circular polarization of the incident X-rays, giving an equivalent effect. Even so, with the recent development of the synchrotron radiation technology, we should be able to perform such an experiment.

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1. Chikazumi, S. Physics of Ferromagnetism. (Oxford Univ. Press, 1997).
2. Van Vleck, J. H. The Theory of Electric and Magnetic Susceptibilities, Sec. 59 (Oxford University Press, 1932).
3. Adachi, H., Ino, H. \& Miwa, H. Effect of conduction-electron polarization on the magnetism of hcp samarium metal. Phys. Rev. B 56, 349-354 (1997).
4. Adachi, H., Ino, H. \& Miwa, H. Separation of the 4f-spin, 4f-orbital and conduction-electron magnetization from exotic thermomagnetic behavior of ferromagnetic Sm intermetallics. Phys. Rev. B 59, 11445-11449 (1999).
5. Legvold, S. et al. Magnetic properties of gadolinium-rich alloys. Phys. Rev. B 16, 4986-4989 (1977).
6. Stewart, A. M. The ordered moment of metallic samarium materials. Phys. Status Solidi B 52, K1-K4 (1972).
7. Koehler, W. C. \& Moon, R. M. Magnetic structures of samarium. Phys. Rev. Lett. 29, 1468-1472 (1972).
8. Givord, D., Morin, P. \& Schmitt, D. Unusual form factor in SmZn. Phys. Lett. A 73, 221-223 (1979).
9. Adachi, H. et al. Evidence for positive polarity of the spin moment in hcp Sm determined from a magnetic Compton-scattering experiment. Phys. Rev. B 56, R5744-R5746 (1997).
10. Williams, H. J., Wernick, J. H., Nesbitt, E. A. \& Sherwood, R. C. Magnetic properties of rare earth aluminum compounds with $\mathrm{MgCu}_{2}$ structure. J. Phys. Soc. Jpn 17 (suppl. B-I), 91-95 (1962).
11. Grover, A. K., Malik, S. K., Vijayaraghavan, R. \& Shimizu, K. Hyperfine fields in $\mathrm{Sm}_{1-x} \mathrm{Gd}_{x} \mathrm{Al}_{2}$ alloys-Microscopic evidence for ferromagnetic coupling between rare earth spins. J. Appl. Phys. 50, 7501-7503 (1979).

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# Unidirectional rotary motion in a molecular system 

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The conversion of energy into controlled motion plays an important role in both man-made devices and biological systems. The principles of operation of conventional motors are well established, but the molecular processes used by 'biological motors' such as muscle fibres, flagella and cilia ${ }^{1-9}$ to convert chemical energy into co-ordinated movement remain poorly understood ${ }^{10-12}$. Although 'brownian ratchets ${ }^{\text {'13-16 }}$ are known to permit thermally activated motion in one direction only, the concept of channelling random thermal energy into controlled motion has not yet been extended to the molecular level. Here we describe a molecule that uses chemical energy to activate and bias a thermally induced isomerization reaction, and thereby achieve unidirectional intramolecular rotary motion. The motion consists of a $120^{\circ}$ rotation around a single bond connecting a threebladed subunit to the bulky remainder of the molecule, and unidirectional motion is achieved by reversibly introducing a tether between the two units to energetically favour one of the two possible rotation directions. Although our system does not achieve continuous and fast rotation, the design principles that we have used may prove relevant for a better understanding of biological and synthetic molecular motors producing unidirectional rotary motion.

A range of molecular devices ${ }^{17-23}$, including turnstiles, shuttles and switches, has been synthesized, but a molecule able to produce unidirectional rotary motion has not yet been reported. Our attempts to design a molecular system able to achieve such motion focused on structure 1 (Fig. 1), which consists of two main components: a three-bladed triptycene (the lighter-shaded unit in Fig. 1b) and a [4]helicene (the darker-coloured component in Fig. 1b). The triptycene and helicene are connected by a single bond (shown as a black wedge in 1; Fig. 1a) that functions as an axle. We have previously established ${ }^{24-27}$ that the barrier to rotation $\left(\sim 25 \mathrm{kcal} \mathrm{mol}^{-1}\right)$ of the triptycene around the triptycene/helicene bond in 1 is substantially higher than the barrier to rotation around typical carbon-carbon single bonds $\left(\sim 3-5 \mathrm{kcal} \mathrm{mol}^{-1}\right)$. The helicene in 1 may be regarded as a stiff (but not entirely rigid) pawl that resists deformation and prevents easy rotation. Molecule 1 cannot be looked upon as a molecular ratchet, however, because when thermally stimulated rotation of the triptycene does occur, it occurs in clockwise and anti-clockwise directions to an equal extent ${ }^{24,25}$. The helicene in 1 might best be pictured as a friction brake ${ }^{28}$ that inhibits, but does not completely prevent, spontaneous rotation of the triptycene.

The essence of achieving unidirectional rotation with a molecular system based on the structure of $\mathbf{1}$ involves continuing the frictionbraking action to prevent anti-clockwise rotation, while using the chemical energy of carbonyl dichloride to lower the energy barrier of this system against clockwise rotation, thereby selectively fostering formally induced clockwise rotation of the triptycene. The unidirectional rotation derives ultimately from the asymmetric skew of the helicene and the use of a monosubstituted triptycene, which result in non-identical energy surfaces for clockwise and anticlockwise rotation. To us, the function of the carbonyl dichloride is reminiscent of that of another energy-rich molecule, ATP, which powers many biological motors.

The thermodynamics of the design are presented in detail in Fig. 2. The basic strategy was to start with a molecule related to 1 , which has a rotational energy barrier of $\sim 25 \mathrm{kcal} \mathrm{mol}^{-1}$ (see Fig. 2b) but can be trapped (schematically represented by a 'brick wall' in Fig. 2d) somewhat above the rotational ground state by using a chemical reaction powered by carbonyl dichloride. The chemically trapped species is therefore energetically closer (compare Fig. 2d


Figure 1 Compound 1, a triptycy|[4]helicene. a, Chemical structure. b, Stereo view of a calculated electron-density surface map of the lowest-energy conformation of $\mathbf{1}$ using the Spartan (see below) version of the AM1 semi-empirical molecular modelling program. The triptycene is shown in lighter tones, the helicene in darker tones. The calculated barrier to rotation $\left(\Delta H^{+}=22 \mathrm{kcal} \mathrm{mol}^{-1}\right)$ around the triptycene/helicene bond in $\mathbf{1}$-calculated using version 4.0 (1995) of the Spartan software (Wavefunction Inc., Irvine, California, USA) -is in good agreement with the experimentally determined value ${ }^{25}$ $\left(\Delta G^{+}=25 \mathrm{kcal} \mathrm{mol}^{-1}\right)$.
with $2 b$ ) to the rotation barrier and requires relatively smaller amounts of thermal activation to reach the summit of the rotational energy barrier. Once the system has reached the summit (Fig. 2e), further rotation brings it into the second rotational ground state (Fig. 2f) and releases $25 \mathrm{kcal} \mathrm{mol}^{-1}$. This energy immediately diffuses through the system, and thus is not directly available to drive the more energy-intensive reverse reaction (which requires $25 \mathrm{kcal} \mathrm{mol}^{-1}$, in contrast to the less energy demanding forward process from the state shown in Fig. 2d to that in Fig. 2f). Put


Figure 2 Schematic representation of the concepts underlying the design of the system. a, Energy diagram representing $240^{\circ}$ of rotation around the triptycene/helicene bond (black wedge in $\mathbf{1}$ ), with a barrier of $\sim 25 \mathrm{kcal}^{\text {mol }}{ }^{-1}$. $\mathbf{b}$, At any given time a single molecule (represented by the filled black circle) will usually exist in a low-energy conformation such as $\sim 120^{\circ}\left(=\sim 0^{\circ}\right.$ and $\sim 240^{\circ}$ because of the three-fold symmetry of the triptycene) around the triptycene/helicene bond. $\mathbf{c}$, Within a very brief time span, random thermal energy temporarily elevates all individual molecules to conformationally excited states (for example, $t_{1 / 2}$ for thermally exciting molecules $10 \mathrm{kcal}_{\mathrm{mol}}{ }^{-1}$ above ground state at $25^{\circ} \mathrm{C}$ is $2.3 \times 10^{-6} \mathrm{~s}$ ). d, Conformationally excited rotamers in $\mathbf{c}$ are trapped, and prevented from rotating back to a lower-energy conformation. e, The trapped molecules are propelled by the random thermal energy to the top of the energy barrier (at energy $E_{\text {act }}$ (reversion to the position in $\mathbf{d}$-but not $\mathbf{b}$-is possible, but readily reversible). f, Descent from the summit in $\mathbf{e}$ to the next energy minimum is easy and virtually irreversible (because the reverse reaction $(\mathbf{f} \rightarrow \mathbf{e})$ has an energy requirement of $+25 \mathrm{kcal}^{\mathrm{mol}}{ }^{-1}$, which is effectively inaccessible $\left(\mathrm{t}_{1 / 2}\right.$ for achieving $+25 \mathrm{kcal}^{\mathrm{mol}}{ }^{-1}$ is 63.2 h at $25^{\circ} \mathrm{C}$ ).
another way, the states shown in Fig. 2 b and f are isoenergetic, and the rates of the $\mathrm{b} \rightarrow \mathrm{f}$ and $\mathrm{f} \rightarrow \mathrm{b}$ conversions will be identical; but by using the chemical energy of carbonyl dichloride to trap (Fig. 2d) the molecule as shown in Fig. 2c, the transformation $c \rightarrow f$ is exoergic, and unidirectional rotation is driven by the negative change in free energy for the $\mathrm{c} \rightarrow \mathrm{f}$ transformation.

Figure 3 provides molecular detail for the concepts outlined in Fig. 2. The demonstration of controlled rotary motion starts with 2 (the synthesis and characterization of all compounds will be reported elsewhere). Compound 2 is one of three low-energy rotational isomers (rotamers) about the axle connecting the triptycene and helicene components ( 7 is a second low-energy rotamer). Rotamer $\mathbf{2}$ is activated by reaction with carbonyl dichloride to give the isocyanate $\mathbf{3}$ via a carbamoyl chloride. Isocyanate $\mathbf{3}$ is chemically prepared to react with the OH group in the hydroxypropyl tether attached to the helicene, but in the rotational ground state 3, the isocyanate and the OH group are too far apart to interact. However, at those instants when a clockwise rotation of the triptycene (not possible with a comparable anti-clockwise rotation because an anticlockwise rotation would bring the reactants further apart and prevent the essential urethane formation) brings the isocyanate and the OH group sufficiently close to react (see $\mathbf{4}$ ), urethane formation $(\rightarrow \mathbf{5})$ can then result, irreversibly trapping the triptycene in a relatively high-energy (compared with 3; also see Fig. 2d versus b) conformation around the triptycene/helicene axle. Ambient thermal energy then drives the exoergic unidirectional rotation from 5 to 6 (in contrast, but as expected, the control experiment involving


8


9


Figure $\mathbf{4}$ Molecules $\mathbf{8 , 9}$ and $\mathbf{1 0}$, referred to in the text and in Fig. 5 .

2
3
4
(corresponds to Fig. 2c)
urethane
formation


7


6


5
(corresponds to Fig. 2d)
Figure $\mathbf{3}$ Sequence of events in the chemically powered rotation of $\mathbf{2}$ to $\mathbf{7}$. See text for discussion. Although $\mathbf{2}$ and $\mathbf{3}$ are not identical, to a first approximation they both
conceptually correspond to Fig. 2b. Compounds $\mathbf{4}$ and $\mathbf{5}$ correspond to Fig. 2 c and d, respectively; compounds $\mathbf{6}$ and $\mathbf{7}$ both correspond roughly to Fig. $2 f$.


Figure 5 Spectroscopic evidence that carbonyl dichloride fuels the unidirectional rotation of 2. Partial ${ }^{1} \mathrm{H}$ NMR spectra (monitoring the bridgehead proton relative to $\left(\mathrm{CH}_{3}\right)_{4} \mathrm{Si}=0$ p.p.m.) indicate the sequence of events as a function of time. Numbers next to peaks in the spectra refer to structures in Fig. 3. a, $\mathbf{2}$ in $\mathrm{CDCl}_{3} ; \mathbf{b}, t_{0}$; addition of $\mathrm{Cl}_{2} \mathrm{C}=0$ and $\mathrm{Et}_{3} \mathrm{~N}$. $\mathbf{2}$ is rapidly converted to intramolecular urethane $\mathbf{5}$ via isocyanate $\mathbf{3}$; the isocyanates $\mathbf{3}$ and $\mathbf{4}$ convert to $\mathbf{5}$ too rapidly to be seen in the spectra. c, After 1.6 h at ambient temperature $\left(\sim 22^{\circ} \mathrm{C}\right), \sim 30 \%$ of $\mathbf{5}$ has rotated "over the hump" (Fig. 2d to Fig. 2f) to $\mathbf{6}$. d, e, $\mathbf{f}$, Over further time, rotation of $\mathbf{5}$ to $\mathbf{6}$ continues, with unidirectional conversion of $\mathbf{5}$ to $\mathbf{6}$ being $>80 \%$ complete in $\sim 6 \mathrm{~h}$. Urethane $\mathbf{6}$ was isolated and shown to be identical to material prepared directly from amine rotamer $\mathbf{7}$ by reaction with $\mathrm{Cl}_{2} \mathrm{C}=0 / \mathrm{Et}_{3} \mathrm{~N}$. Control experiments established that $\mathbf{6}$ does not convert to $\mathbf{5}$; that is, that the conversion of $\mathbf{5} \rightarrow \mathbf{6}$ is unidirectional. The assignment of structures to $\mathbf{3 - 6}$ is corroborated by infrared spectroscopic monitoring of the relevant reactions of 2,7 and $\mathbf{9}$ with $\mathrm{Cl}_{2} \mathrm{C}=0 / \mathrm{NEt}_{3}$ (and also $\mathbf{1 0}$ in the case of $\mathbf{9}$ ), performed using ReactIR technology (ASI Applied Systems, Millersville, Maryland, USA); this equipment makes it possible to record in situ, and in real time, the infrared spectra of reaction mixtures and to thereby assay functional group changes as they occur.
treatment of $\mathbf{7}$ with $\mathrm{Cl}_{2} \mathrm{C}=\mathrm{O} / \mathrm{Et}_{3} \mathrm{~N}$ leads rapidly to $\mathbf{6}$, but $\mathbf{6}$ does not detectably convert to 5). Finally, 6 is cleaved to give 7, thereby completing the chemically driven rotation of 2 to 7 . Control experiments demonstrate that in the absence of $\mathrm{Cl} 2 \mathrm{C}=\mathrm{O} / \mathrm{Et}_{3} \mathrm{~N}$, pure 2 slowly converts (over several days) to an approximately 1:0.8:1 equilibrium mixture of 2,7 and 8 (the third low-energy rotamer: see Fig. 4). In Fig. 5 we show the experimental data which establish that the events in Fig. 3 proceed as indicated.

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1. Rayment, I. et al. Structure of the actin-myosin complex and its implications for muscle contraction. Science 261, 58-65 (1993).
2. Abrahams, J. P., Leslie, A. G. W., Lutter, R. \& Walker, J. E. Structure at $2.8 \AA$ resolution of $F_{1}$-ATPase from bovine heart mitochondria. Nature 370, 621-628 (1994).
3. Dominguez, R., Freyzon, Y., Trybus, K. M. \& Cohen, C. Crystal structure of a vertebrate smooth muscle myosin motor domain and its complex with the essential light chain: visualization of the prepower stroke state. Cell 94, 559-571 (1998).
4. Block, S. M. Real engines of creation. Nature 386, 217-219 (1997).
5. Noji, H., Yasuda, R., Yoshida, M. \& Kinoshita, K. Jr Direct observation of the rotation of $F_{1}$-ATPase.

Nature 386, 299-302 (1997).
6. Boyer, P. D. The ATP synthase-a splendid molecular machine. Annu. Rev. Biochem. 66, 717-749 (1997).
7. Shingyoji, C., Higuchi, H., Yoshimura, M., Katayama, E. \& Yanagida, T. Dynein arms are oscillating force generators. Nature 393, 711-714 (1998).
8. Berg, H. C. Keeping up with $\mathrm{F}_{1}$-ATPase. Nature 394, 324-325 (1998).
9. Vale, R. D. \& Oosawa, F. Protein motors and Maxwell's demons: does mechanochemical transduction involve a thermal ratchet? Adv. Biophys. 26, 97-134 (1990).
10. Stryer, L. in Biochemistry Ch. 15, 4th edn (W. H. Freeman, New York, 1995).
11. Howard, J. Molecular motors: structural adaptations to cellular functions. Nature 389, 561-567 (1997).
12. Huxley, A. How molecular motors work in muscle. Nature 391, 239-240 (1998).
13. Faucheux, L. P., Bourdieu, L. S., Kaplan, P. D. \& Libchaber, A. J. Optical thermal ratchet. Phys. Rev. Lett. 74, 1504-1507 (1995).
14. Travis, J. Making light work of Brownian motion. Science 267, 1593-1594 (1995).
15. Astumian, R. D. Thermodynamics and kinetics of Brownian motion. Science 276, 917-922 (1997).
16. Rousselet, J., Salome, L., Ajdari,k A. \& Prost, J. Directed motion of brownian particles induced by a periodic asymmetric potential. Nature 370, 446-448 (1994).
17. Mislow, K. Molecular machinery in organic chemistry. Chemtracts—Org. Chem. 2, 151-174 (1989).
18. Bedard, T. C. \& Moore, J. S. Design and synthesis of molecular turnstiles. J. Am. Chem. Soc. 117, 10662-10671 (1995).
19. Balzani, V., Gomez-Lopez, M. \& Stoddard, J. F. Molecular machines. Acc. Chem. Res. 31, 405-414 (1998).
20. Sauvage, J.-P. Transition metal-containing rotaxanes and catenanes in motion: toward molecular machines and motors. Acc. Chem. Res. 31, 611-619 (1998).
21. Bissell, R. A., Cordova, E., Kaifer, A. \& Stoddart, J. F. A chemically and electrochemically switchable molecular shuttle. Nature 369, 133-137 (1994).
22. Benniston, A. C. \& Harriman, A. A light-induced molecular shuttle based on a [2]rotaxane-derived triad. Angew. Chem. Int. Edn. Engl. 32, 1459-1461 (1993).
23. Mao, C., Sun, W., Shen, Z. \& Seeman, N. C. A nanomechanical device based on the B-Z transition of DNA. Nature 397, 144-146 (1999).
24. Kelly, T. R., Tellitu, I. \& Sestelo, J. P. In search of molecular ratchets. Angew. Chem. Int. Edn. Engl. 36, 1866-1868 (1997).
25. Kelly, T. R., Sestelo, J. P. \& Tellitu, I. New molecular devices: in search of a molecular ratchet. J. Org. Chem. 63, 3655-3665 (1998).
26. Davis, A. P. Tilting at windmills? The second law survives. Angew. Chem. Int. Edn. Engl. 37, 909-910 (1998).
27. Musser, G. Taming Maxwell's demon. Sci. Am. 280, 24 (1999).
28. Kelly, T. R. et al. A molecular brake. J. Am. Chem. Soc. 116, 3657-3658 (1994).

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## Light-driven monodirectional molecular rotor

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Attempts to fabricate mechanical devices on the molecular level ${ }^{1,2}$ have yielded analogues of rotors ${ }^{3}$, gears ${ }^{4}$, switches ${ }^{5}$, shuttles ${ }^{6,7}$, turnstiles ${ }^{8}$ and ratchets ${ }^{9}$. Molecular motors, however, have not yet been made, even though they are common in biological systems ${ }^{10}$. Rotary motion as such has been induced in interlocked systems ${ }^{11-13}$ and directly visualized for single molecules ${ }^{14}$, but the controlled conversion of energy into unidirectional rotary motion has remained difficult to achieve. Here we report repetitive, monodirectional rotation around a central carbon-carbon double bond in a chiral, helical alkene, with each $360^{\circ}$ rotation involving four discrete isomerization steps activated by ultraviolet light or a change in the temperature of the system. We find that

