

PHYSICS

Fullerides in a Squeeze

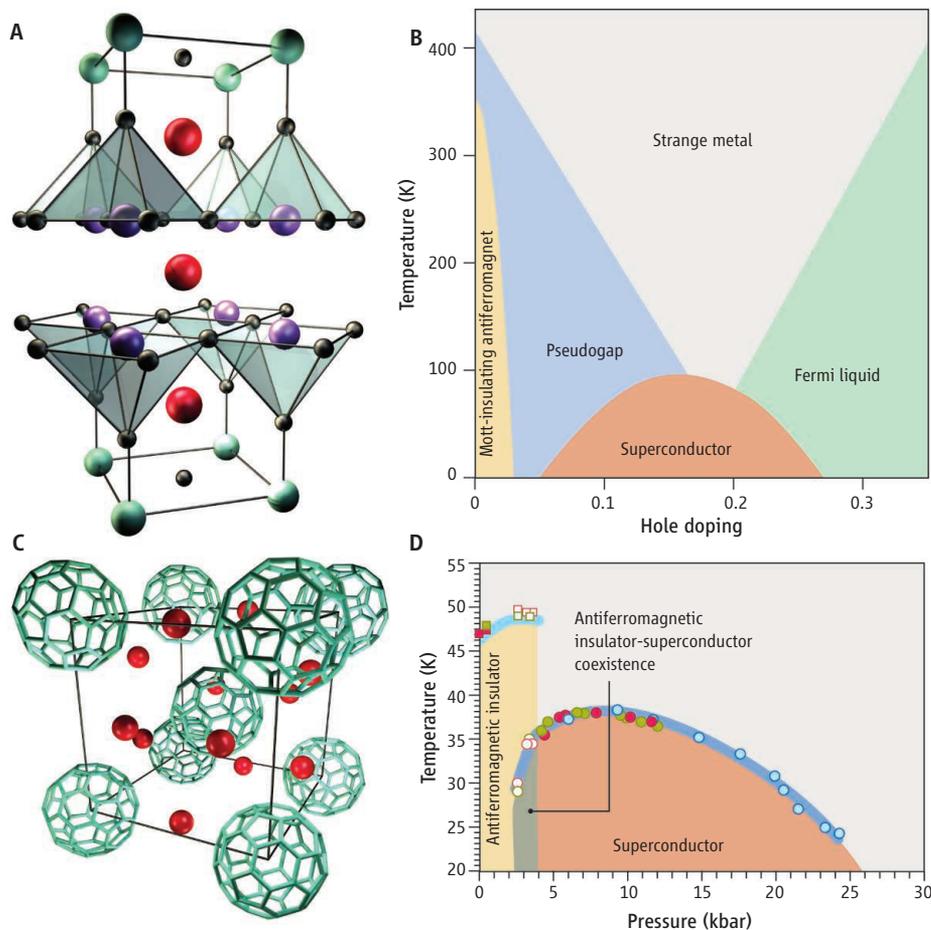
Erio Tosatti

Before the discovery of cuprate superconductors, superconducting metals and Mott insulators—would-be metals turned insulating by repulsion between electrons—seemed to have nothing to do with one another. Yet in cuprates, superconductivity popped up by simply doping Mott insulators with some impurities (see the figure, panels A and B), opening up perhaps the most controversial physics field of the past 25 years. As Takabayashi *et al.* show on page 1585 of this issue (1), pressure works very much the same feat in a completely different material: the hyperexpanded body-centered-cubic A15-structured fulleride Cs_3C_{60} , an insulator that is turned into a superconductor by giving it a light squeeze. What else, if anything, do cuprates and fullerides have in common? And if they do, could one of them teach us something about the other?

In fullerides, electron-donating alkali atoms are regularly interspersed in a lattice of C_{60} molecules (see the figure, panel C). The donated electrons are mobile between one C_{60} molecule and the next, turning the whole system into a metal. Upon cooling, these metalized fullerene crystals turn superconducting, and they do so at respectably high critical temperatures T_c of 20 to 30 K (2–4).

At first sight, this is no big deal, because superconductivity in fullerides appears similar in many ways to that of conventional superconductors and unlike that in cuprates. For example, the symmetry of electron pairs—whose condensation gives rise to superconductivity—is conventional (*s*-wave) in fullerides but unconventional (*d*-wave) in cuprates. In addition, the mechanism that glues the two electrons together to form the superconducting pair is conventional (phonon exchange) in fullerides (3, 4), whereas an electronic and magnetic mechanism is more probable in cuprates, because electron correlations are strong in these systems (5).

However, according to proponents of the “strongly correlated superconductivity” theory, the difference between fullerides and cuprates may be more superficial than substantial (6, 7). This theory identifies two basic elements that



Different yet similar. Cuprates such as $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ (13) (A) show a bell-shaped dependence of superconducting transition temperature T_c on doping density (14) (B). Takabayashi *et al.* now report that in the fulleride A15 Cs_3C_{60} (C), a similar behavior can be induced through applying pressure (D).

are common to fullerides and cuprates: First, the contiguity between a Mott insulating and a metallic phase; and second, some spin selective electron-electron interaction—be it phononic or electronic in origin—favoring singlet spin pairing in the insulating state.

It has been known for about a decade that fullerides can indeed be changed from metallic to Mott insulating by expanding the lattice. This was achieved in the past by inserting additional neutral molecules such as ammonia between the buckyballs; these molecules acted as spacers, exerting a kind of negative pressure and prying the lattice open. In these expanded compounds—exemplified by $(\text{NH}_3)_\text{K}_3\text{C}_{60}$ (8)—theory has long shown how the role of electronic repulsion is enhanced by expansion, tilting the fine balance between

The superconducting behavior of very different materials—fullerides and cuprates—could have more in common than previously believed.

metallic and Mott insulating state (3, 4, 7). The Mott insulating state is antiferromagnetic (nearest spins point opposite to one another), but the spin of each C_{60} site is only 1/2 instead of 3/2 as one might have expected for three electrons per molecule. The low spin state is due to coupling to phonon vibrations, known in molecular physics as the Jahn Teller effect. Under pressure, such a “Mott Jahn Teller” insulator (9, 10) should, according to theory, turn into a strongly correlated superconductor; and indeed it does (11). However, the lattice expansion caused by inserted molecules also changes the lattice symmetry and introduces disorder relative to the parent compound K_3C_{60} , introducing some ambiguity into the assessment of this insulator-superconductor transition.

International School for Advanced Studies and CNR-INFN Democritos National Simulation Center; and International Centre for Theoretical Physics, Trieste, Italy. E-mail: tosatti@sissa.it

The novel fulleride reported by Takabayashi *et al.* is born expanded, because the large Cs ions force the C_{60} lattice into a body-centered-cubic arrangement, which is more open than the face-centered-cubic structure of previous compounds (12). Takabayashi *et al.* show that the zero-pressure state of this fulleride is a true Mott Jahn Teller insulator; thus, it possesses both ingredients required by the strongly correlated theory. The insulating state is experimentally destroyed by a modest 2.5- to 4-kbar pressure—with no doping, no disorder, and no change of lattice symmetry. In the squeezed metal, magnetism disappears and is replaced by superconductivity below a T_c that rises from ~30 k at 2.5 kbar, peaks at ~38 k for 7 kbar, and then drops at higher pressure. This bell-shaped behavior (see the figure, panel D) is a general feature predicted by the strongly correlated theory (7) and is similar to that seen in cuprates upon doping (see the figure, panel B).

In this mapping between fullerides and cuprates, the superconducting A15 Cs_3C_{60}

fulleride between 2.5 and 7 kbar corresponds to the “underdoped” cuprates (with a hole doping between 5 and 15; see the figure, panel B). Above T_c , the low-pressure fulleride normal state should, according to the strongly correlated theory, behave quite differently from the regular metal of conventional superconductors. For example, it should show a depression of electronic states near the Fermi level (a pseudogap) reminiscent of that of underdoped cuprates, and detectable, for example, through photoemission or tunneling spectroscopy.

What makes A15 Cs_3C_{60} particularly exciting is that it allows these and other predicted properties of a state claim to be akin to underdoped cuprates to be measured without the complications caused by doping, and that its properties seem easier to model and calculate than those of cuprates—and of other molecular superconductors, too (13). The hope is that we may finally make progress in grasping what is important and what is irrelevant in all strongly correlated superconduc-

tors, by scrutinizing and understanding the expanded fullerides.

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MATERIALS SCIENCE

Stiffer Than Steel

John D. W. Madden

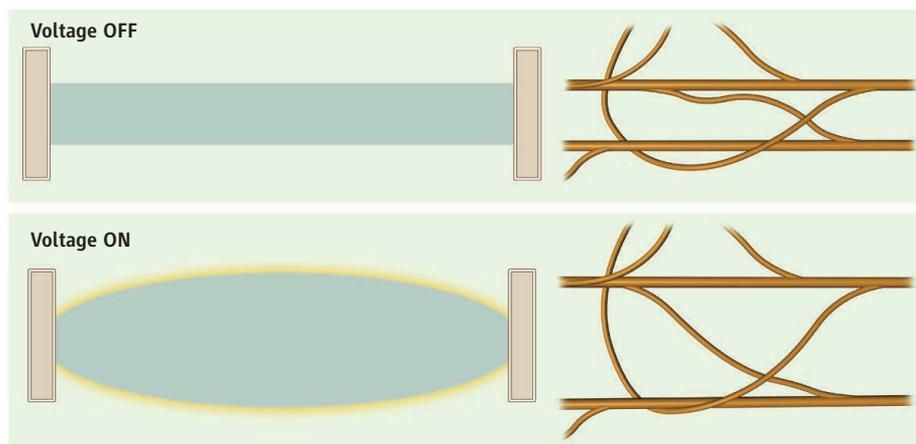
The ultralow-density ribbons described by Aliev *et al.* on page 1575 of this issue (1) have the strength and stiffness of steel by weight in one direction and are more compliant than rubber in the other two. When charged, two dimensions quickly and reversibly triple in size while the third contracts. This response is virtually the same from liquid-nitrogen temperatures up to the melting point of iron. The ribbons are also transparent and flexible, yet conductive. The work is an exciting example of how nanostructuring can lead to combinations of properties that are not possible in bulk materials.

Nature provides the best examples of the power of nanostructuring. For example, human hair is as strong as some steels (much stronger when scaled by density), and unlike steel can be stretched by 30% before breaking. These properties are enabled by the alignment and crosslinking of bundles of protein helices. Similarly, the use of micrometer- and nanometer-diameter fibers dramatically

increases the strength of materials. Carbon fiber-reinforced plastics used in sports equipment and aircraft parts are both strong and light thanks to the incorporation of aligned fibers into a much less stiff epoxy resin. These composites can be about one hundred times as compliant perpendicular to the fiber axis as parallel to it.

A new material is as light as air and expands like rubber, yet is stiffer than steel by weight.

Carbon nanotubes have attracted a lot of interest as reinforcing materials because individual tubes are almost as stiff as diamond, are low in density, and have a tensile strength that is far greater than any bulk material. Carbon nanotube-containing fibers are gradually approaching the stiffness and strength of their component tubes. Aliev *et al.* now show that



Intertwined tubes. Application of a voltage to ultralow-density carbon nanotube sheets produces a dramatic expansion in width and thickness (left). The sheets are highly compliant in the width and thickness directions, perhaps held together by the bending stiffnesses of intertwined nanotubes, enabling large deformations of the ribbon in these axes (right).

Department of Electrical and Computer Engineering, Advanced Materials and Process Engineering Laboratories, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada. E-mail: jmadden@ece.ubc.ca

nanotubes also enable highly anisotropic material properties. The authors have grown forests of 11-nm-diameter carbon nanotubes and then pulled the entangled tubes into ribbons composed of oriented bundles. Their densities are extremely low—a little higher than that of air, and similar to that of the lightest materials known. The ribbons are very stiff for their weight in the stretch direction. Perpendicular to the stretch direction, they may be as much as one million times less stiff, and are far more compliant than rubber (2). This apparently unprecedented degree of anisotropy is akin to having diamond-like behavior in one direction and rubber-like behavior in the others. If the ribbons are stretched along the orientation axis, the other axes collapse dramatically—20 times as much as most materials do—leading to an overall shrinkage that is again unique in its magnitude and direction.

The nanotube ribbon's combination of the high stretch-direction modulus and low density is well suited for creating thin, stiff beams and plates for aerospace and other applications, in which minimizing mass is critical. The ribbons would require less than 10% of the mass needed by composites, wood, metals, or other materials, but are bulkier because of their extremely low densities (3).

The application of a voltage charges and expands the ribbons in milliseconds, as the repelling charges maximize the surface area by pushing apart loosely interconnected bundles (see the figure). Although carbon nanotube actuators have previously been activated by charging in an electrolyte, the resulting relative changes in length were much smaller. The large strains of the new actuation mechanism suggest that high electromechanical coupling and efficiency should be achievable. This is because large changes in the distance between charges lead to a substantial change in electrical potential energy that can be converted to work.

The actuators can deflect light, but are otherwise so compliant in their large strain axis that applications requiring large displacement and any appreciable force are excluded. This limitation might be overcome by greatly increasing the transverse stiffness of the ribbons by densification of the nanotube ribbons and increasing the degree of interconnection between adjacent fibres. When forces are increased, the ribbon artificial muscles will become candidates for use in medical devices, robots, and perhaps even implants.

How can a material that is so stiff in one direction be so compliant in the others? Entanglement of adjacent bundles might be expected to lead to a rubber-like elasticity, in

which thermal agitations resist the uncoiling of weakly intertwined tubes. However, the nanotubes are much too stiff to bend due to thermal energy, and their response shows virtually no temperature dependence—the elasticity is “enthalpic” rather than entropic in origin. So what keeps the films together? Small bundles wind around and perhaps interconnect with the larger oriented fibers [supporting figure S10 in (1)]. These tiny but stiff wires may act as springs that bend to provide a restoring force when the ribbons are deformed (see the figure). If so, then altering the density and stiffness of interconnects should allow tuning of the mechanical properties of the ribbons.

The discovery of the stiff yet compliant, light yet strong, electrostatically deformable ribbons should inspire the development of new nanostructured materials whose stiff, long, and carefully arranged elements enable exquisite tailoring of material properties. For

example, it may be possible to create custom materials with unique properties by assembling nanometer-thick beams into carefully designed three-dimensional structures. The beams in this case are stiff macromolecules or nanowires that can resist attractive surface forces from neighbors. Creating the desired property combinations is a challenge, but reports of engineered three-dimensional structures composed of stiffened DNA (4), zinc oxide ribbons, and other stiff materials suggest that it will ultimately be possible.

References and Notes

1. A. E. Aliev et al., *Science* **323**, 1575 (2009).
2. Aliev et al. do not report modulus in the compliant axes; I have estimated the modulus from the resonant frequency during actuation.
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CHEMISTRY

Copper Puts Arenes in a Hard Position

Robert E. Maleczka Jr.

Copper catalysts enable substitution reactions on a benzene ring to occur at positions that normally are unfavorable.

As a professor of chemistry, I have written many letters of recommendation for nonchemistry majors. This task gives me the opportunity to ask what the students remember most from their year of organic chemistry. Electrophilic aromatic substitution—the replacement of hydrogen atoms on aromatic rings, or arenes, with substituents—often tops the list. With surprising regularity, students can recall the rules (or at least remember that rules exist) predicting whether substituted benzenes will react at their ortho, meta, or para positions (see the figure, panel A). A report by Phipps and Gaunt on page 1593 of this issue (1) might give my students pause. The authors show how ortho/para-directing amido groups can facilitate a difficult reaction, carbon-carbon (C–C) bond formation, at the less favored meta position, courtesy of a novel copper(I)/copper(III) catalytic sequence.

The problem addressed by Phipps and Gaunt is a long-standing one. Shortly after

Faraday isolated benzene, chemists began to explore its reactivity. These studies soon revealed that benzene reacts in a way that replaces a hydrogen atom with a functional group such as NO₂ or Cl (2). Moreover, even before Kékulé suggested benzene's structure, a number of disubstitution reactions were known to yield three different isomers. Assigning the absolute structures of such isomers fell to Körner, who in 1869 introduced the terms ortho, meta, and para.

In 1877, Friedel and Crafts discovered reactions that formed C–C bonds at aromatic rings (3). By the turn of the 20th century, reliable predictions could be made of how substituent effects govern the reactivity and selectivity of reactions that would later be described as electrophilic aromatic substitutions (4).

A substituent on a benzene ring influences both where a second substituent will preferentially react and whether these reactions will be accelerated or inhibited. Benzene molecules bearing groups that release electron density into the ring, which include alkylbenzenes, as well as anilides and phenols, activate electrophilic aromatic substitution reactions and

Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA. E-mail: maleczka@chemistry.msu.edu

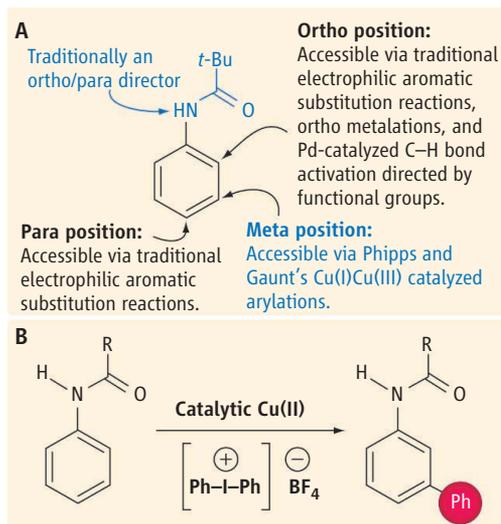
favor substitution at the ortho or para positions, or both (see the figure). Halides also direct substituents to these positions, but because they pull electron density from the ring relative to H, the reactions are relatively slower. Lastly, benzenes bearing electron-withdrawing groups (such as NO₂) are deactivating and direct substituents to meta positions.

These “rules” made preparation of many arene substitution reactions predictable and also practical on an industrial scale. The benzene nucleus can be found in ~30% of all industrial chemicals and over half of the top 50 drugs (5). Unfortunately, arenes in which the substitution patterns do not fit these rules (and which are said to be contra-electronic) can be extremely difficult to prepare. For example, obtaining only ortho products in the presence of a para- or meta-directing group was long considered a challenge. Multistep syntheses, which tend to be time consuming, more expensive, and lower yielding, were often needed to achieve the desired substituted benzene.

In the 1980s, directed metalation chemistry, developed by Snieckus, emerged as a powerful tool for selective ortho substitution to certain functionalized groups, including some that are normally meta directors, such as carbamides (6). In this approach, an existing group guides a base to the nearby ortho proton. Acid-base chemistry leaves a metal such as lithium at the ortho position, which then exchanges with a nonmetal substituent. More recently, functional group-directed carbon-hydrogen (C–H) bond activation, especially with palladium catalysts in the Pd(II)/Pd(IV) oxidation states, has allowed the introduction of various atoms, such as carbon, oxygen, and halogens, at ortho positions (1, 7).

The complementary problem of achieving selective substitution meta to ortho/para donors has been more aggravating to chemists. For example, one relatively simple and synthetically useful (8) molecule, 3-bromo-5-chlorophenol, has three ortho/para directors, two of which are deactivating, and all occupy meta positions with respect to the others. Thus, phenol and either halobenzene are poor starting materials—each would direct the next substituent to the wrong position. Until recently (9), the best effort at synthesizing this contra-electronic molecule was a 10-step procedure reported in the 1920s that used the explosive TNT (trinitrotoluene) as the starting material.

Partial solutions to this meta problem have relied on steric preferences, catalyst choice, acidity differences, and, most often, multistep syntheses (1, 10). Some of these approaches



Location, location, location. (A) Many reactions readily add a second substituent to a benzene molecule at the positions across from the first substituent (para) or next to it (ortho), but addition at the remaining meta positions is usually slow and low in yield. The copper-catalyzed route described by Phipps and Gaunt forms carbon-carbon bonds to arene substituents at positions meta to an amide group; *t*-Bu is a tertiary butyl group. (B) The overall reaction; Ph is a phenyl group.

are quite clever, including Wilhem and Lautens' palladium-catalyzed alkylation hydride reduction sequence (10). Sterically guided iridium-catalyzed C–H borylations also afford meta-substituted products regardless of the electronic preferences (11). However, none of these methods could start with benzene bearing a single ortho/para donor and directly afford a single meta-substituted benzene.

Phipps and Gaunt changed that landscape by tapping into the electrophilicity of Cu(III) (see the figure, panel B). In their scheme, a Cu(III) species is generated from Cu(I) and a bisarylated hypervalent iodine (that has lost two electrons to form two bonds and developed a positive charge). That reagent apparently does not undergo traditional electrophilic aromatic substitution without the aid of the amide. The electrons on the basic amide oxygen attack the ortho position of the benzene. The ring electrons are effectively then pushed out to form the C–Cu bond, which breaks the ring's aromaticity in the process. Further reaction with base rearomatizes the ring, and then the aryl group, originally bonded to iodine, forms a C–C bond at the meta position occupied by the Cu(III) group. The Cu(I) is regenerated, and the whole process begins anew.

Cross-coupling reactions are among the most common C–C bond-forming reactions used for the preparation of drug candidates

(12). Cross-coupling reactions that avoid the preparation of haloaromatics are among the aspirational reactions recently identified by the American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable (13). The organo-copper components of Phipps and Gaunt's reaction need not be isolated, nor do the anilides require a halogen to effect C–Cu bond formation, so this part of the method can be considered green.

Phipps and Gaunt's methodology also represents new advances in both C–H activation and Cu(III) chemistry. Although their approach builds on their previous studies on copper-mediated indole arylations, the work does open a new chapter in electrophilic aromatic substitution chemistry. The chapter is still being written; the authors' putative mechanism is speculative, and there are drawbacks to hypervalent iodides (such as availability, by-product formation, and cost). Relatively small changes to the reaction conditions can change the products (14). Moreover, the yield of an anilide disubstituted with a deactivating meta director was a disappointing 11%.

Nonetheless, this study inspires the imagination. What besides aryl groups can be transferred? Can the approach be used in combination with other Cu(III) methods (15)? Finally, the role of Cu(III) in biological systems suggests that there may be biochemical or biosynthetic implications to these findings.

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