analysis of the resulting products showed a marked increase in ultraviolet light absorption associated with the tag.

Although this confirmed that the products of the mechanochemical process were reacting with the chemical trap, it didn't provide information about the structure of those products or about the mechanism that yielded them. To address this problem, the authors labelled the trap molecules with ^{13}C atoms, which can be detected by nuclear magnetic resonance (NMR) spectroscopy. The NMR spectra of the products from both benzocyclobutene isomers showed the same single peak, suggesting that the trap reacts to form identical products regardless of which isomer is used as the starting material. This aberration strongly supports the authors' theory that mechanochemistry can alter reaction pathways and formally break the laws of orbital symmetry.

Although chemists might not immediately rush to adopt this technique, the work is a remarkable first step in using mechanical stress to break bonds in a synthetically useful organic reaction. The applications of polymers in chemistry have come a long way — from the resins that act as supports in solid-phase peptide synthesis[9] to the DNA templates that systematically bring reactants together[10]. In Moore and colleagues' study[1], the role of polymers has evolved further to that of a scaffold, not only encouraging reactions but also moulding the subsequent reaction pathway. The authors have provided a glimpse into a possible future where mechanical deformation, mediated by reactants attached to polymer chains, will allow access to previously unattainable molecules and materials, reducing the need for expensive and often environmentally unfriendly catalysts. ■

Brad M. Rosen and Virgil Percec are in the Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA.
e-mail: percec@sas.upenn.edu

1. Hickenboth, C. R. *et al. Nature* **446,** 423–427 (2007).
2. Kang, J. & Rebek, J. *Nature* **385,** 50–52 (1997).
3. Leung, D., Fiedler, D., Raymond, K. & Bergman, R. G. *Angew. Chem. Int. Edn* **43,** 963–966 (2004).
4. Percec, V. *et al. Nature* **391,** 161–164 (1998).
5. Percec, V., Ahn, C.-H. & Barboiu, B. *J. Am. Chem. Soc.* **119,** 12978–12979 (1997).
6. Beyer, M. K. & Clausen-Schaumann, H. *Chem. Rev.* **105,** 2921–2948 (2005).
7. Beyer, M. K. *J. Chem. Phys.* **112,** 7307–7312 (2000).
8. Woodward, R. & Hoffmann, R. *The Conservation of Orbital Symmetry* (Academic, New York, 1970).
9. Merrifield, R. B. *Angew. Chem. Int. Edn Engl.* **24,** 799–892 (1985).
10. Gartner, Z. J. & Liu, D. R. *J. Am. Chem. Soc.* **123,** 6961–6964 (2001).

ASTEROIDS

Spun in the sun

William F. Bottke

Two asteroids have been observed gradually spinning faster and faster, and the hot tip is that sunlight is the cause. If so, this could give us a handle on the dynamics and evolution of the asteroid belt in general.

"Captain, something is spinning up these asteroids, and there's no way we can stop it!" What might sound like an excerpt from a long-lost episode of *Star Trek* is, in fact, a pretty precise description of a genuine scientific mystery. On page 420 of this issue, Kaasalainen *et al.*[1] show that asteroid (1862) Apollo, a 1,400-metre-diameter near-Earth asteroid (one whose orbit intersects that of Earth), has noticeably increased its rate of rotation over 25 years of observation*. And in papers published in *Science*, Lowry *et al.*[2] and Taylor *et al.*[3] report ground-based optical and radar observations showing that (54509) 2000 PH5, a 114-metre-diameter near-Earth asteroid, is also spinning up.

So what's the cause, if it is not tractor beams or dilithium crystals? The answer, it seems, is sunlight. The measurements might be the first direct detection of a long-hypothesized phenomenon known as the Yarkovsky–O'Keefe–Radzievskii–Paddack (YORP) effect. This is a torque produced when sunlight from an asteroid's surface is reflected and re-emitted at thermal, infrared wavelengths[4,5]. According to the theory, these thermal torques can cause small asteroids to spin up or down with time, the direction and acceleration of the spin being determined by the shape and orientation of each body (Fig. 1). Given enough time, the YORP effect can even flip a body so it ends up spinning in the opposite direction.

The idea that solar radiation can affect asteroid dynamics goes back to the first of the eponymous YORP scientists, Ivan Osipovich Yarkovsky, a Polish civil engineer who worked for a Russian railway company by day, and bent his mind to scientific problems by night[6]. Shortly before his death in 1902, Yarkovsky published a pamphlet describing how infrared heat that was re-radiated away from the surface of an asteroid could provide a small thrust. In much the same manner, ices sublimating to their gaseous state off the surface of a comet create a 'rocket effect' that propels the comet strongly enough to change its orbit. Yarkovsky's effect works much more slowly, mainly because the angular momentum of a body changes more easily when comparatively massive gas and dust are thrown off than when infrared photons are radiated away. Nevertheless, it is now recognized that the thermal forces of the Yarkovsky effect can cause small bodies to drift slowly towards or away from the Sun to an extent determined by their size, the direction of their spin axis and several other parameters[7].

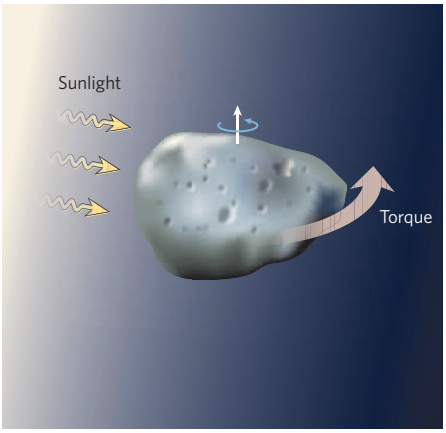

Figure 1 | YORP in action. An unevenly shaped asteroid heating up in sunlight re-radiates the energy away at right angles to its surface. The resultant net torque can both provide a small thrust (the Yarkovsky effect), causing the asteroid to drift towards or away from the Sun, and also change the asteroid's spin rate — the YORP effect, now seemingly observed for the first time[1–3].

After languishing in obscurity for several decades, Yarkovsky's work began to inspire several experiments in the 1970s, which included shining light on centimetre-sized meteoroids in a vacuum chamber[8]. The results seemed to show that sunlight reflecting off an asymmetrical object of asteroid size would not only give it an additional thrust, but also cause it to spin up over geologically short timescales. Objects spinning too fast might even undergo 'rotational bursting', shedding mass to slow themselves down.

The modern pioneer of the YORP effect is David Rubincam, who in 2000 derived the theory of how thermal torques affect real asteroids, and performed numerical simulations[4]. An important conclusion was that asteroids spin up much faster if they have some windmill-like asymmetry. In other words, propeller-shaped asteroids are more affected by YORP than are spheres or ellipsoids.

This brings us back to the contemporary YORP observations[1–3]. As irregularly shaped asteroids turn in space, they reflect different amounts of light to Earth. By carefully measuring how this light changes[1,2] — or, equivalently, how the returned beam strength from a well-aimed radar signal varies[3] — astronomers can determine the body's rotation rate and shape. Such measurements should also allow a prediction of the asteroid's orientation at any time in the future, whether it looks like a flattened

*This article and the paper concerned[1] were published online on 7 March 2007.

skipping stone (like Apollo) or a pulled tooth (like 2000 PH5). But Kaasalainen *et al.*[1] found that, 25 years after the first observations, the long axis of Apollo, around which the asteroid spins once every 3 hours, was 125° ahead of where it should have been. Similarly, Lowry *et al.*[2] and Taylor *et al.*[3] found that the 12-minute-spinner 2000 PH5 was 240° ahead of expectation after only 4 years. YORP theory not only predicts these changes, but it also explains why 2000 PH5, a smaller body more susceptible to thermal forces, was spun up faster.

So why should we care? Collisions among asteroids mean that they are already spinning in many different ways, so what does it matter if thermal radiation adds a few more twists and turns?

One answer is that the YORP effect is more efficient at changing the spin rates of irregularly shaped, kilometre-sized asteroids than are collisional impacts[5]. Indeed, it is so efficient that rotational bursting could well be an important mechanism for creating asteroid satellites both of near-Earth asteroids[9,10] and of asteroids in the main belt between Mars and Jupiter. The presence of a 75-m asteroid in Apollo's tow might well be a case in point. At the other extreme, some asteroids are spun down so far that they lose virtually all of their rotational angular momentum. This provides a firm explanation for how some asteroids enter into tumbling rotation states[5] — for example, (4179) Toutatis, which made a particularly close approach to Earth in September 2004.

A second answer is that the Yarkovsky and YORP effects work together to deliver asteroids and meteoroids to a state of so-called orbital resonance, and thence possibly to Earth[5]. When a small asteroid is created by a collision in the main belt, it immediately begins to drift inwards or outwards as a result of Yarkovsky thermal forces. The body's speed and direction, however, are controlled by the orientation of its spin axis, which is in turn determined by the YORP effect. Given long enough, these bodies will drift into regions where perturbations due to the gravity of the planets, especially those of Jupiter and Saturn, are enhanced. One such region, called a region of mean motion resonance, occurs where the orbital periods of two bodies are in a simple integer ratio. Resonances frequently act as dynamical escape hatches from the asteroid belt and are responsible for continually replenishing the population of near-Earth asteroids.

The distance traversed by fragments from an asteroid break-up can also, if carefully modelled, be used as a clock to determine when the collision took place[5]. Studying the Yarkovsky/YORP evolution could therefore also eventually allow us to explain the precise history of collision events in the asteroid belt over the past several billion years. Finally, the YORP effect can do extremely strange things in tandem with planetary perturbations. For example, consider the Koronis asteroid family: its known prograde-rotating bodies (that is, those spinning in the same direction in which they are moving) all have nearly identical spin rates, and have spin axes that roughly point towards the constellation Cassiopeia[11]. Rather than signifying some message from deep space, however, it seems that these asteroids were captured in special spin states after billions of years of similar YORP-driven evolution[12].

Thus, when it comes to asteroid dynamics, a light touch might be all that is needed to set big changes in motion. Although we may not be any closer to stopping the spinning up of those asteroids, we at least think we understand what's behind it. ■

William F. Bottke is in the Department of Space Studies, Southwest Research Institute, 1050 Walnut Street, Boulder, Colorado 80302, USA.
e-mail: bottke@boulder.swri.edu

1. Kaasalainen, M., Ďurech, J., Warner, B. D., Krugly, Y. N. & Gaftonyuk, N. M. *Nature* **446,** 420–422 (2007).
2. Lowry, S. C. *et al. Science* doi:10.1126/science.1139040 (2007).
3. Taylor, P. A. *et al. Science* doi:10.1126/science.1139038 (2007).
4. Rubincam, D. P. *Icarus* **148,** 2–11 (2000).
5. Bottke, W. F., Vokrouhlický, D., Rubincam, D. P. & Nesvorný, D. *Annu. Rev. Earth Planet. Sci.* **34,** 157–191 (2006).
6. Beekman, G. *J. Hist. Astron.* **37,** 71–86 (2006).
7. Chesley, S. R. *et al. Science* **302,** 1739–1742 (2003).
8. Paddack, S. J. Thesis, Catholic Univ. Am., Washington DC (1973).
9. Ostro, S. J. *et al. Science* **314,** 1276–1280 (2006).
10. Scheeres, D. J. *et al. Science* **314,** 1280–1283 (2006).
11. Slivan, S. M. *Nature* **419,** 49–51 (2002).
12. Vokrouhlický, D., Nesvorný, D. & Bottke, W. F. *Nature* **425,** 147–152 (2003).

ORGANIC CHEMISTRY

Synthesis undressed

John A. Porco Jr

Fragile chemical groups can be shielded from harsh reaction conditions by temporary protection. This approach is conventional wisdom for organic synthesis, but is it always the best solution?

Ask any organic chemist about their worst nightmare, and they'll probably give you the same answer: not being able to remove 'protecting groups'. These handy chemical groups are used to safeguard parts of a molecule that would otherwise be destroyed under the reaction conditions of a synthesis. The final step of a complex synthetic route often involves removing protecting groups to unmask the target compound. But if the wrong groups have been chosen, they might stay stubbornly attached to the molecule — or worse still, the molecule might be destroyed in the attempt to remove them. Years of work are frequently ruined in this way. On page 404 of this issue[1], Baran *et al.* show that complex, naturally occurring compounds can be constructed without using a single protecting group. This approach opens up avenues of research for discovering reactions that harness the intrinsic reactivity of unprotected organic molecules.

Protecting groups are ubiquitous in organic synthesis and often seem essential for performing multi-step sequences of reactions[2,3]. Not surprisingly, chemists have become reliant on these groups to access interesting molecules, especially naturally occurring compounds (generally referred to as natural products) with complex structures that are much loved as targets for synthesis[4]. But each group used adds two additional steps to any given reaction sequence — a protection step, where the groups are attached to the molecule, and a de-protection step, where they are removed. Because several different protecting groups are often used in one molecule, this can greatly decrease

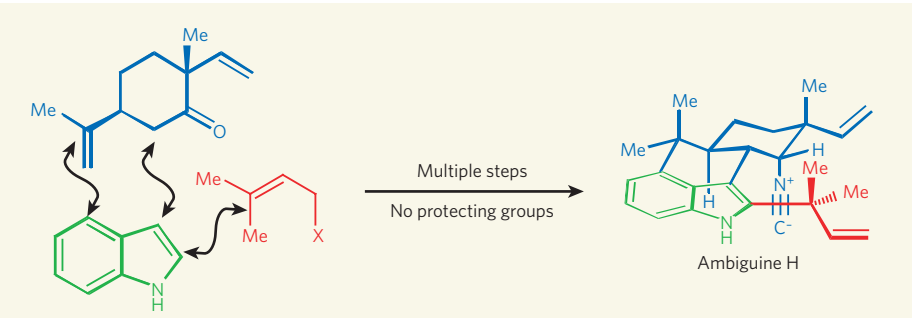

Figure 1 | Synthesis without protection. Baran *et al.*[1] have prepared ambiguine H, a naturally occurring compound originally extracted from marine organisms. Because they used no 'protecting groups' — temporary chemical groups that are attached to fragile parts of the molecule to shield them from destructive reaction conditions — the authors' synthesis is the shortest ever devised for this compound. The molecule is constructed from three fragments: an indole (green), a terpene (blue) and a prenyl unit (red). Curly arrows indicate where bonds are formed between the fragments; Me represents a methyl group (CH_3).