] Only half a year later, a series of exciting new findings require that yet another Highlight article be written (closing date May 20, 1991).

X-ray Crystal Structure Analysis of Osmylated C_{60}

Although the icosahedral-cage structure of C_{60} was strongly suggested by ^{13}C NMR[3], IR[3-6], Raman[6], and photoelectron spectroscopy,[7] as well as by scanning tunneling microscopy (STM) imaging,[8-10] the ultimate confirmation and detailed parameters of the soccerball-shaped framework had to await X-ray crystallography. However, rapid isotropic rotational motion of the orderly packed spherical molecules in the crystal to temperatures down to 100 K[11,12] have so far prevented a successful high resolution X-ray crystal structure analysis. To break the symmetry of C_{60} and prevent its rapid spinning in the crystal, *Hawkins* et al. prepared by osmylation [Eq. (a)] a remarkable 1:1



(a)

C_{60}–osmium tetraoxide adduct.[13,14] The crystal structure of this adduct was subsequently solved by the Berkeley group and clearly confirms the soccerball structure of C_{60}, composed of 20 six-membered rings fused to 12 five-membered rings (Fig. 1).[14] All tricoordinate carbon atoms of C_{60} are pyramidalized and lie at an average distance of 3.512(3) Å from the center of the sphere. The unfunctionalized five- and six-membered rings are all planar within ± 0.05 Å. The two bond lengths in these rings are 1.388(9) Å for the fusion between two six-membered rings and 1.432(5) Å for the fusion between a six- and a five-membered ring. Values of 1.40 (± 0.015) Å and 1.45 (± 0.015) Å were determined for the two bond lengths in C_{60} by solid-state ^{13}C NMR.[15]

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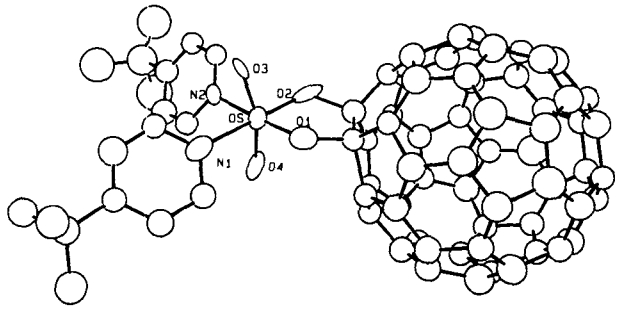


Fig. 1. Structure of the C_{60}-osmium tetraoxide-di(*p-tert*-butylpyridine) adduct in the crystal [16].

Reactivity of C_{60}

The chemistry of C_{60} promises to develop rapidly in the coming months. Initial reactivity studies with this fully delocalized closed-shell molecule[17] might have been of limited success since they probably relied too much on analogy to the chemistry of polycyclic aromatic hydrocarbons. However, C_{60} differs in many aspects from these planar molecules and shows "ambiguous"[18] aromatic character. The C_{60} structural framework is highly stable. Ion-beam collision experiments, in which $C_{60}^{\oplus}$ or $C_{60}^{\ominus}$ collide with silicon or graphite surfaces at speeds up to 50000 km per hour ($\triangleq$ 250 eV impact energy) show high inelasticity of the ions, but no evidence for impact-induced fragmentation.[19] This behavior differs from those of any other molecule or similar-sized cluster ions that have been tested, including benzene and naphthalene ions, which show fragmentation under these drastic conditions. The electronic properties predicted by *Elser* and *Haddon*[20] were confirmed. C_{60} possesses a vanishingly small π-electron ring-current magnetic susceptibility χ, far below that of graphite or benzene, resulting from accidental cancellation of the diamagnetic and paramagnetic contributions to χ.[18, 21] Electrochemical studies showed that C_{60} is a very strong oxidizing agent, comparable to methyl viologen and flavin chromophores, and its first reduction potential ($E^{\circ} = -180$ mV in THF against Ag/AgCl) is at least 1 V more positive than those of most polycyclic aromatic hydrocarbons.[3, 4, 22] This electron-deficient character of C_{60} determines much of the chemistry that is currently being pursued. C_{60} does not react with electrophiles or as a diene in Diels–Alder and other cycloadditions. Rather, it is easily reduced and reacts readily with nucleophilic agents.[23, 24] In an exploratory investigation, *Olah* et al. obtained deep red-brown solutions of diamagnetic polyanions of C_{60} upon reaction with lithium in THF.[23] Subsequent alkylation with methyl iodide led to polymethylated C_{60}; according to mass spectrometric analysis, one or more (all the way up to 24) methyl groups were covalently added to the sphere. *Wudl* et al. observed multiple additions of amine nucleophiles to C_{60} and were able to prepare polyaminated derivatives that are soluble in water.[24] In sharp contrast to rigid aromatic polycycles, C_{60}, upon excitation, exhibits no significant fluorescence or phosphorescence despite a richly structured optical spectrum in the red and violet regions;[25-27] luminescence observed for neat C_{60} films is probably due to solid-state interactions between spheres.[28] Besides being a strong oxidizing agent, C_{60} is a potent sensitizer of singlet oxygen and, therefore, should be handled with caution.[25]

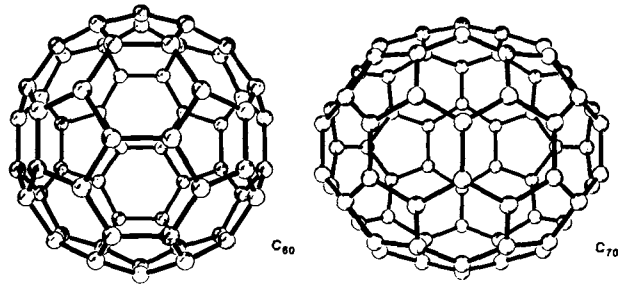
Superconductivity of Alkali-Metal-Doped C_{60}

Recent reports from AT&T Bell Laboratories on the conductivity and superconductivity of C_{60} are breakthrough results with potentially significant technological implications.[29, 30] Today, doped C_{60} is the molecular superconductor with by far the highest onset temperature of superconductivity T_c. It is not difficult to predict in view of extremely rapid developments that the following information might well be outdated when this article is published.

Earlier, the *Wudl* group used C_{60}'s high electron affinity to prepare a crystalline semiconducting (10^{-5}–10^{-7} Scm^{-1}) $Ph_4P^{\oplus}/C_{60}^{\ominus}$ salt by bulk electrolysis.[31] *Haddon* et al. found that C_{60} films doped with alkali-metal vapor become organic metals that exhibit conductivities at ambient temperature comparable to those of *n*-type doped polyacetylene (100 Scm^{-1} for Rb/C_{60} and 500 Scm^{-1} for K/C_{60}).[29] Doping is presumed to occur in the tetrahedral interstices between C_{60} molecules. Soon after, a report from the same laboratory appeared on the superconductivity of potassium-doped C_{60}, both in forms of thin films and polycrystalline powders.[30] The powder samples showed a well-defined, yet small (circa 1%), diamagnetic shielding (Meissner effect) with an onset temperature T_c of 18 K. The C_{60} group at the University of California in Los Angeles (UCLA) subsequently characterized the composition of the stable superconductive phase as K_3C_{60}, and $T_c = 19.3$ K.[32] Controlled sample preparation raised the Meissner effect to above 40% of the perfect diamagnetic shielding, which is a high value for a powder sample. This should probably be regarded as a stoichiometric compound ($K_3^{\oplus}C_{60}^{3\ominus}$) rather than a doped molecular solid. The UCLA group also found that Rb_xC_{60} shows an even higher onset temperature for superconductivity ($T_c = 30$ K); diamagnetic shielding was 7% at the time of manuscript preparation.[32] An onset temperature of $T_c = 28$ K for a Rb-doped C_{60} sample was measured by the Bell Lab group.[33] Theoretical models for the superconductivity of doped fullerenes are already appearing.[34]

The Fullerene and Heterofullerene Family

Buckminsterfullerene (C_{60}) and C_{70}, whose ellipsoidal-cage structure with D_{5h}-symmetry is now firmly supported by a variety of spectroscopic methods,[3, 4-6, 22, 35] are both



major, but not the only products that can be isolated from the toluene-soluble fraction of the fluffy soot produced by resistive heating of graphite. By repeated chromatography on alumina, *Diederich* et al.[36] obtained small quantities of C_{76}, C_{84}, C_{90}, and C_{94}, which, like C_{60} and C_{70}, are mem-

bers of the same family of hollow-cage all-carbon molecules called the fullerenes.[37] In addition, they also showed that the toluene-insoluble fraction of the soot contains a variety of larger fullerenes in the range between C_{100} and C_{212} that dissolve in boiling 1,2,4-trichlorobenzene.[36, 38] The structures of the higher fullerenes above C_{70} have yet to be determined. The UCLA group also isolated $C_{70}O$, a stable oxide of D_{5h}-C_{70} with the oxygen atom covalently attached to the convex external surface of the ellipsoid.[36] Apparently, this oxide forms from trace oxygen impurities in the helium gas used as the inert atmosphere during the resistive heating process. A recent study by *Smalley* et al. suggests the existence of heterofullerenes, and it should not take long before such compounds are actually isolated.[39] Supersonic beams produced by laser vaporization of a graphite pellet containing boron nitride powder were found to contain heterofullerenes, e.g. $C_{58}B_2$ and $C_{59}B$, in which presumably one or more atoms of the soccerball are replaced by a boron atom. The doped carbon balls are Lewis acidic and readily chemisorb one ammonia molecule per boron atom.

It is obvious from this short account that research on C_{60} and the other fullerenes is about to revolutionize chemistry within a rather short period of time. Since these new materials are readily prepared[3, 22, 40] as well as commercially available,[41] the exploration of their tremendous basic research and technological perspectives is now limited only by the imagination of the individual investigators.[42]

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[41] Commercial sources of fullerenes: a) Texas Fullerenes Corporation, 2415 Shakespeare, Suite 5, Houston, TX 77030-1038 (Tel. 713-227-9003, FAX 713-686-5139). Crude Soot: 20 $ per gram, 10 $ with University discount. Benzene-soluble extract (mainly C_{60} and C_{70}): 500 $ per gram. Pure C_{60}: 6 $ per milligram. b) Materials and Electrochemical Research (MER) Corporation, 7960 S. Kolb Road, Tucson, AZ 85706 (Tel. 602-574-1980, FAX 602-574-1983). Crude Soot: 80 $ per gram. C_{60}/C_{70} mixture: $ 1250 per gram. c) Research Materials Incorporated, 1667 Cole Blvd., Building 19, Suite 400, Golden, CO 80401 (Tel. 303-238-9369, FAX 303-237-1103). All three companies deliver worldwide.

[42] Editorial note: We have just learnt of some exciting results of a group at the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104. In press are the following articles: Fluorinated Fullerenes (H. Selig, C. Lifshitz, T. Peres, J. E. Fischer, A. B. Smith III, A. R. McGhie, W. J. Romanow, J. P. McCauley, Jr., *J. Am. Chem. Soc.*); Orientational Ordering Transition in Solid C_{60} (P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., A. B. Smith III, D. E. Cox, *Phys. Rev. Lett.*); Compressibility of Solid C_{60} (J. E. Fischer, P. A. Heiney, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., A. B. Smith III, *Science (Washington, D. C.)*); Structure and Bonding in Alkali-Metal-Doped O_{60} (O. Zhou, J. E. Fischer, N. Coustel, S. Kycin, Q. Zhu, A. R. McGhie, W. J. Romanow, J. P. McCauley Jr., A. B. Smith III, D. E. Cox, *Nature (London)*).