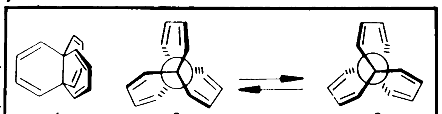
Putting a spin into chemistry

Chemists have found a way to build a molecular propeller. The recently synthesized molecule, consisting of three six-membered rings made up of carbon atoms radiating from a central axis (diagram 1), looks like a three-bladed propeller. Its name, appropriately, is propellahexaene.

Paquette/JACS



1 2 3

"It's a very attractive molecule," says chemist Leo A. Paquette of Ohio State University in Columbus. "It's nicely symmetric and has all the features one would expect if one were to describe a molecular propeller." Paquette and Liladhar Waykole report their successful synthesis in the May 13 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

Achieving the synthesis was no simple matter. It took about 20 steps and many years of work to end up with the correct ring structure. Locking three rings together was relatively easy. The trick was to strip away any unnecessary molecular appendages hanging from the rings without causing a major rearrangement of the molecular structure.

The new compound turns out to be remarkably stable in air. It appears in the form of fine, colorless, needle-like crystals, which melt at 48°C.

Paquette and his colleagues are hoping to produce larger quantities of the hexaene to study its crystal structure and its chemical reactivity. In terms of its chemistry, he says, "we don't know what to expect – except complications."

Propellahexaene is also of interest to chemists because it comes in two forms: a right-handed and a left-handed conformation. The rings are strongly curved, and the whole system rapidly flips back and forth between one form and the other (diagrams 2 and 3). Chemists are interested in the factors that determine how easily this switching occurs and how much energy is involved.

It may be possible to lock such a molecular propeller in one position, says Paquette, perhaps by making the rings heavier. That could be done by using double instead of single rings for each blade. Paquette says he can also imagine stacking hexaene molecules to create a molecular screw, "but I wouldn't want to come to grips yet with the task of making them." *– I. Peterson*

Volcanic history in the Aleutian arc

Benjamin Franklin was probably the first to suggest a correlation between volcanic eruptions and changes in the global climate when he proposed that a 1783 volcanic eruption on Iceland had induced abnormally cold temperatures later that year. More recently, scientists have accused volcanic eruptions of causing the yearly depletions of polar ozone and even the extinction of the dinosaurs. However, to support volcano-climate theories, scientists must rely on an incomplete and often sketchy list of the major eruptions in the earth's history, says Thomas P. Miller of the U.S. Geological Survey (USGS) in Anchorage, Alaska.

In the May GEOLOGY, Miller and Robert L. Smith, a USGS colleague from Sacramento, Calif., report results that fill in some of the gaps in the eruption chronology. Their study will help climatologists confirm or deny that volcanoes had caused certain prehistoric climate changes, says Miller. He and Smith have identified and dated 12 large eruptions – 11 of them previously undated or poorly documented – in the eastern Aleutian arc, a volcanically active boundary between the Pacific plate and the North American plate.

Using carbon-14 dating, the researchers pinpointed the age of organic material either charred by the eruptions or buried under the debris. From these dates, they determined that most of these eruptions occurred relatively recently, within the last 10,000 years. Eight of those eruptions and two earlier ones were large enough "that they must be considered in hypotheses linking large eruptions and climate changes in the late Quaternary [last 100,000 years] time," write the USGS researchers.

M. Woodbridge Williams/NPS

View of Alaska's Aniakchak caldera, formed by the collapse of a volcanic cone during an eruption about 3,400 years ago.

Volcanic eruptions influence global climate by ejecting sulfur dioxide into the stratosphere. When this combines with water, it forms small, stable droplets of sulfuric acid, which interact with solar radiation and radiation from the earth, thereby affecting global temperatures.

This study of the Aleutian volcanic history, says Thomas Simkin, a geologist with the Smithsonian Institution in Washington, D.C., will also aid those who assess the potential hazard from future volcanic eruptions. *– R. Monastersky*

Plant hormone: Key to ozone toxicity?

Ozone, a photochemical oxidant in smog, is considered by the government's National Crop Loss Assessment Network to account for about 90 percent of U.S. crop losses from air pollution. According to Walter W. Heck, a scientist with the Agricultural Research Service in Raleigh, N.C., which oversees the network, the pollutant's economic toll on U.S. corn, soybean, wheat and cotton producers is estimated at between $1 billion and $5 billion annually. What has remained a mystery is how the pollutant exacts its toll on plants.

Now a pair of biologists in England report stumbling onto what may be an important clue: that dramatically increased production of a hormone, in response to stress, appears to increase a plant's ozone vulnerability. Moreover, the hormone-triggering stress in this case was a one-shot dose of ozone; long-term ozone exposure actually had the opposite effect on young seedlings, reducing hormone levels.

The researchers found that pea seedlings exposed to between 50 and 150 parts per billion of ozone for seven hours daily throughout their first three weeks of growth showed no visible leaf injury. However, when seedlings grown in the absence of ozone for three weeks were given just one similar seven-hour exposure on day 21, they immediately developed severe leaf-tissue death.

The researchers, Horst Mehlhorn and Alan R. Wellburn of the University of Lancaster, wondered why the two sets of plants were responding so differently. They measured the plants' production of the hormone ethylene and discovered that the single-exposure group produced double the amount of ethylene produced by unstressed (control) plants. Plants in the three-week-exposure group, on the other hand, seemed to combat the ozone by producing 92 percent *less* ethylene than the controls.

"These two quite different responses to ozone suggest that the rate of ethylene production may have an influence on and modify the extent of visible leaf injury caused by ozone," the researchers write in the June 6 NATURE. As a further test of ethylene's role, they pretreated plants with an ethylene inhibitor on the day before the 21-day-old seedlings' single seven-hour ozone exposure. Not only did the treatment reduce by 85 percent the plants' ethylene production during ozone treatment, but it "also almost abolished the visible leaf injury normally caused by this short ozone fumigation," they report.

Mehlhorn says it's not clear how or why the seedlings exposed to three weeks of ozone reduce their ethylene production. But from the study, he says, this accommodation appears to be permanent.

"Since they both perform similar functions in terms of making [leaf] membranes leaky, it seems both reasonable and interesting" that ozone and ethylene could interact, according to botanist Joseph Sullivan of the University of Maryland in College Park. Heck says he is unconvinced, largely because his research with other plants indicates that many days of exposure produce more damage than one-day exposures.

– J. Raloff

Will livestock drug cause dung crisis?

Dung beetles and earthworms don't tend to get a lot of respect – except when they're not around. Ecologically, these invertebrates provide a valuable housekeeping service. Not only do they break down and carry away dung, but in the process they also aerate soil and enhance the ability of water to percolate into the ground. For these reasons, growing veterinary use of the drug ivermectin in livestock to control parasites – such as roundworms – could have unintended environmental repercussions. A new British study shows that the drug, excreted in the feces, can exert a dramatic insecticidal effect on dung fauna.

While feces of nontreated calves were immediately colonized by dung beetles in the field – sometimes by hundreds per "pat" – and later by earthworms, the dung of ivermectin-treated animals remained largely devoid of such invertebrates, according to a report in the June 4 NATURE by zoologists Richard Wall and Les Strong of Bristol University in England. Within 100 days, the researchers say, the control pats had "largely disappeared," whereas the drug-containing dung samples "were still largely intact." This situation could spell a serious, impending problem, especially to livestock farmers, Wall believes, because "for every pat [of dung] you have, you reduce available pasture land; cows won't graze up to the edge of their cow pat."

Bill Hill, a spokesperson for the Rahway, N.J.-based MSD-AGVET (a division of Merck & Co.), the drug's maker, says there have been no anecdotal reports from ivermectin users of problems with dung degradation. Moreover, he says, because the drug is registered only for infrequent administration by injection or as a paste, its effects on dung beetles would be limited to feces passed in the few days after each treatment. But Wall says while that may be true today, it would not be true if the drug were administered from a controlled-release implanted pellet, which he says is now under development – an application that would shed the drug into the feces daily for months.

– J. Raloff

Superconductivity and quantum mechanics

The new high-temperature form of superconductivity that is currently setting the physics world on its ear may also illustrate the problems of applying quantum mechanics to small numbers of objects, Edward Teller of Lawrence Livermore (Calif.) National Laboratory told the Loyola Conference on Mathematical and Interpretational Problems in Relativistic Quantum Theory, meeting in New Orleans last week.

Quantum mechanics makes statistical predictions, and the statistics are most easily understood when applied to ensembles of large numbers – millions, billions – of individuals. Classical mechanics, which usually governs the macrocosm, makes absolute predictions for individuals. Somewhere, somehow, the two must come together, a serious question that has been largely avoided. Teller suggests that because superconductivity in these high-temperature materials is accomplished by the action of only a few electrons – far fewer than in the long-known low-temperature form – this may be a place where the statistical and the individual shade into each other.

Electrical conduction of any kind depends on the substance having a supply of electrons that are not tightly bound to given atoms but free to drift through the material. Ordinary metals have such conduction electrons in great abundance, but the new superconducting materials are ceramics with far fewer free electrons in them. As Teller says, "If you put together a barium oxide, a copper oxide and an yttrium oxide and cook them together in the right proportions, you don't get superconductivity. But cook at 950°C for an hour and cool it. The oxygen has gone up from 6.5 to 7. You don't get superconductivity either. Stop a little too soon [so that the proportion of oxygen is 6.9], and you get superconductivity. Anybody can do it."

The 6.9 means that in an occasional cell of the crystal, an oxygen present in other cells is missing. The omissions seem randomly distributed. This missing oxygen ion leaves behind two electrons, says Teller, and these add crucially to those contributed by other atoms, particularly the copper, to make the superconducting effect go. The oxygens that are present are also critical, as they are the intermediaries that make the electrons behave in a superconducting way.

To get superconductivity, electrons must cooperate in pairs, called Cooper pairs. The pairs obey a different statistical law from single electrons, making resistanceless passage possible. In low-temperature superconductors the pairs form through an interaction with an acoustical wave in the crystal lattice called a phonon. As an electron proceeds through the crystal, it draws the atomic nuclei toward itself. As it passes, the nuclei move back to their previous position. Thus the lattice ripples as the electron moves along. A proper interaction between two such ripples brings the electrons into a Cooper pair. Characteristically the members of a pair are a few hundred angstroms apart, Teller says.

In the high-temperature superconductors, he suggests, it is not an acoustical vibration of the lattice, but a vibration of oxygen atoms at frequencies characteristic of light – ultraviolet to be precise – that makes the Cooper pairs. The mobile electrons are particularly those extracted from a certain orbital level of the copper atoms, and they move preferentially in what crystallographers call the y direction, thus accounting for the strong tendency for supercurrents in that direction that experiment has found. These electrons form Cooper pairs with members in adjacent unit cells.

The electrons are not evenly distributed. There is a probability for them to prefer certain locations to others, and these locations form a kind of checkerboard three-dimensional pattern through the crystal. The preferred locations along a given line are offset from those in adjacent parallel lines so as to form a stable three-dimensional "superlattice," in which the absolute positions are unknown but the positions relative to each other are known. In this structure the electrons move in "lockstep." A slight disturbance of the superlattice will produce a lot of current for very little energy.

The "optical" quality of the high-temperature superconductivity can make the Josephson effect appear at temperatures above those where resistanceless conduction sets in, Teller proposes. In the Josephson effect a supercurrent passing through a slightly insulating junction between two superconducting contacts generates a radio wave. Some experimenters have found the Josephson effect at temperatures as high as 260 kelvins in these materials, and some have claimed that that means superconductivity is present. However, actual resistanceless current flow has not been confirmed above 100 K.

Low-temperature superconductors are fully superconducting when the Josephson effect appears. In the high-temperature materials, Teller believes, a combination of the optical frequency of the vibrations and a variation of the photoelectric effect can produce a Josephson effect at temperatures above those where true resistanceless flow begins. As Teller puts it, "The electrons are not yet moving in lockstep; conductivity is not yet zero, but a dozen or 100 are correlated" – enough to make a Josephson effect.

– D. E. Thomsen