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Ultrafast X-ray Diffraction Tracks Molecular Shape-Shifting

"If you want to understand function, study structure," exhorted Francis Crick. But knowing a molecule's static structure is often only the first step toward unraveling how the molecule works, especially in the world of biology. The molecular grappling hook that HIV uses to latch onto its cellular prey, for example, depends on a change of structural shape to initiate infection.

The structural changes that accompany chemical reactions have been studied with fast spectroscopy for the past 50 years. And since the mid-1980s, ultrafast lasers have been the tool of choice in this approach (see PHYSICS TODAY, December 1999, page 19). But with spectroscopy, structure has to be inferred, which is tough to do without a deep and robust understanding of the physics linking spectra to three-dimensional structure.

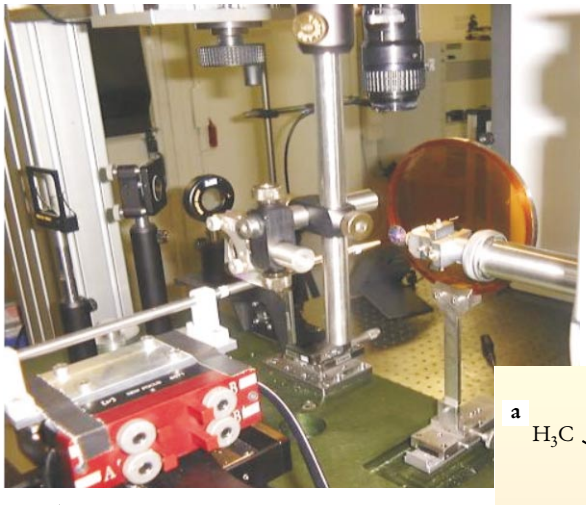
X-ray diffraction yields structural information directly. In 1982, Ben Larson (Oak Ridge National Lab) and Denny Mills (Argonne National Lab, but then at Cornell University) became the first to couple a nanosecond laser with a synchrotron x-ray source (the Cornell High Energy Synchrotron Source). Their aim was to settle a controversy about the physical mechanism behind the laser annealing of silicon.

The molecular workings of photosynthesis, vision, and other light-driven processes can now be studied on the time scales on which they occur.

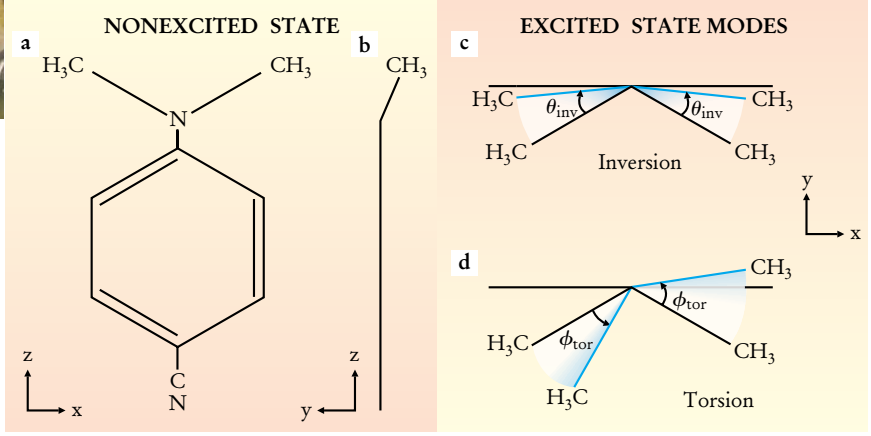
In the two decades since that pioneering experiment, the x-ray pulses produced by synchrotrons have become briefer and more intense, lasers have become faster, and the clocks that synchronize the pumping lasers and the probing x rays have become more precise. Exploiting all those developments, Simone Techert, Friedrich Schotte, and Michael Wulff have used ultrafast x-ray diffraction to follow how an organic molecule changes shape in response to light on a time scale of tens of picoseconds.[1] Measuring such rapid conformational changes is "really a tremendous step forward," says Philip Coppens, who studies laser-generated molecular states at SUNY Buffalo.

Techert's team did its experiment last year at the ID09 station of the European Synchrotron Radiation Facility in Grenoble, France. At that time, Techert was a postdoc at ESRF (she's now at the Max Planck Institute for Biophysical Chemistry in Göttingen) and Schotte was a graduate student at the University of Düsseldorf (he's now at the National Institute of Diabetes and Digestive and Kidney Diseases in Bethesda, Maryland). Wulff developed and directs the ID09 station.

ID09 was built for time-resolved (and high-pressure) studies. After the station's various insertion devices have intensified, filtered, and focused the bunched x-ray beam, a rotating chopper picks out one 150-ps pulse every revolution of the beam, creating a train of pulses separated by 1.1 ms. Keeping track of the x-ray pulses is a so-called bunch clock, which also controls a femtosecond laser. With a timing accuracy of 3 ps, the bunch clock triggers the laser pulses to excite the



▲ **FIGURE 1. EXPERIMENTAL SETUP** at the European Synchrotron Radiation Facility's ID09 station. The thin metal pipe is the x-ray collimator; above it are the laser optics. The goniometer holds the sample (a small purple disk), above which is an optical microscope. The amber disk is a beam stop, which protects the image plate detector behind it from high x-ray fluxes. (Courtesy of Simone Techert.)



▼ **FIGURE 2. THE SHAPE** of *N*,*N*-dimethylaminobenzonitrile ($C_9H_{10}N_2$) changes in response to light. In the nonexcited state, the two methyl groups remain tilted out of the plane of the benzene ring, as shown here from above the molecule (**a**) and from the side (**b**). When the molecule absorbs a photon, the methyl groups undergo both an inversion, in which their out-of-plane tilt decreases (**c**), and a torsion (**d**), in which they twist about the molecule's long axis. (Adapted from ref. 1.)

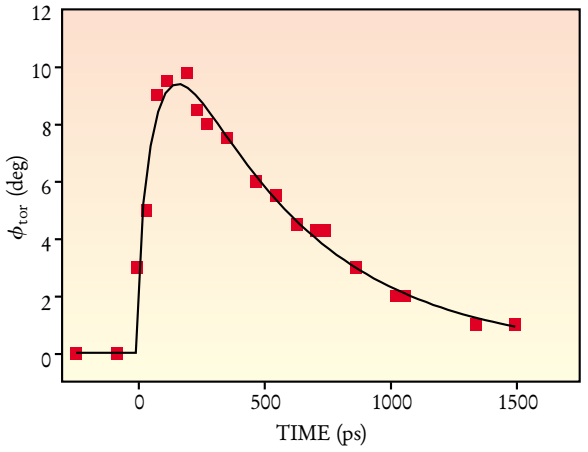


FIGURE 3. AS MEASURED by Techert, Schotte, and Wulff, the torsion angle rapidly attains its maximum value and then decays more slowly. (Adapted from ref. 1.)

sample just before the x-ray pulses arrive to probe it. By varying the delay between the pump and probe pulses, it's possible to watch the sample in various stages of post-excitement relaxation. Standard analysis techniques yield the structural information from the series of diffraction patterns, which are accumulated by a charge-coupled device camera. Figure 1 shows the setup.

The full name of the molecule that Techert chose to work on is *N*, *N*-dimethylaminobenzonitrile ($C_9H_{10}N_2$; see figure 2). Known as DMABN for short, the molecule began to attract the attention of spectroscopists in the 1960s when Ernst Lippert discovered that it fluoresced in two distinct bands in polar solution.

A considerable amount of subsequent work, both experimental and theoretical, has outlined the sequence of events that occurs when a DMABN molecule in solution absorbs a photon. First, the molecule is excited into the S_2 state. Fast internal conversion ensues, and then, with a branching ratio that's thought to be close to unity, the molecule enters a second excited state S_1. Finally, if the surrounding solution is sufficiently polar, DMABN can deexcite further by transferring charge from its $N(CH_3)_2$ amino group to its CN group at the other end of the molecule. In the process—so the prevailing theory goes—the two methyl groups twist 90° about the bond that connects them to the benzene ring.

It was the prospect of observing DMABN's methyls twisting that inspired Techert and her coworkers to do their experiment. Their diffraction measurements reveal exactly how DMABN moves—not in solution, but in its solid state. Following excitation, the two methyl groups rapidly twist about the bond connecting them to the benzene, reaching their maximum torsion angle of 9.5° by 80 ps. Meanwhile, the methyls, which are normally inclined 13° below the plane of DMABN's benzene ring, rise by 10°. By 1500 ps, the two distortions have returned to normal, as shown in figure 3.

Although the charge transfer transition, with its full 90° twist, is off-limits to DMABN in the solid state, some twisting was thought to accompany the S_2 transition, which doesn't require a solution. Indeed, calculations made by Wolfgang Rettig of Berlin's Humboldt University actually predicted some of the behavior observed by Techert's team. "When I read their paper, I was astonished!" says Rettig. "Techert's observation is the first to directly show the degree of twisting and that the molecule becomes less pyramidal."

Klaus Schulten of the University of Illinois at Urbana-Champaign shares Rettig's enthusiasm: "It's great that we now have a report on the observed molecular dynamics of a single organic molecule. For such a simple system, the opportunities for a thorough understanding of the observed dynamics are much better than for an entire protein."

Thanks to its light-induced twisting, DMABN might one day be used as a molecular switch in an optical circuit, but it's only one of many kinds of molecules whose structural response to light can be measured with ultrafast diffraction. The University of Chicago's Keith Moffat believes that "any and all" light-driven systems are fair game, among them the molecules responsible for photosynthesis in plants and vision in animals.

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