Totally Tubular

John H. Weaver

Carbon in its pure form exhibits a wide variety of complex structures with properties that range from insulating for three-dimensionally coordinated diamond to metallic for planar graphite. Recent attention has focused on C_{60} and the higher fullerenes, particularly in the condensed state, which represents the third form of crystalline carbon (*1*, *2*). Another extremely exciting form of pure carbon is the object of the report by Amelinckx *et al.* (*3*) on page 635 of this issue. This form consists of a carbon tube as would be produced when a sheet of graphite is closed upon itself, resembling a seamless roll of chicken wire. Such structures have diameters of only a few nanometers, have a central cavity, and generally appear as tubes within tubes. Most are straight, but they can be bent, kinked, and spiral-shaped as well (Figs. 1 and 2). In their report, Amelinckx *et al.* discuss tube growth, offering insight into the formation of the different structures.

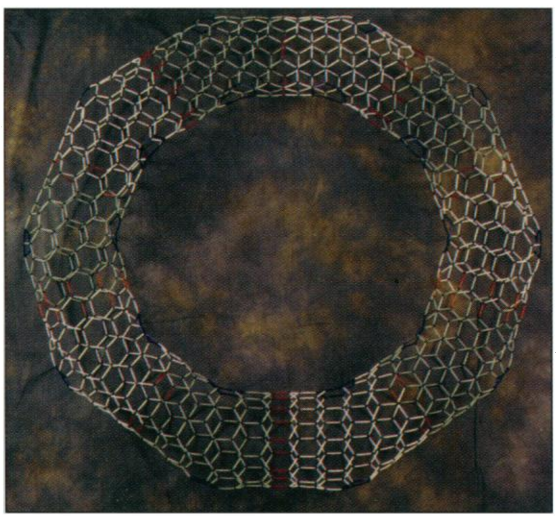

Fig. 1. A fivefold torus made of five (5,5) tubule segments and five (9,0) segments connected to each other by a pair of 5-7 rings. These tubes have the C_{60} radius. This structure contains 10 pentagons and 10 heptagons and closes onto itself perfectly with minimal strain. It has been considered in the theoretical literature but has not yet been observed.

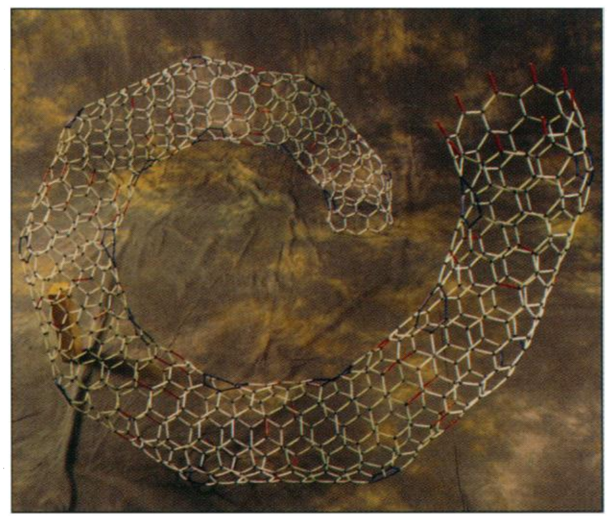

Fig. 2. One helix turn of a coiled tubule made of the same segments as in Fig. 1 except that each segment is rotated by a fixed angle with respect to the previous segment. Hence, the line connecting the opposed 5-7 rings has a rotated azimuth on progressing along the helix. [Figures courtesy of A. A. Lucas, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium]

Carbon nanotubes that were closed (as opposed to being continuous like a scroll) were first reported by Iijima (*4*). He investigated the deposit that grew on the cathodic carbon rod in an arc discharge of the sort used to produce fullerenes. From elegant electron microscope images, it was clear that structures that were tubular had formed on the cathode. Moreover, these tubes contained multiple coaxial layers, separated from one another by about 3.4 Å, the separation that one finds between layers of carbon in crystalline graphite. Within the tubes, there were faults that resulted in changes in direction or diameter of a given tube, an effect attributed to the presence of a pentagon (introducing positive curvature) or a heptagon (introducing negative curvature) in the otherwise perfect hexagonal mesh (*4*). When Iijima and co-workers examined the ends of the tubes, they deduced that capping was achieved by the introduction of pentagons of carbon, as in the fullerenes.

These nearly perfect tubes sparked speculation regarding applications in nanotechnology as tips for scanning tunneling microscopes, as electrodes in energy storage devices, as components in lightweight composites, and as one-dimensional wires in microelectronics. Many groups have tried to produce long tubes of uniform diameter free of amorphous carbon, but this has proven to be a daunting task. Considerable insight has come from theoretical studies, including the prediction that nanotubes of specific diameters might be metallic, whereas others might be semiconductors (*5*), suggesting electronic applications if only such tubes could be isolated and connected to external probes.

Two other developments in carbon nanotube research have astounded the community. In one, Ajayan and Iijima (*6*) demonstrated that a tube could be opened by exposing it to air at elevated temperature, allowing a chemical reaction to occur at sites of lowest stability (the caps). They then demonstrated that material could be drawn into the tubes, offering possibilities for quantum confinement and dimensionally constrained structures. The second development was realized when the carbon electrodes used in fullerene synthesis were loaded with Fe or Co. Electron microscope images of material deposited on the chamber walls showed tubular carbon structures that had been catalyzed by the metal particles (*7*), often as single shells with a diameter of 1 nm.

Amelinckx *et al.* show high-resolution images of carbon structures grown when they exposed cobalt particles distributed on a silica support to a flowing gas of acetylene at 700°C. Such conditions led to catalytic decomposition (*8*). By optimizing the parameters for nanotube production, this group was able to produce straight tubes that were equivalent to those grown by the arc discharge method with lengths up to tens of micrometers (*9*). As can be seen in their figure 1, they also observed planar spirals, helices of variable pitch, structures resembling the eye of a needle, and objects that reflect interacting straight and helical nanotubes.

The helical structures are most amazing. By diffraction studies, Bernaerts *et al.* (*10*) demonstrated that the helix was actually made of straight tubular sections that were joined at an angle in a periodic fashion. In one set of measurements, they found that this angle was about 30°, so that 12 such straight sections constituted a single turn of the helix. Each straight section, in turn, was made up of multiple coaxial carbon tubes.

Remarkably, two theory groups had already developed considerable expertise in forming helices from carbon sheets. Dunlap (*11*) had considered the optimal angle at which two tubes should meet, finding that

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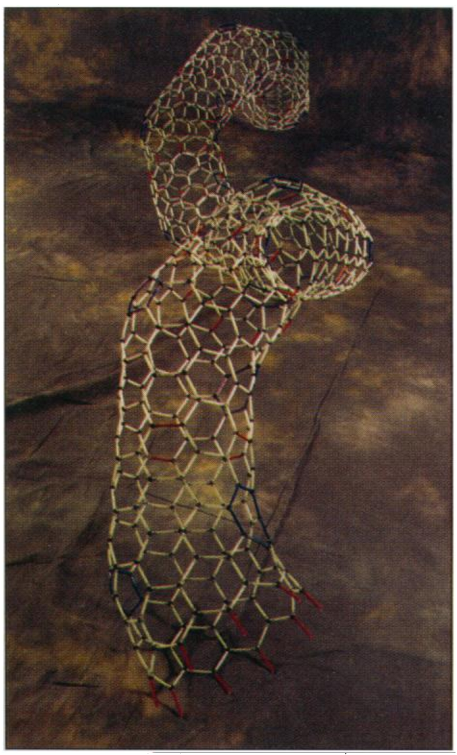

Fig. 3. Two helix turns of the same coiled, polygonized tubule as seen more longitudinally. [Figures courtesy of A. A. Lucas, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium]

the intersection of like-sized tubes at 30° could be accomplished by introducing a five-membered ring on the outer point of contact and a seven-membered ring at the inner point. Inspired by this model, Amelinckx *et al.* deduced that their structures could, in fact, be derived from periodic pentagon-heptagon arrays that served as joints for straight tubes. In calculations of structural stability, Ihara *et al.* (*12*) had deduced that curvature could be accomplished by an appropriate array of pentagons and heptagons in the hexagonal mesh and had predicted that some structures would be favored over others.

The mechanisms of tube growth, like those responsible for fullerene growth, have long stimulated the imaginations of those dealing with such structures. Although much remains to be learned, Amelinckx *et al.* have provided considerable food for thought, at least with respect to the kinetics of the process. In their report, they have described "extrusion" of carbon from the metal particle as though it were a continuous medium, considering the kinds of shapes that could be produced. They have examined straight tube extrusion from a circular starting configuration under the assumption that growth proceeds from the contact area with the metal particle. The more interesting geometries that they discuss involve greater quantities of carbon being supplied at one part of the tube base than another, resulting in a curved tube, and the effects of noncircular contact areas with the particle.

Future investigations, both theoretical and experimental, must resolve issues related to the interaction of the carbon atoms with the catalyzing particle at the point of contact. From early studies of filament growth, it was concluded that carbon atoms dissolve in the catalyst and diffuse through it to the point where the tube is grown (*13*). It is fascinating to imagine the nucleation of a tube on a metal surface, that is, considering the movement of carbon atoms and the pathways that lead them to produce chains from which the first complete rings form. The assembly of this ring must reflect surface interactions with the particle and, as Amelinckx *et al.* (*3*) conclude, this structure defines the orientation of the nascent tube. The motion of carbon atoms as they pop through the surface or diffuse to the growth point would make a most stimulating video, although the time scale of such processes is not amenable to even the fastest imaging probe.

As Baker, one of the seminal figures in carbon research, recently noted, "filamentous carbon is a material which fulfills the axiom that one man's garbage is another man's treasure" (*13*), referring to the fact that carbon deposits can lead to undesirable performance in many applications. It continues to be the case that carbon structures offer exciting new perspectives into the state of matter, now with nanoscale dimensions.

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Phage Assembly: A Paradigm for Bacterial Virulence Factor Export?

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Because they are so genetically and biochemically tractable, bacterial viruses (bacteriophages) have long been used as tools for investigating fundamental biological processes—identifying signals, proteins, and mechanisms that govern replication, transcription, and translation. Now, analyses of protein-protein interactions that occur during assembly of filamentous phage are likely to be relevant to a complex cell biological question—how many bacterial pathogens export the proteins that enable them to interact with and exploit their plant and animal hosts? The unexpected parallels between these processes confirm the power of basic research in one area to fertilize another and, perhaps, to generate useful ideas.

At least three distinct systems mediate extracellular export of proteins in Gram- negative bacteria. Two of them are complex, with 12 to 14 different proteins required in the Type II systems of plant pathogens like *Erwinia* and *Klebsiella oxytoca* (*1*) and probably 13 or more Ysc proteins in the Type III system exemplified by pathogenic *Yersiniae* (*2*). Each contains a protein with an adenosine triphosphate (ATP)–binding motif, but the constituents of these two export systems are otherwise unrelated, with one notable exception. The exception is a protein also homologous to an essential morphogenetic protein (pIV) of filamentous phage. A third system present in *Haemophilus influenzae* may mediate export and assembly of a cell surface structure, the "transformasome"; transformation in these bacteria requires a homolog of pIV, as well as proteins that are unrelated to the other Type II or III proteins (*3*). Filamentous phage also encode an essential morphogenetic protein (pI) with an ATP-binding motif.

Several bacteria export virulence factors by means of the Type III set of proteins, even though they interact with their eukaryotic hosts quite differently to cause disease (*4*). Thus, pathogenic *Yersiniae* (including Y. *pestis*, the agent of the plague or

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