

The Curling Crystal Club

By IVAN AMATO

Just as Halley's comet faintly painted the night skies in February 1986, medicinal chemist Tamime F. Braish first noticed the most remarkable crystal formations he had ever seen. Under the laboratory's ventilation hood sat a glass vial containing a helical crystal construction so bizarre that Braish, his colleagues at Purdue University in West Lafayette, Ind., and others who have seen it are still scratching their heads.

Only two weeks earlier, Braish had finished his analyses of a then-unassuming compound designated as "46." The material started out just like the other minor chemical by-products that organic chemist Philip L. Fuchs and his graduate students at Purdue produced over the years in their efforts to make exact copies of naturally occurring chemicals called jolkinols. Rubber trees and many other plants routinely manufacture these structurally complex and biologically active compounds in their cells. Nature's own chemicals often make for top-notch medicines, adhesives and other products. Natural-product chemists like Fuchs and Braish not only develop laboratory sources of such compounds, but often discover techniques for making chemical structures never before made in a laboratory. As he had done many times, Braish stored the dissolved 46 in a vial and temporarily set it aside under the hood, often a kind of purgatory for chemicals most likely destined for storage and obscurity. Something quite different lay in store for compound 46.

"Over the course of two weeks' time, it was found that the solvent had evaporated and 46 had crystallized in a unique and unprecedented helical manner," Braish, Fuchs and John C. Sandler noted (almost parenthetically) in the Aug. 5, 1988 *JOURNAL OF ORGANIC CHEMISTRY*. As the solvent slowly disappeared from the incompletely sealed vial, thousands of small crystalline needles of compound 46 grew and assembled into an unmistakably helical form, twisting round three and more times and spanning the entire height of the vial (see cover). Over the next month, Braish redissolved and recrystallized the material six or seven times in different-sized containers. Each time, it did the same thing with the same direction of twist.

"I was completely amazed," says Braish, who now works as a pharmaceutical chemist with Pfizer, Inc., in Groton, Conn. So were Fuchs and others whom the scientists had invited into the lab for a peek. "We're sitting with this curiosity that may be something fundamentally important screaming out at us," says Fuchs. Even after three years, the re-

searchers remain nearly clueless about the phenomenon that Fuchs says "stuns" conference audiences. So far, the published record on 46 and its peculiar behavior consists of two paragraphs and a couple of footnotes in last August's article.

That the helix always formed with the same twist direction particularly teased the imagination, Fuchs told *SCIENCE NEWS*. Many organic compounds are chiral, which means they usually form in equal amounts of two mirror-image structures known as enantiomers. The researchers knew from their chemical and crystallographic analysis of 46 that it consisted exclusively of one enantiomer, a consequence of the reaction scheme the researchers chose in their attempts to synthesize jolkinol compounds. "This got us musing that if we only had the opposite enantiomer, the helix might curl in the opposite direction," Fuchs says. Unfortunately, making the other enantiomer would take a year and a half, a far too costly and time-consuming research tangent, Fuchs decided.

"So we did the next best thing," Fuchs says. They sent their entire several-gram sample of 46 to the Australian National University in Canberra, where Bruce Twitchin recrystallized it four times. In the first three Southern Hemisphere attempts, 46 recrystallized in the opposite helical twist. The fourth trial yielded "a Northern helix," an inconsistency that still stumps the scientists. If enough material existed to perform hundreds of crystallizations in both halves of the globe, the anomaly could well disappear, Fuchs suggests. Still, the small-scale experiment points to a possible physical explanation for the curious curling phenomenon.

Fuchs' best hypothesis involves the Coriolis force—a horizontally acting force that works in opposite directions in the Northern and Southern Hemispheres and partially governs rotational motions such as the vortex of draining water—counterclockwise in the north, clockwise in the south. Compound 46 begins crystallizing at the top of the container, where hundreds of 2- to 3-millimeter needle crystals form a semipermeable meshwork. And that traps an air bubble. According to Fuchs' speculations, as the underlying solvent slowly evaporates, the bubble limits the locations at which new needles can attach to the growing crystal assembly.

Presumably, the Coriolis effect keeps the bubble moving to the right in the Purdue labs and to the left in the Australian labs. "But we really don't know what's going on here," Fuchs stresses. If

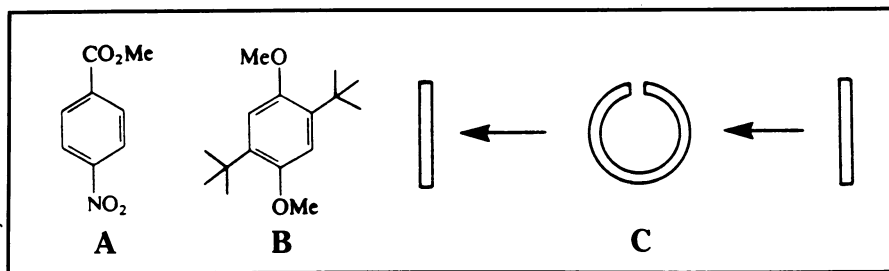
the physical effect were the entire story, he notes, many other chemists would have observed similar helical formations with other crystallizing compounds.

If chemical factors play a role as well as physical ones, they are not obvious. Compound 46 is pretty ordinary chemically, Fuchs says. Although it is chiral, and also a complex carbon-based chemical with several interconnected ring structures, he sees nothing that suggests these molecules would link into a helix. Even crystallographic data yield no clues. "I was hoping that when we saw the crystal structure of the needles, we would see a lock-and-key phenomenon" accounting for the helicity of the aggregate, Fuchs says. No luck here either. "It's the kind of thing you just grin and look at and try to get some idea of what nature is saying."

Linus Pauling of the Linus Pauling Institute of Science and Medicine in Palo Alto, Calif., a longtime student of crystal phenomena, finds this one a bit odd himself. "If the helical form of aggregated needle crystals had a sound chemical basis, it surely would be connected to the chirality of the molecules themselves," he argues. If so, the hemisphere that hosts the crystallization would have no bearing on the helical direction of the crystal aggregate; only the geometric structure of the enantiomer undergoing crystallization would matter. For this reason, Pauling seriously doubts that chemical factors shape Fuchs' material.

The August paper, which mentioned compound 46 only in passing, did turn the heads of perhaps the only other admitted veterans of curling crystals. Soon after the Purdue scientists' article appeared, Neil Buckley, an organic chemist at the University of California, San Francisco, sent Fuchs a letter welcoming him "to the smallest known scientific subdiscipline—those who have published on curling crystals."

In the May 1986 *CHEMISTRY AND INDUSTRY*, just a few months after Braish made his discovery, Buckley had published a short account of separate experiments by him and others involving two simple organic compounds that have their own repertoire of bizarre antics. As part of a long sequence of chemical reactions, Buckley prepared one of the compounds—para-nitromethylbenzoate (figure A)—in a large flask containing more than a gallon of methanol. Flat, thin, orange crystals formed when he filtered and cooled the solution. These drifted down some in the beaker before curling into little cylinders. After descending a little more, the cylinders suddenly snapped open, sometimes turning into projectiles that would "ping" faintly against the



beaker. Some of the crystals fractured when they uncurled. Those that remained intact were almost always thicker after they uncurled than before.

Although Buckley judged this as unusual behavior indeed, he knew his observation was not unique. In the mid-1960s, he and John Larsen, now a physical chemist at Lehigh University in Bethlehem, Pa., were grad students together at Purdue — where Fuchs works now. Some years earlier, when Larsen was an undergrad at Tufts University in Medford, Mass., he and his chemistry professor Robert Stolow reported in *CHEMISTRY AND INDUSTRY* on crystals of the compound 2,5-di-*t*-butyl-1,4-dimethoxybenzene (figure B) that “changed ‘conformation’ in a most dramatic manner.”

Like Buckley’s crystals, the Stolow-Larsen crystals start out as thin plates, curl into cylinders and then suddenly uncurl into somewhat thicker plates (figure C). “Some of the crystals were rolling right up,” Larsen says. “Others would

have one stiff end and the other end would flex. Sometimes they would propel themselves across the solution as they uncurled.”

“I went into Stolow’s office and asked: ‘Do crystals normally swim around when they’re growing?’” Larsen recalls. Amazed by the behavior, Stolow counseled Larsen to write down his observations. Stolow and several others who witnessed the crystals promptly authenticated the written records with their signatures. After publishing a short note on this observation in the March 1963 *CHEMISTRY AND INDUSTRY*, neither Stolow nor Larsen pursued the curling crystal phenomenon.

Three years later, though, two English chemists published a paper in *TRANSACTIONS OF THE FARADAY SOCIETY*, attempting to explain the curling behavior in a number of ways. They suggest, for example, that crystal growth might occur preferentially on one face of the plates, giving rise to “a difference between the

surface energies of the two faces” that exceeds what they define as the “curling energy,” or the amount of energy required to curl the thin plates. Then additional growth could lead to a total energy of the crystal lattice that exceeds the surface energies that first caused the curling. The crystals respond to the additional growth by uncurling. An alternative explanation involves preferential adsorption of solvent molecules on one face due to slightly expanded or contracted lattice spacings caused by such things as “convective currents in the solution.” But without further experimental verification of such theories, Larsen points out, they remain little more than stories.

Had Buckley and Larsen not been students together, Buckley suspects he never would have known that his crystals were more than a fluke. Another odd coincidence: The two were graduate students of organic chemist Richard A. Sneen, who occupied a fourth-floor suite in the chemistry building at Purdue—the very same lab suite in which Braish happened onto the helical crystal formations years later.

In his August 1988 letter to Fuchs, Buckley puckishly offered the following advice: “You might consider an immediate and thorough search for gnomes that we may have left behind.” In lieu of gnomes, Braish wonders in good humor if the comet has had anything to do with his baffling crystals. □

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