Tilting at Windmills? The Second Law Survives

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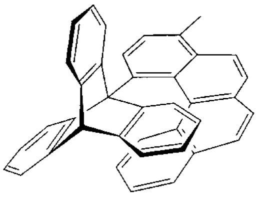
The Second Law of Thermodynamics is surely among the most annoying of scientific principles. In puritan tones it dictates that we cannot do what we would so like to—extract useful work from the vast reservoirs of thermal energy surrounding us at ambient temperature. To counterbalance this stricture, it promises no reward or redemption. Ultimately we are condemned to perish in a sea of bleak uniformity, as entropy pursues its dismal end.[1] Sadly the Second Law seems also to be among the most secure of principles. The notion of a device which breaks it, exhibiting "perpetual motion of the second kind", has long been considered beyond the pale of respectable science, evidence of foolishness and perhaps even quackery.

In this context, it is remarkable and refreshing to see, within the pages of *Angewandte Chemie*, a piece of work that challenges the Second Law in a subtle and elegant fashion. Perhaps wisely, the authors make no explicit reference to the thermodynamic consequences of their experiments. However, their intentions are surely clear. Kelly and co-workers, of Boston College, Massachusetts, designed the molecule **1** as a "molecular ratchet".[2] Its polycyclic structure is largely rigid, but has one degree of internal rotational freedom, about the single bond between the triptycene and benzophenanthrene units. As in the earlier "molecular brake" **2** from this group,[3] rotation about this bond is hindered by interference of the "pawl" with the "spokes" of the triptycene.



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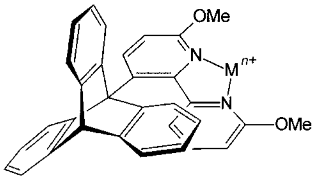

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In the case of **2**, interest was centered on the controllability of the hindrance. In the presence of metal ions (as shown) the brake was "on", while in their absence rotation within the bipyridyl unit minimized its effect, so that the brake was "off". In the case of **1** the focus is on the *asymmetric* nature of the helicene pawl. Because of its chiral, helical structure, its effect on the rotating triptycene depends strongly on the direction of rotation. As the triptycene rotates clockwise (as pictured in **1**), resistance builds up steadily, while for anticlockwise rotation a much steeper barrier intercedes (Figure 1). The situation bears a close resemblance to that in a macroscopic ratchet (Figure 2). For the latter, motion in one direction is effectively prohibited, while motion in the other is relatively free. If the wheel were subjected to small, rapidly varying torques, rotation in the favored direction would presumably accumulate.

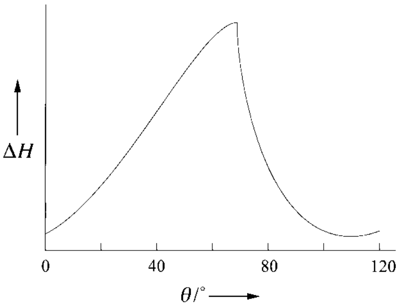

Figure 1. Calculated energy profile (AM 1) for rotation about the helicene-triptycene bond in **1**. Increase in θ refers to clockwise rotation of the triptycene as viewed in the formula.

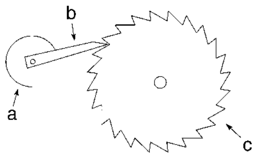

Figure 2. A macroscopic ratchet composed of a) spring, b) pawl, and c) wheel with asymmetric indentations.

So can this macroscopic picture be transferred to the microscopic scale? Will a "molecular ratchet" such as **1**, harboring thermal energy and therefore in constant motion, rotate preferentially in one direction? Before answering that question it is important to consider the consequences of a positive answer. Suppose that a molecular ratchet were linked to a microscopic pulley. If no load is applied to the system it would clearly rotate in one direction. If a very small load were applied this motion would slow, but not stop. The load would be raised, work would be done, and the only source of energy would be the thermal energy of the ratchet (which would cool).[4] The thermal energy could of course be replaced from the environment, so

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that the motion would continue until the environs of the ratchet dropped below a critical temperature.

Less fancifully, the success of a molecular ratchet would imply the possibility of other devices, notably a "one-way membrane". Such a membrane would present asymmetric barriers to the passage of gas or liquid molecules, varying in energy profile depending on the direction of approach ("molecular trap-doors", to draw analogy with the macroscopic world).[5] Molecules would pass through more rapidly in the preferred direction, creating a pressure differential. The differential could be used to drive a turbine to generate electricity, with the thermal motion of the gas again the only source of energy. Although the gas would cool below ambient temperature, resupply of energy from the outside world would not be difficult. Our energy problems would be at an end.

Of course, the Second Law of Thermodynamics says that this cannot be achieved, just as the Principle of Microscopic Reversibility (which is connected to the Second Law through the above arguments) says that the rates of passage across a free energy surface between isoenergetic states must be equal in both directions. Can they be wrong? To determine the directional preference of **1**, Kelly et al. made elegant use of the NMR technique of spin polarization transfer.[6] Rotation of the triptycene is slow on the NMR timescale, so that separate signals are observed for the three aromatic "spokes". By polarizing a signal on one ring, then observing the spectrum after successive delays, the triptycene can be followed in its travels. Rotation with no directional preference results in polarization transfer at equal rates to both other environments. Transfer to just one of the other environments would imply unidirectional rotation, or racemization (a possibility that would then need to be discounted). The answer, sadly, is disappointing but predictable. Rotation occurs in both directions with equal ease, the principle of microscopic reversibility is upheld, and the Second Law survives.

Some would argue that this experiment was misconceived. To challenge the Second Law may be seen as scientific heresy (a nice irony, considering the Jesuit origins of Boston College), and the theoretical arguments against molecular ratchets and trapdoors are well-developed.[4, 5, 7] However, as scientists we should take the view that nothing is sacred, that experimental results outweigh all theoretical considerations, and that it is quite appropriate to revisit old questions as new techniques become available. The Boston College group should be congratulated on their courageous, if perhaps Quixotic, attempt at the "impossible". Wishful thinking will not make the Second Law disappear, but if there is any chance we can escape its deathly grip, surely we should take it.

German version: *Angew. Chem.* **1998**, *110*, 953–954

Keywords: molecular devices · molecular modeling · NMR spectroscopy · thermodynamics · triptycenes

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[1] For alternative (and more authoritative) perspectives on the Second Law, see: P. W. Atkins, *The Second Law: Energy, Chaos and Form*, W. H. Freeman, New York, **1994**, and references therein.

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[4] For a theoretical analysis of a related mechanism, see: R. P. Feynman, R. B. Leighton, M. Sands, *The Feynman Lectures on Physics, Vol. 1*, Addison-Wesley, Reading, MA, USA, **1963**, chap. 46.

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[6] F. W. Dahlquist, K. J. Longmur, R. B. Du Vernet, *J. Magn. Reson.* **1975**, *17*, 406.

[7] For example, Feynman[4] points out that motions at the molecular level are perfectly elastic, and that, at thermal equilibrium, the pawl is in constant motion. When it lifts, rotations can occur in either direction with equal probability.