

Halley's Whiskers: First Space Polymer Detected

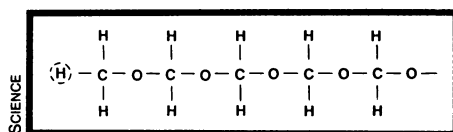
Over the last half-century, radio-telescopes and other earth-based tools have revealed the presence of more than 60 different kinds of molecules in space, plus nearly as many of their isotopic variations. They have ranged from simple molecular hydrogen (H_2)—composed of two atoms of the most ubiquitous element in the universe—to increasingly complex forms such as ethyl alcohol (CH_3CH_2OH) and cyanodecapentene ($HC_{11}N$). Yet all have been found as individual molecules, never as the kind of linked, molecular chains well known on earth as polymers.

Now, however, one of the results of last year's multi-national, multi-spacecraft encounter with Comet Halley has turned out to be the first identification of a polymer in space. The find is based on measurements from the European Space Agency's Giotto craft, which went closest of all to the comet as the first European space mission ever to get beyond earth-orbit. The substance appears to be the polymeric form of formaldehyde [$(H_2CO)_n$], also known as polyoxymethylene, or POM.

The polymer was identified by Walter F. Huebner of Los Alamos (N.M.) National Laboratory, now on leave at the Southwest Research Institute in San Antonio, Tex. Huebner analyzed the atomic masses of ions detected during Giotto's approach to the comet by an instrument called the positive ion cluster composition analyzer. What the device had measured was a succession of spectral peaks whose regular, alternating pattern seemed to show a mass of 14, then a mass of 16, then 14 again, then 16, then 14—like a chain with one link consisting of an oxygen ion, followed by an ionized group comprising two atoms of hydrogen and one of carbon, then another oxygen ion and so on. This is the "signature" of POM.

Though it is the first such identification in space, the find was not entirely unexpected. In 1969, ordinary "monomeric," or nonchained, formaldehyde (H_2CO) had become the seventh addition to the list of known "space molecules," and within five years it had been detected in more than 100 interstellar clouds. On earth, the polymer had been synthesized as long ago as the turn of the century, and in 1974, N.C. Wickramasinghe of University College, Cardiff, in Wales, proposed on the basis of his own and others' studies that POM was a natural candidate to exist as an interstellar polymer.

He maintained that it could condense onto silicate grains in space, of the sort ejected by cool, giant stars, and that with the grains at temperatures below about 20 kelvins ($\sim 253^\circ C$), the result would be



The first polymer identified in space is shown by this length of the molecular "chain" of polymerized formaldehyde, $(H_2CO)_n$. It was identified from ion-mass spectra measured by the Giotto spacecraft on the way through the coma of Comet Halley. The chain's free ends could bond with various species, such as the hydrogen atom in the dashed circle.

"polymerization into chains." Reporting in the Dec. 6, 1974 NATURE, Wickramasinghe concluded that "POM grains must clearly be regarded as a strong candidate for the main component of interstellar dust."

The new find supports the view of many scientists that comets are repositories of some of the most primitive material in the solar system. Huebner notes in the Aug. 7 SCIENCE that "since POM is still being released from the comet, it appears

that the dust that contains POM is also deep in the interior of the nucleus. The POM must have been created in interstellar space, the presolar nebula or the solar nebula and was then incorporated into the cometesimals [particles from which the comet formed] at the time of their formation."

POM may also have played a role in one of the more surprising findings revealed in the photos taken by Giotto and the two Soviet Vega spacecraft that also took part in the encounter: the surprising darkness of parts of the nucleus, which was expected to be ice-bright throughout. It is unclear just how long the POM polymer chains coming from the nucleus actually were, but relatively short ones, says Huebner, tend to attach themselves to grains of carbon or silica in thin, "whisker-like" structures. If these grizzly particles fall back onto the nucleus, he suggests, they could trap incoming sunlight in the spaces between whiskers, scattering it in different directions rather than reflecting it brightly as would a smoother ice "complexion." — J. Eberhart

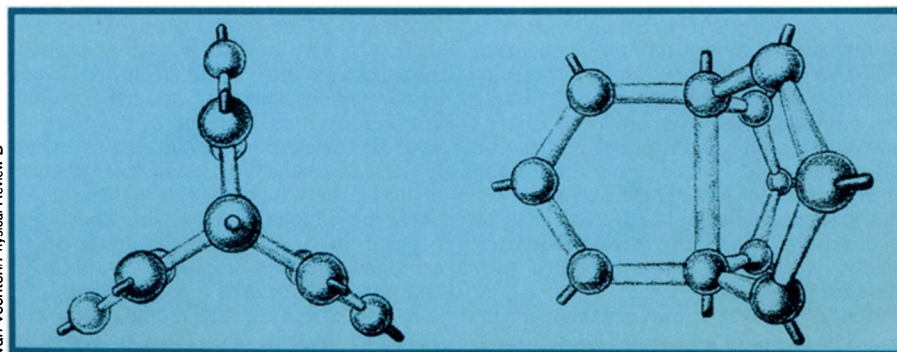
Explaining carbon-cluster magic numbers

When graphite is vaporized by a laser, the liberated carbon atoms are found to be clumped together in remarkably specific numbers: If more than 40 atoms make up a cluster, then an even number will be in the clump, while in smaller clusters, certain "magic numbers"—11, 15, 19 and 23—are most common. For years chemists have debated the origin and structure of these clusters, especially those in the 40-plus range. To explain the high prevalence of C_{60} clusters, for example, some researchers have proposed a soccer-ball-like structure called buckminsterfullerene (SN: 11/23/85, p.325).

Now two scientists at Oregon State University in Corvallis have come up with a carbon structure that they believe may explain the magic numbers of the smaller clusters. Materials scientist James A. Van

Vechten and chemist Douglas A. Keszler also suggest that their new structure could form the basis of a novel and industrially important material that would have all the strength of graphite, but none of its brittleness. Their work will appear in the Sept. 15 PHYSICAL REVIEW B.

Van Vechten and Keszler happened upon the structure when they were analyzing fine "whiskers" of carbon that they had made by "sputtering" or bombarding a graphite target with ions. Transmission electron microscopy revealed that the whisker material is crystalline, but that the carbon atoms in it are arranged in neither a diamond's nor graphite's pattern. Van Vechten says that after spending months thinking up atomic arrangements that could be reconciled with the experimental data, he found only one model



Two views of the proposed 11-atom paddle-wheel structure.

that would fit: an 11-atom, paddle-wheel-like structure consisting of two "hub" atoms along an axle surrounded by three paddles, each containing an additional three atoms.

In the midst of the whisker work, Van Vechten realized that this structure could also be "a natural explanation for the strong prominence of 11-atom clusters in laser [vaporization]," since that process is as violent as sputtering. Support for the stability of the structure comes from the recent synthesis of similarly shaped molecules such as propellane (SN: 6/6/87, p.357).

To explain the other carbon-cluster magic numbers, Van Vechten says each addition of four carbon atoms to the 11-atom molecule would allow a stable graphite six-member ring to form along the side of one paddle. The magic number series stops at 23, he believes, because there are only three paddles in the molecule. He also thinks this molecule—unlike the chain and ring structures proposed before to explain small clusters—can account for why 11, 15, 19 and 23 are observed to be magic numbers for neutral and positively charged clusters but not for negatively charged ones.

While Princeton (N.J.) University's Leland Allen says this work is "interesting and impressive," he and others caution that it is conjectural and that the chains and rings are still very much in the running. Moreover, says Richard E. Smalley at Rice University in Houston, Van Vechten's molecule is much more reactive than the other candidate structures. This property appears to be inconsistent with experiments indicating that the 11-atom clusters are not very reactive.

Van Vechten hopes to use the 11-atom structure as the basis for making a new low-density material that improves upon the properties of graphite. "Graphite is extremely strong, but there are difficulties using it as a structural material because it tends to fracture," he says.

Van Vechten would like to try to grow carbon crystals in which the 11-atom structure is stacked into a honeycomb pattern, interlocked by carbon chains. This interlocking would prevent the honeycomb planes from slipping past one another, which is at the root of graphite's brittleness. "It looks as though this material would have an order of magnitude higher tensile strength than titanium and about a third the density," he says.

"Also, the material is clearly a metal and it's nonmagnetic, so it ought to have a superconducting-transition temperature," says Van Vechten. "Its features lead one to think that it [the temperature] would be high." If so, then he says it would have vastly better structural properties than the high-temperature superconducting materials (see p.106) that are getting so much attention now, but that are difficult to form into wires because of their brittleness. — S. Weisburd

Hereditary highway map: Assessing the toll

Momentum is building among U.S. scientists to create a detailed road map of the entire human gene system, or genome. Last week, geneticists, molecular biologists and computer scientists convened in Washington, D.C., at the request of the Office of Technology Assessment (OTA) to help estimate the cost of such an undertaking — a biological mission so complex it has been likened to the 1960s effort to put a man on the moon. Congress is to consider funding for the project in the fall.

Scientists expect that human-gene mapping will lead to improved diagnosis of hereditary diseases, the development of new drugs and a host of unforeseen benefits. Enthusiasm for the project has grown in the past year with the mapping of genes responsible for muscular dystrophy and neurofibromatosis, and with the discovery that certain genetic sequences are related to manic depression (SN: 10/25/86, p.261; 6/6/87, p.359; 3/28/87, p.199). But a high-resolution map showing every human gene has only recently become feasible with the development of specialized automated technologies.

Recent advances in automation have made DNA sequencing both cheaper and faster. Until recently, according to scientists at the meeting, the cost has been \$1 to \$2 per nucleotide base; these bases spell out the genetic code. New technologies have lowered the costs to as little as 6¢ or 8¢ per base, says Leroy Hood of the California Institute of Technology in Pasadena. And within six months, he predicts, the cost could drop to a penny a base. Such differences are significant, he says, as there are approximately 3 billion bases in the human genome, and each base will have to be mapped at least two or three times to confirm its location.

Researchers at the meeting also noted progress in the number of genetic markers — key chromosomal reference points — that have been identified (SN: 8/31/85, p.140). To date, 300 to 400 "reasonably informative" markers have been identified, says Helen Donis-Keller, a senior research director at Collaborative Research Inc., a Bedford, Mass.-based biotech research laboratory. An additional 300 to 400 such markers will be needed to develop a genetic map that would have a marker every 5 million bases — a scale that would be very useful for locating the sites of disease-causing genes, Donis-Keller says. She predicts that such a map will be completed in the next two years. Detailed nucleotide sequencing, with its ability to determine exactly which proteins are coded for by defective genes, would take many more years.

Scientists say it will be necessary to develop highly sophisticated computer programs to make sense of the huge

amount of genetic data that will be generated by the mapping project. It is not unreasonable to assume that a supercomputer may be needed, according to some scientists at the meeting. And millions of dollars may be needed to train specialists with combined skills in molecular biology and computer science.

How much would the gene mapping project cost? It will be some time before OTA analysts add up the numbers. But several scientists express surprise that while much of the mapping itself could be done for \$100 million, the costs of simply freezing "signpost" cell lines for future use might amount to a quarter of a billion dollars or more. "At that price," says Harvard researcher and Nobel laureate Walter Gilbert, "it would be cheaper to make the stuff all over again instead of storing it."

If in fact every important cell line were to be cloned and stored, "it would take 12 of the largest liquid-nitrogen refrigerators now available," says Robert E. Stevenson, of the American Type Culture Collection, a cell-storage bank in Rockville, Md. "We're talking about a large [liquid-nitrogen] tank farm."

Total cost of the project will also hinge on the total number of human genomes mapped, says Paul Berg, Stanford biochemist and Nobel laureate: "Whose DNA are we going to sequence? Are you satisfied with one? Is that *the* human genome?" — R. Weiss

High-cadmium diet: Recipe for stress?

When laboratory rats consume a diet that includes relatively large doses of cadmium, a common metal and environmental pollutant, there is increasing evidence that they become more anxious and unable to deal with stress. The latest such study, conducted by psychologist Jack R. Nation and his colleagues at Texas A&M University in College Station, finds a link between exposure to cadmium and increased alcohol consumption.

Given a choice of drinking water or a 10-percent alcohol solution, rats put on a cadmium-laced diet preferred the liquor, whereas rats munching cadmium-free food favored the water. The former group may have turned to alcohol to ease cadmium-induced anxiety, says Nation. There are other indications of increased anxiety among rats who ingest cadmium, he notes, such as an exaggerated startle response and freezing in their tracks when a loud tone is presented.

But the connection between anxiety and alcohol use is tentative, say the researchers in the September NEUROTOXICOLOGY AND TERATOLOGY, since "there is