Nanocomputers from Organic Molecules?

The ultimate in miniaturized electronics is a computer whose elements are molecules that may even reproduce and assemble themselves

A wide-screen thinker is someone who boldly speculates about the general features of the future without being held back by all the detailed reasons why it cannot work. Some of the wider screens these days belong to an interdisciplinary brood comprising biologists, chemists, physicists, materials scientists, electrical engineers, and computer scientists who are establishing the new field of molecular electronics. Their goal is to replace the transistors and other devices of solid-state electronics with molecular functional groups, either organic or inorganic, that are constructed to exhibit the appropriate electrical behavior when hooked together in networks. A recent workshop on the subject at the Naval Research Laboratory in Washington, D.C., showed that there is a considerable gap between the cinemascope pictures of the thinkers and what they can do right now.*

Begin with the dreams, although these were largely not discussed at the workshop. First, the molecular computer. If one could be built, it would pack an enormous computing power into the tiniest of volumes. The smallest characteristic features of solid-state microelectronic circuits are measured in micrometers, whereas the dimensions of molecules are expressed in units a thousand times smaller, nanometers. Present silicon integrated circuits made of silicon are planar or two-dimensional affairs, so the molecular equivalent of a chip could contain a million times as many transistors. If true three-dimensional molecular nanocircuits were made, the device density would increase another 1000-fold (or even more, since the vertical spacing between silicon chips is at least a few millimeters).

A very tiny computer implies the possibility of its being implanted in the human body. One idea that has gotten a lot of attention comes from James McAlear and John Wehrung of EMV Associates, Inc., in Rockville, Maryland. The researchers want to use a miniaturized television camera mounted on eyeglasses as the "eyes" of a blind person. In itself this is not a new idea, but the way it would be implemented is imaginative. A tiny molecular "chip" would convert the signals from the digital camera into a pattern of current pulses in an array of miniature electrodes implanted in the brain. The electrodes would be coated with a protein to which cultured nerve cells would be affixed. The nerve cells would grow into the brain to make the final connections with neurons in the visual cortex. A radical extension of this notion is the human-computer hybrid, in which the computational power of an implanted computer would (one hopes it is not the other way around) tremendously augment a person's intellectual capabilities.

Finally, there is the question of how to construct computers whose elements are nanometer-sized molecules. One of the proposed ways to accomplish this is by means of an ambitious extension of genetic engineering technology that Kevin Ulmer of the Genex Corporation in Gaithersburg, Maryland, has called protein engineering (*Science*, 11 February, p. 666). Ulmer's idea is to generate new proteins not found in nature by altering the genes that control the structure and function of natural proteins. Ultimately it may be possible to learn the gene structure appropriate for proteins that act as enzymes to catalyze the production of molecules that can perform the electronic functions of a computer. The machine would be self-assembling and could even reproduce itself, according to this line of thinking.

"If we had more support, we would have more results," says the Navy's Carter.

Forrest Carter, the Navy laboratory chemist who organized the workshop and who has been energetically promoting the concept of molecular electronics, smiles but does not disavow such visionary applications when asked about them. He prefers to emphasize that the biochip or biocomputer is not necessarily the direction molecular electronics will take, especially at first. Carter also touts a way of assembling molecules with particular electronic functions that he calls modular chemistry. The method is an adaptation of the technique for the synthesis of polypeptides that was developed by Robert Bruce Merrifield of Rockefeller University in the 1950's. A suitably prepared, very clean surface is exposed to reagents that add only one subunit of a molecule to specific areas on the surface during the course of the reaction. A series of reactions with the same or different reagents builds up molecular "wires" or conductors, insulating regions, and switching and memory devices. Since only one subunit is added per reaction, control is in principle very precise, in contrast to batch chemical processes of today.

For the moment, fact considerably trails fiction. There has been no demonstration of any molecular electronic device, for example. At the workshop, Robert Metzger presented a paper, coauthored with his colleague Charles Panetta of the University of Mississippi, that illustrated some of the difficulties.

The investigators are trying to implement an idea proposed in 1974 by Ari Aviram of the IBM Yorktown Heights laboratory and Mark Ratner, who is now at Northwestern University, for a molecular diode. Diodes pass current easily in one direction but not in the other. The proposed molecule consisted of three parts: an electron donor complex, an electron acceptor complex, and an insulating bridge that separates them. A particular example considered by Aviram and Ratner, and the one being worked on at Mississippi, involves tetrathiofulvalene (TTF) as the donor and tetracyanoquinodimethane (TCNQ) as the acceptor. When TTF and TCNQ come together, an electron from the TTF donor immediately jumps to the TCNQ acceptor. The purpose of the insulating bridge is to prevent the electron transfer.

Diode action can occur when the molecule is placed between two metal electrodes and a voltage is impressed. In the forward or high-current direction, the donor electrode is positive with respect to the acceptor electrode. In the reverse or low-current direction, the polarity is the opposite. Somewhat surprisingly, given the natural inclination of electrons to go from the donor to the acceptor, the key to the diode is that electrons can relatively easily transfer by quantum mechanical tunneling from the acceptor to the donor when the forward voltage is

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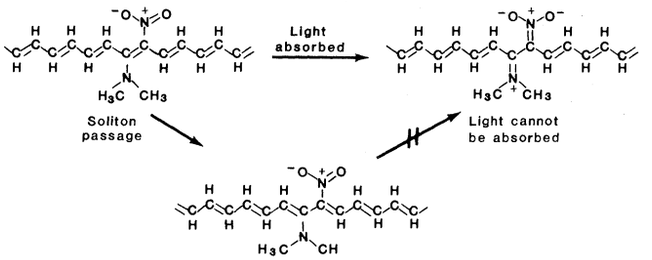
applied but they cannot so easily go from the donor to the acceptor when the reverse voltage is applied. This unintuitive asymmetry is the consequence of a shift in the positions of the energy levels of the quantum mechanical states in the donor and acceptor relative to one another during the synthesis of the molecular diode. IBM holds the patent for this concept.

The trick, as Metzger pointed out in his talk, is to find a way to attach the insulating bridge between the donor and the acceptor in a shorter time than it takes for the donor electron to naturally transfer to the acceptor. Once this transfer occurs, none of the molecular energy levels match up in the right way and the diode scheme will not work. The Mississippi researchers say they have now synthesized two molecules of the form TTF-urethane-TCNQ. Apparently, the urethane was able to tranquilize the electron transfer process, although the investigators have not been able to extract pure material and test its electrical properties.

As Metzger pointed out, the distance across the molecule from one metal electrode to the other is about 2 nanometers. Such a small structure could be very vulnerable to overheating. "An excessive voltage would fry an organic molecule," said Metzger. Another kind of proposed molecular electronic device could avoid this problem because there would be no dissipation at all. The idea is to use the theoretically popular but experimentally unproven idea of solitons.

Mathematically, solitons are solutions of nonlinear, partial differential wave equations. Unlike the waves in linear equations, solitons are both localized in space and do not smear out with time; that is, they do not dissipate energy as they travel. In nature, certain types of water waves have the properties of solitons. In theory, the magnetic monopoles that fall out of some elementary particle field theories are solitons. Solitons are also hypothesized to occur as fractionally electrically charged entities in so-called organic linear chain or one-dimensional conductors. The crystalline form of TTF-TCNQ is one such material.

For molecular electronic devices, the material of more interest is polyacetylene, and *trans*-polyacetylene in particular. The polymer consists of a zig-zag–shaped carbon chain with alternating single and double bonds. Each carbon has two hydrogen atoms bonded to it, but it is the pattern of carbon-carbon bonds that are relevant to solitons. One can imagine two patterns as follows: if one follows the chain to the right, one either ascends the zig-zag on double bonds and descends on single bonds, or just the opposite. Four years ago, Wu-pei Su of the University of Pennsylvania and J. Robert Schrieffer and Alan Heeger of the University of California at Santa Barbara considered what would happen in the region of a polyacetylene chain where the two patterns met. They calculated that a new quantum state with the properties of a soliton would be created. It would also have a fractional electronic charge of $\pm 1/2$ except for the fact that electrons exist in two states of spin angular momentum, which has the effect of multiplying the 1/2 by a factor of 2.



Soliton switch

Absorption of light in a "push-pull" olefin transfers an electron from the amine nitrogen at the bottom of the molecule to the oxygens in the nitro group at the top. Here the olefin is imbedded in a trans-*polyacetylene chain. When the double bond of the polyacetylene is between the two carbons of the olefin, light can be absorbed as described. After passage of a soliton, the double bond becomes a single bond. Light cannot then be absorbed because there is no path for the electron transfer. [Source: F. Carter, Naval Research Laboratory]*

The boundary between the two bonding patterns can move along the chain; that is, the soliton can propagate along the chain. This feature can be exploited in molecular electronics, or so it is asserted. As yet, experimental evidence that solitons exist in polyacetylene is suggestive but not conclusive.

One key to the use of solitons can be seen by considering three polyacetylene chains that meet at a point. Since carbon has its bonding requirements satisfied with four electons, at the carbon atom where the three chains join there can be one double bond and two single bonds. This means that a soliton passing down a chain toward the junction may be able to continue down either both or only one of the others, depending on the pattern of single and double bonds at the junction. Moreover, once a soliton has passed, it changes the pattern of bonds. At the workshop, Michael Groves of the University of Adelaide, South Australia, used this notion and others developed previously by Carter to demonstrate how soliton propagation in polyacetylene chains could be used to replicate the logic and memory functions of solid-state electronics.

The closest thing to a molecular electronic device reported at the workshop was an optically driven switch made of a metal-TCNQ polycrystalline thin film by Richard Potember and several co-workers from the Johns Hopkins University Applied Physics Laboratory in Laurel, Maryland. Copper and silver figured as the metal in most of the experiments. Four years ago, investigators there showed that films in an initially high resistivity state switched in less than 5 nanoseconds to a low resistivity state when a sufficiently large voltage was applied. Removal of the voltage resulted in restoration of the high resistivity state either immediately (threshold switch) or after a long period (memory switch). The change in the resistivity was by a factor of 10^4.

Optically driven switching means that rather than an applied high voltage, a laser beam induces the switching. Irradiation with laser wavelengths both above and below the optical absorption edge will work, so the researchers are proposing that it is the electric field in the laser light wave that is causing the effect and not the absorption of the light. Their model is that the high resistivity material is metal-TCNQ in which there is electron transfer from the metal to the TCNQ. Under the action of the electric field in the laser light, part of the material effectively has the charge transfer reversed to create neutral metal atoms and TCNQ complexes that are responsible for the high conductivity.

In addition to a change in the resistivity, the laser-induced switching also produces a change in the optical properties of the irradiated material. For example, a swept, focused laser beam can write patterns in the film. A second infrared laser pulse can "erase" the patterns. The Johns Hopkins investigators are therefore looking into the possibility of information storage devices, akin to the newly popular laser disks, that would be erasable, unlike the disks, and therefore could be candidates to replace magnetic disks in computers.

In his talk, Mississippi's Metzger pointed out that working molecular electronic devices would need to be assembled into arrays. The Mississippi researchers have in fact made Langmuir-Blodgett films from one of their product TTF-urethane-TCNQ molecules. The

Langmuir-Blodgett technique dates from the work of Irving Langmuir and Kathleen Blodgett in the 1930's and is a way to make films only one molecular layer in thickness. By successive repetition, scientists can build up multilayer films with different molecules in different layers. The technique is thus a variant of Carter's modular chemistry notion.

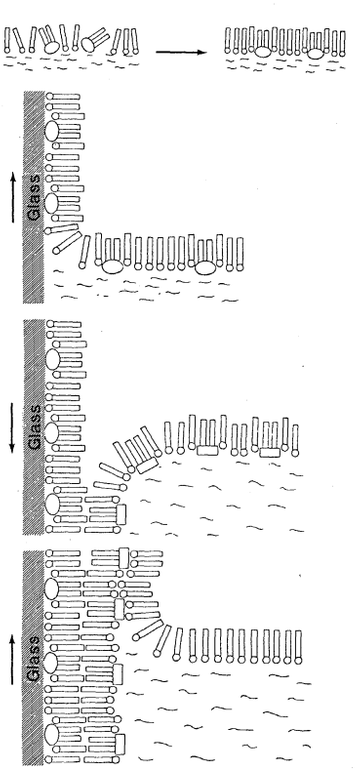
To make a film, chemists prepare molecules with a polar, hydrophilic moiety and a long-chain hydrocarbon, hydrophobic moiety. These are spread on a water surface. A movable barrier compresses the molecules together so that the hydrophobic ends are all lined up, pointing out of the water. When a glass slide or other substrate is immersed in the water and then pulled out, it is covered with a monolayer of oriented molecules. One of the modern-day apostles of the Langmuir-Blodgett technique, Hans Kuhn of the Max-Planck Institute for Biophysical Chemistry in Göttingen, West Germany, showed movies at the workshop that beautifully illustrated what could be done. By incorporating different dyes in successive molecular layers so that they glowed with different colors, Kuhn was able to demonstrate the mechanical robustness of the films as they were peeled apart and reassembled. He also presented concepts for making optical switches by incorporating light-emitting and -absorbing dye molecules into Langmuir-Blodgett films.

One of the problems relative to molecular electronic devices is that the molecules in Langmuir-Blodgett films studied to date generally have not had interesting electronic properties. A start on addressing that issue was presented by Donald J. Freed of ICI Americas, Wilmington, Delaware, on behalf of several researchers from Imperial Chemical Industries and the University of Durham in the United Kingdom. These investigators were able to generate multilayers of derivatives of two organic semiconductors, anthracene and phthalocyanine.

In the nearer term, Langmuir-Blodgett films may find use in electron-beam or x-ray resists for conventional microcircuitry. Resists are polymers that are sensitive to ultraviolet light, to x-rays, or to electron beams. Radiation from a scanning beam or through a mask can thereby "write" a pattern in the resist that can subsequently be transferred to the underlying semiconductor by various means. One of the limitations in making patterns with features very much smaller than 1 micrometer is that the thickness of the resist restricts the narrowness of the features in the pattern. To write a narrow line, for example, one needs a thin resist, but commercial resists are not easily applied to make uniformly thin coatings of less than a micrometer.

Langmuir-Blodgett films provide a possible answer to this predicament because they can be any desired thickness from one molecule on up. A number of groups, especially in Europe, are looking into this approach. At the workshop, Scott Rickert of Case Western Reserve University presented preliminary results of an investigation carried out in collaboration with Jerome Lando and G. Fariss, also of Case Western. These researchers fabricated mono- and multilayers of α-octadecylacrylic acid. Multilayers were deposited on both silicon and gallium arsenide surfaces and were virtually free from pinholes. In one set of experiments with a 20-layer coating that was 69 nanometers thick, patterns drawn with a 25-nanometer diameter electron beam were 50 nanometers wide. These are by no means the narrowest lines ever drawn but they are an encouraging start for a new technology.

An altogether different approach for assembling molecular electronic devices in arrays was presented to the workshop by Don Kendall of the National Institute of Astrophysics, Optics and Electronics in Puebla, Mexico. Kendall's idea takes advantage of the difference in the etching speed of different crystallographic directions in silicon. For example, potassium hydroxide solutions will etch vertically downward into grooves in the (110) surface of silicon 400 times faster than the lateral etching rate. The futuristic structure that Kendall would fabricate by these methods he calls a multiple-use substrate. It would be an array of tiny (as small as 50 nanometers on a side) cells etched into a silicon block. Each cell could be connected by a network of discretionary resistive or conducting links. And each cell would be reachable from outside the substrate, so that it forms a two- rather than a three-dimensional array. The electrically active devices would sit in the cells.



Langmuir–Blodgett multilayers

By successively raising and lowering a glass slide into a water-filled trough covered by a monolayer of fatty acid molecules, one can build up multiple-layer films. Molecules with oval and rectangular heads contain light absorbing and emitting dyes. [Source: H. Kuhn, Max-Planck Institute for Biophysical Chemistry]

However, even if exceedingly tiny molecular electronic devices could be manufactured and assembled into a computer or some other system, it may still be for nought unless a new way to organize them is discovered, according to two speakers at the workshop, Robert Grondin of Colorado State University and John Barker of the University of Warwick, United Kingdom. One problem is that electrical devices that are very close together are no longer treatable as isolated, independent entities. All of the circuit models developed for larger scale devices have to be discarded. To take a simple example, the capacitance of a logic device begins to be determined primarily by the capacitance between the conductors connecting the device to a neighbor when devices shrink below 0.3 micrometer, said Grondin. A second problem, emphasized by Barker, is the sheer complexity of arranging things so that so many electrical components work together harmoniously and reliably.

All in all, for all their high-tech razzle-dazzle, the semiconductor microelectronics wizards are remarkably conservative. They began with silicon and no other semiconductor has come close to replacing it. Most computer designers chortle when advanced alternatives such as superconducting Josephson junction electronics are mentioned. Molecular electronics, then, is not a high-priority item, as the Navy's Carter admits. "If we had more support, we would have more results," he says. Rather than a molecular computer, a possible outcome of molecular electronics research is that in trying to bring their dreams to fruition, researchers will uncover new micro- or nanofabrication technologies with applications quite different from those they now imagine.—**ARTHUR L. ROBINSON**