Light-Driven Molecular Rotor: Unidirectional Rotation Controlled by a Single Stereogenic Center

Nagatoshi Koumura, Edzard M. Geertsema, Auke Meetsma, and Ben L. Feringa*

Department of Organic and Molecular Inorganic Chemistry, Strating Institute, University of Groningen, Nijenborgh 4
9747 AG Groningen, The Netherlands

Received July 26, 2000

Controlled motion by the conversion of chemical energy into mechanical energy is a key feature of living organisms and recent studies on biomolecular motors not only revealed fascinating structures and functions but also offered a formidable challenge for the bottom-up construction of molecular motors. A number of systems have been designed in which movement or change in shape occurs in response to external-chemical, electrochemical, or photochemical stimuli. Recently Kelly et al. and Harada, Feringa, and co-workers reported the first examples of unidirectional rotary motion in molecular type motors. In our initial design, helical shaped overcrowded alkenes (biphenanthrylidenes), featuring identical chiral upper and lower halves, were used. Two photochemical cis-trans isomerizations are each followed by a thermal irreversible helix inversion and the 4-step cycle completes a full 360° rotation process. We envisioned that in the next stage toward molecular machinery the construction of rotor type molecules with distinct upper and lower halves as well as tuning of the helix inversion steps by structural modifications had to be addressed.

Here we wish to report a second generation of unidirectional light-driven molecular rotors, the adjustment of the thermal isomerization barriers, and the remarkable finding that the presence of a single stereogenic center is sufficient to control unidirectional rotary motion.

The new type of molecular rotor contains a chiral 2-methyl-2,3-dihydrothiopyran upper part and a (thio)xanthene lower part. The overcrowded alkenes were prepared by diazo-thioketone coupling and a subsequent desulfiturization using copper powder. Trans-1 and cis-2 were separated by HPLC on silica gel (hexane: EtOAc = 50:1) and detailed 1H NMR analysis, molecular modeling studies, and X-ray analysis of trans-1 (Figure 1) resulted in the assignment of the geometrical isomers11 and revealed the preferred conformation of the molecules. In particular the coupling constants of H(2') and H(3') of 7.3 and 2.9 Hz (trans-1) and 7.3 and 3.3 Hz (cis-2), respectively, prove that the methyl groups at the 2'-position of both isomers adopt a pseudo axial orientation.

Enantiomeresolution of both isomers was independently achieved by chiral HPLC (Chiralpak OD, heptane:2-propanol = 99:1). The absolute configuration of [CD]-2772-trans-olefin 1 was unequivocally determined to be (2'R)-M by X-ray diffraction (Figure 1). The CD spectrum of (2'R)-(M)-trans-1 exhibits intense Cotton effects (Figure 2).12

Irradiation of (2'R)-(M)-trans-1 in n-hexane at 365 nm and 10°C resulted in the formation of (2'R)-(P)-cis-4, with the methyl group at the 2'-position adopting an equatorial orientation as determined by 1H NMR. A (2'R)-(P)-(cis-4 to (2'R)-(M)-trans-1 ratio of 86:14 was observed. This photochemical cis-trans isomerization induced an M to P helicity inversion which was detected by CD measurement (Figure 2, trace A to B). When the temperature of the solution of (2'R)-(P)-cis-4 was raised to 60 °C, a complete conversion to (2'R)-(M)-cis-2 was observed and the concomitant change in CD absorption showed the helix reversal, from P to M helicity, associated with this thermal interconversion (Figure 2, trace B to C). Subsequent irradiation of (2'R)-(M)-cis-2 in n-hexane at 365 nm resulted in formation of (2'R)-(P)-trans-3 with the methyl group at the 2'-position again in an equatorial orientation as determined by 1H NMR. A (2'R)-(P)-trans-3 to (2'R)-(M)-cis-2 ratio of 89:11 was observed and the change in CD absorption that accompanies this photochemical cis to trans isomerization is due to simultaneous M to P helicity reversals (Figure 2, trace C to D). When the temperature of the solution of (2'R)-(P)-trans-3 was increased to 60 °C, a complete conversion to (2'R)-(M)-trans-1 was observed and the CD absorption again changed sign (Figure 2, trace D to A). The inset of Figure 2 shows the change of ∆ε value at 272 nm as monitored during these three full cycles clearly demonstrating the repetitive nature of the rotary motion that can be induced.16 The X-ray structural analysis of (2'R)-(P)-trans-3 confirmed that the methyl group at the 2'-position adopts an equatorial


Published on Web 11/11/2000

10.1021/ja002755b CCC: $19.00 © 2000 American Chemical Society
unidirectional rotation is induced in the system. Compared to the wavelength (365 nm) and temperature (60 °C), a continuous adopted the more favorable axial orientation and the reverse original molecular rotor, based on biphenanthrylidenes, it is rotation pathway is effectively blocked. At the appropriate (R generating the more stable isomers {(2´ R)} chemical step is followed by an energetically downhill process isomers {(2´ P)} around the central double bond and generate the less stable R process that is observed starting with (2´ P). Inset, changes in Δε value during a full rotation cycle monitored at 272 nm.

Figure 3. PLUTO drawing of racemic (2´ R*)-(P*)-trans-3.

orientation in accordance with the results of the 1H NMR study (Figure 3).

Scheme 1 shows the different stereoisomers and the dynamic processes that are observed starting with (2´ R)-(M)-trans-1. The experimental results show that the upper naphthothiopyran moiety undergoes a full 360° rotation in a counterclockwise sense relative to the lower thioxanthene part. Two photochemical conversions, which are both energetically uphill processes, induce rotations around the central double bond and generate the less stable isomers (2´ R)-(P)-cis-4 and (2´ R)-(P)-trans-3. Each photochemical step is followed by an energetically downhill process generating the more stable isomers (2´ R)-(M)-cis-2 and (2´ R)-(M)-trans-1. In the two thermal steps the 2´-methyl-substituent adopts the more favorable axial orientation and the reverse rotation pathway is effectively blocked. At the appropriate wavelength (365 nm) and temperature (60 °C), a continuous unidirectional rotation is induced in the system. Compared to the original molecular rotor, based on biphenanthrylidenes, it is remarkable that the presence of a single stereogenic center (C(2´)) is a sufficient condition to accomplish unidirectional rotation.

(16) After three cycles a mixture of trans-1-cis-2 with a ratio of 6/4 is observed due to the photoequilibria. However, this does not affect the repetitive unidirectional behavior of the molecules and each photochemical and thermal step still implies a helix inversion.

The rotation rate is governed by the activation energy of the two thermal isomerization steps. To tune the activation energies of the thermal pathways three related molecules 5, 7, and 9, which have different lower parts, were synthesized. Irradiation of toluene-δ6 solutions of olefins 5 and 7, which have symmetric thioxanthene lower parts, resulted in the formation of unstable forms 6 (ratio 5:6 = 8:92) and 8 (ratio 7:8 = 13:87), respectively, with the methyl group at the 2´-position adopting an equatorial orientation. Irradiation of 9, with a symmetric xanthene lower part, yielded the unstable form 10 with an equatorial methyl group in a 23:77 ratio. Since these molecules have symmetric lower parts, heating of the unstable forms 6, 8, and 10 resulted in complete conversion to their respective starting olefins 5, 7, and 9. 1H NMR studies in the range 35-65 °C revealed first-order kinetics for the conversions of 6 to 5 and 8 to 7, and Δε values of 24.9 and 24.2 kcal/mol were found, respectively. These results show that methoxy substituents (R1, R3 = OCH3) at the lower half of the molecule do not influence the activation energy drastically and compared to the biphenanthrylidene molecular rotor we succeeded in lowering the thermal barrier by approximately 1.5 kcal/mol. A further decrease of the thermal barrier for helix inversion by 2 kcal/mol was achieved with 9 featuring a xanthene lower part. The activation energy of 22.7 kcal/mol, found for the conversion of 10 to 9, implies that changing the bridging heteroatom X at the lower part from sulfur to oxygen reduces the steric hindrance in the “fjord region” of the molecule resulting in more favorable thermal helix inversion steps (Scheme 1).

In conclusion a new type of molecular motor with a distinct upper and lower half—a feature essential for coupling the rotor unit to e.g. a surface—showing unidirectional rotation controlled by a single stereocenter was developed. Relative to the bottom part (the stator) the upper propeller unit undergoes a repetitive 360° rotation in four distinct steps with light of the appropriate wavelength and it was shown that the energy barriers for the thermal steps in the rotary motion can be adjusted by structural modification.

Acknowledgment. We thank M. van Gelder for carrying out HPLC separations. Financial support from the Netherlands Foundation for Scientific Research is gratefully acknowledged.

Supporting Information Available: Experimental details and X-ray structural information (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA002755B