

# Nanotechnology: Molecular wheel within a supramolecular bearing observed!

K. L. Sebastian

In 1959, Nobel Laureate physicist Richard P. Feynman<sup>1</sup> gave a talk at the California Institute of Technology entitled 'There's Plenty of Room at the Bottom'. In it he pointed out that it should be possible to fabricate devices much smaller than the ones that existed and that the possibilities of such molecular-scale engineering were immense. To spur work in this direction, he posed two challenges with \$1,000 prizes attached to them. The first was to construct a working electric motor 1/64 inch or less on a side, and the second to produce written text at 1/25,000 scale in comparison with the normal. This would mean that it would be possible to print the entire *Encyclopedia Britannica* on the head of a pin!

The first challenge turned out to be easier than Feynman thought. The prize was paid in 1960 to an engineer who found a way to construct a very small motor using conventional mechanical techniques. In 1985, Thomas Newman, a Stanford University graduate student, won the other prize. He did the required writing using electron beam lithography.

Now the race is on to produce more and more microscopic machines or to

fabricate molecular devices, which may be used as parts for tiny machines. This new technology has been referred to as nanotechnology by Eric Drexler<sup>2</sup> in his visionary book, *Engines of Creation*. Proponents of nanotechnology believe that eventually one would be able to construct supercomputers which are so small that their total volume would be less than one cm<sup>3</sup> and to make nanorobots that could repair damage inside human cells! The smallest motor in nature that we know of is made of macromolecules. It works with chemical energy<sup>3</sup> and is based on H<sup>+</sup> adenosine triphosphate synthase (an enzyme) and is ~10 nm in size. Nature has provided swimming bacteria with chemically driven flagellar motors, but these are bigger, being ~50 nm.

In an article in *Science*<sup>4</sup>, the authors have demonstrated a 'molecular wheel' of size 1.75 nm. The molecule is hexa-*t*-butyl decacyclene (HB-DC), a propeller-shaped molecule which, when placed on a copper surface at room temperature, would either rotate freely or stay still depending on its contacts with neighbouring molecules. They claim that their experiments 'open the way to fabricate, spatially define, and test the

proposals involving mechanical devices fabricated in molecular structures'.

The molecule HB-DC consists of three naphthalene rings attached to a central benzene ring. Each naphthalene has two *t*-butyl groups attached to it (see Figure 1). Steric interactions between adjacent naphthalene rings distort the molecule and give it the shape of a propeller of diameter 1.75 nm. The molecule was chosen because of its shape and molecular mechanics calculations showed that it has some characteristics needed to produce unidirectional rotation by a 'ratchet and pawl' mechanism.

Gimzewski *et al.*<sup>4</sup> deposited the HB-DC molecules on atomically clean Cu(100) surfaces and visualized them by STM (scanning tunneling microscopy) in ultrahigh vacuum. Because of the twisted shape of the molecules, the aromatic rings are somewhat away from the surface and the molecule is held to the surface by the very weak van der Waals interactions of the hydrogens of the *t*-butyl group with the metal atoms of the surface. Hence at very low coverages, the molecules move freely on the surface. At a monolayer coverage, they formed a two-dimensional crystal. The molecules were immobile and were held in place by van der Waals interactions with their neighbours. The STM pictures then show the images of the *t*-butyl groups as six distinct lobes, surrounding the central core. See the image in Figure 2a, for the molecule whose central core is marked with two concentric circles. Figure 3a gives an enlarged view of the image of just this molecule.

At slightly less than monolayer coverage, there are voids present in the two dimensional crystal lattice. A HB-DC molecule near such a void had enough room around it, making the rotation of the molecule possible. However, the neighbours were not that far that the molecule could move away by diffusion. In such cases, due to the rotation of the molecule, the six *t*-butyl groups were imaged as a smooth torus (see Figures

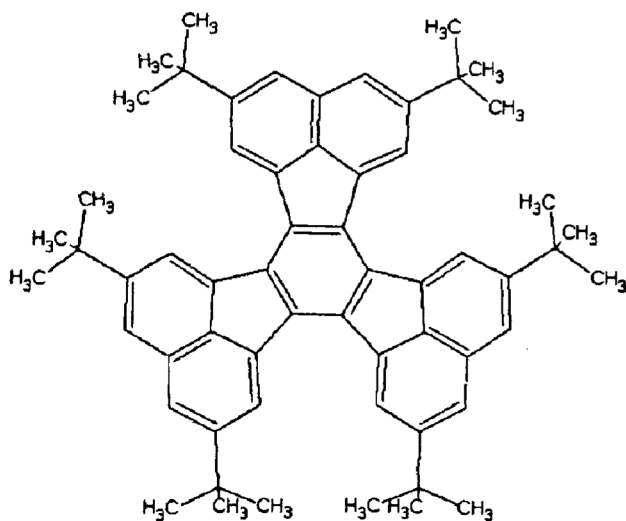
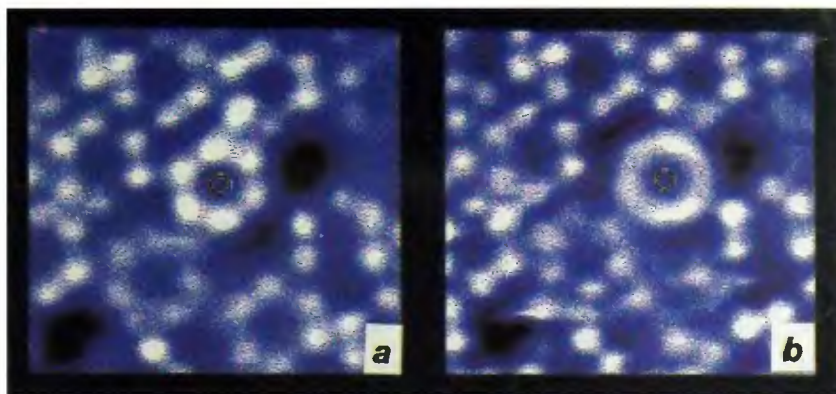
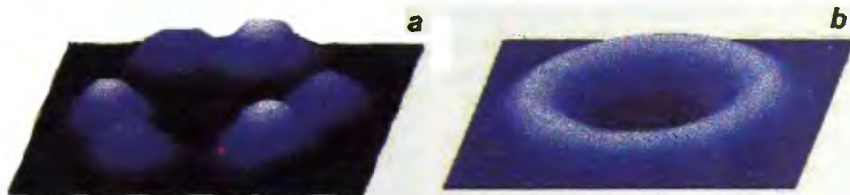


Figure 1. Hexa-*t*-butyl decacyclene (HB-DC) molecule, used in the experiment.



**Figure 2.** The STM image of the surface covered with HB-DC molecules. Compare the images for the molecule whose core is indicated by circles in the two figures (reproduced with permission of IBM Zurich).



**Figure 3.** *a*, STM view of an immobilized molecule which is not rotating; *b*, the torus-like image that results when the molecule rotates (reproduced with permission of IBM Zurich).

2 *b* and 3 *b*) rather than as six distinct lobes around the center of the molecule. The molecule can switch between being held immobile and rotating and back by a movement of only 0.26 nm across the surface. It was found to do so on its own. It is also possible for the experimenter to move it, using the STM tip!

Molecular mechanics calculations indicate that supramolecular interactions of the molecule with its neighbours cause the energy barrier to rotation. While confined by its neighbours, the energy barrier to rotation was 117 kJ/mol. Shifting it out of registry with the lattice by 0.26 nm lowered the barrier to rotation to only 29 kJ/mol.

This barrier is low enough to cause rotation of the molecule by thermal energy, on a time scale faster than can be resolved with their scanning tunneling microscope. The barrier to the 0.26 nm shift was 42 kJ/mol, rationalizing why the molecule could switch slowly between the two states on its own.

Rotors micro-machined from silicon are more than 10,000 times larger in diameter and have limited lifetimes, possibly because they are irregular at the atomic scale. In comparison, the authors claim the HB-DC motor to be wearless. It operates in a dry state. The aim in this kind of work has been to design a molecular motor, which will rotate only in one direction, by a ratchet

and pawl-like mechanism, and to use it as a motor. Computations indicate that the molecular structure of HB-DC is not in a form as to allow rotation only in one direction. Even when the molecular structure has the form, it has not been possible to observe unidirectional rotation<sup>5</sup> if the molecule is kept in a constant temperature bath. This is not surprising because if it did, then we should, in principle, be able to derive work from this rotation and that would violate the second law of thermodynamics! (See the Feynman lectures for a detailed discussion<sup>6</sup>.) So to be a motor, the ratchet should be able to convert energy from some source (heat from a source at a higher temperature, chemical or other forms of energy) into work. Obviously, much further research is required to attain these aims.

1. The full text of the talk is available at the site <http://nano.xerox.com/nanotech/feynman.html>.
2. Drexler, K. E., *Engines of Creation*, Oxford University Press, Oxford, 1990. See also <http://foresight.org/homepage.html>, particularly the news items.
3. Noji, H., Yasuda, R., Yoshida, M. and Kinosita, K. Jr., *Nature*, 1997, 386, 299. See also the commentary by Block, S. M., *Nature*, 1977, 386, 217.
4. Gimzewski, J. K., Schlittler, R. R., Langlais, V., Joachim, C., Tang, H. and Johansson, I., *Science*, 1998, 281, 531–533.
5. Kelly, T. R., Tellitu, I. and Sestelo, J. P., *Angew. Chem. Int. Ed. Engl.*, 1997, 36, 1866. See also commentary on this paper by Davis, A. P., *Angew. Chem. Int. Ed. Engl.*, 1998, 37, 909.
6. Feynman, R. P., Leighton, R. B. and Sands, M., *The Feynman Lectures on Physics*, Addison Wesley Publishing Co., Reading, 1963, vol. 1.

*K. L. Sebastian is in the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India.*