Light-Driven Molecular Hinge: A New Molecular Machine Showing a Light-Intensity-Dependent Photoresponse that Utilizes the Trans–Cis Isomerization of Azobenzene
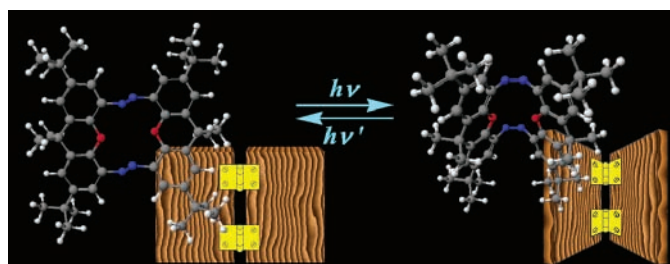
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ABSTRACT

A new class of molecular machine exhibits a hingelike motion upon photoirradiation. The motion (close and open) can be operated by alternate irradiation with UV and visible light. The trans/trans and cis/cis isomers are thermally stable at 40 °C, and the photochemical closure reaction (from trans/trans to cis/cis isomer) is dependent on the intensity of the light used because of the short-lived intermediate (trans/cis isomer).

Controlling the motion and reactivity of photoreactive molecules is a major challenge for photochemists, who have developed many kinds of molecular machines and switches whose motion can be induced by light.[1] Trans−cis isomerization of azobenzene has been the basis for many functional molecules[2] and materials[3] with applications in photonics and data storage in various media.

In this paper, we describe a new class of molecular machine that has a hingelike motion, so-called "light-driven molecular hinges".[4] The characteristic structure of a hinge is two planes that are connected at their edges through an axis; the motion of the hinge allows a transformation between open and closed states. When two hinges connect the two rigid planes, efficient motion of the hinges must occur in a cooperative manner; i.e., a configuration in which one hinge is open and another is closed either will not exist or will be very unstable. To the best of our knowledge, molecules that

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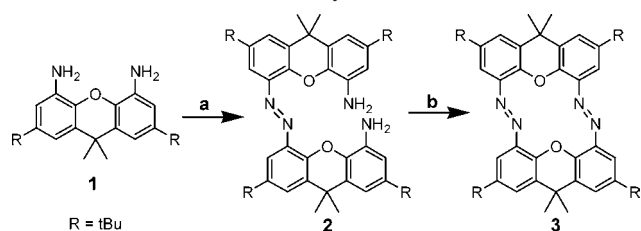
operate with a hingelike motion upon irradiation with light have not been reported previously. The molecular motion in our system is induced by photochemical trans−cis isomerization of azobenzene units; cooperative effects and ring strain restrict the molecular motion.

Scheme 1 presents the structure of molecular hinge **3** and the synthetic route we used for its preparation. The two xanthene rings in **3** are connected by two −N═N− linkers that act as hinges. By heating **1**[5] and MnO$_2$ in benzene under reflux, we did not obtain **3** directly but instead isolated **2**. The ring closure reaction from **2** to **3** was achieved using tBuOK in DMSO/tBuOH (4:1, v/v) under an atmosphere of dry oxygen. This stepwise reaction sequence avoids the formation of polymers.

Figure 1 displays the structures of the trans/trans (**3**tt) and cis/cis (**3**cc) isomers of **3** that were optimized using AM1
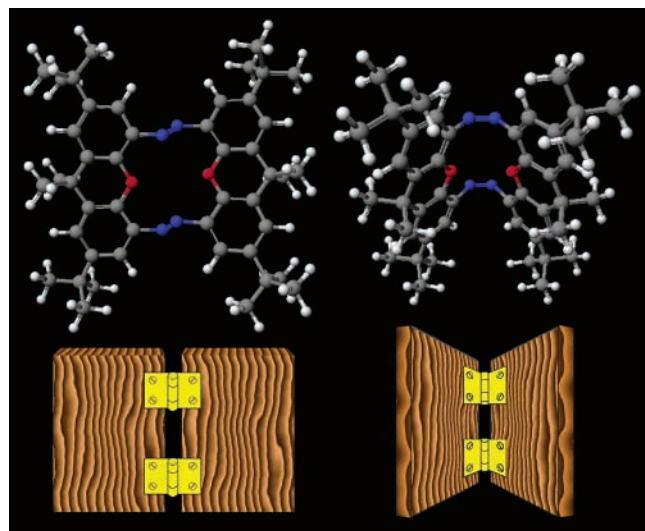
Figure 1. Molecular structures of **3**tt (left) and **3**cc (right), optimized by AM1 calculations (top), and graphical representations of these two isomers (bottom).

calculations. When both of the azobenzene units are in trans configurations (**3**tt), the two xanthene rings are almost coplanar and the overall molecular shape is flat. In **3**cc,
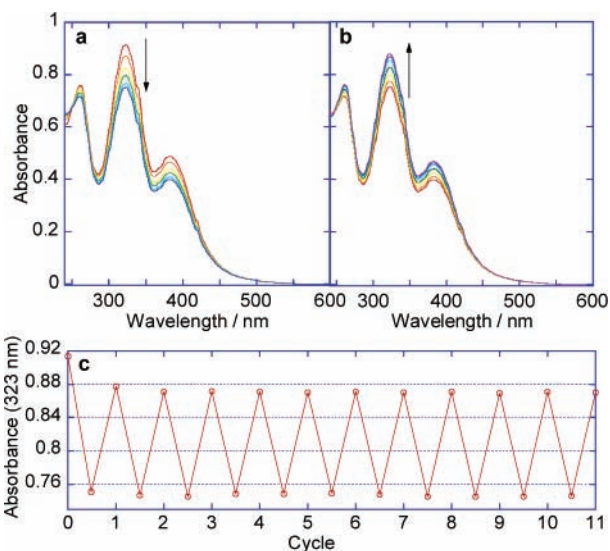
Figure 2. Changes in the absorption spectra of **3** in chloroform upon irradiation at (a) 366 and (b) 436 nm. (c) Absorption changes observed at 323 nm after alternating irradiations at 366 nm (half integers) and 436 nm (integers) over 11 complete cycles.

however, the two xanthene planes are nearly perpendicular to one another. Structure **3**cc seems to be quite thermally robust because the two −N═N− bridges act cooperatively to stabilize the configuration. On the other hand, the trans/cis isomer (**3**tc; structure not shown) seems to have significantly more ring strain than the other two isomers, and the result is that **3**tc is expected to be thermally unstable and have a relatively short lifetime.

Figure 2a presents the absorption spectrum of **3**tt; the absorption maxima (λ_{max}) occur at 383, 323, and 261 nm (ϵ = 14 300, 26 900, and 21 900 M^{-1} cm^{-1}, respectively). The spectrum is different from that of azobenzene[6] itself, which exhibits absorption maxima at 444 nm ($n{\rightarrow}\pi^*$, ϵ = 440 M^{-1} cm^{-1}) and 316 nm ($\pi{\rightarrow}\pi^*$, ϵ = 22 000 M^{-1} cm^{-1}). Presumably, the $n{\rightarrow}\pi^*$ band of **3**tt overlaps with the tail of the band at 383 nm. Upon irradiation of a chloroform solution of **3**tt at 366 nm, the intensity of absorption spectra decreases, as indicated in Figure 2a. On the other hand, we observed recovery of the absorption intensity upon irradiation at 436 nm (Figure 2b). By alternating irradiations at 366 and 436 nm, we verified that the photochemical processes are highly reproducible over more than 10 cycles (Figure 2c). To confirm the formation of the isomer of **3**cc, we measured ^{1}H NMR spectra after irradiation at 366 nm. Two new signals of equal intensity for aromatic protons appear at 6.97 (d, J = 2.2 Hz) and 6.48 ppm (d, J = 2.2 Hz) alongside the initial peaks for **3**tt appearing at 7.79 (d, J = 2.3 Hz) and 7.52 ppm (d, J = 2.3 Hz). It is reasonable to assign the two new peaks to the aromatic protons of **3**cc because the signals of

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aromatic protons of azobenzene units generally shift to higher magnetic fields upon their isomerization from trans to cis configurations,[7] as a result of the magnetic shielding effect of aromatic rings, which face each other to a greater extent in *cis*-azobenzenes.

To investigate the thermal isomerization of **3cc**, a chloroform solution of **3** was kept in the dark at 40 °C after irradiation at 366 nm. The absorption spectra did not change during the next 2 weeks, which indicates that thermal isomerization from **3cc** to **3tc**, or to **3tt**, barely occurs. To explain this stability of the **3cc** isomer, the heats of formation of the three isomers were estimated by ab initio quantum chemical calculations. The HF/6-31G* method[8] was used, and the geometries were fully optimized. The results show that **3tt** and **3cc** are 28 and 2.6 kcal mol^{-1} more stable than **3tc**, respectively. An experimental study on the heat of combustion of trans- and *cis*-azobenzene showed that *trans*-azobenzene is about 10 kcal mol^{-1} more stable than *cis*-azobenzene.[9] The extraordinarily large energy difference between **3tt** and **3tc** indicates that **3tc** is destabilized due to the ring strain, which prohibits the thermal isomerization from **3cc** to **3tc**. A further study on calculation of the energy of the transition state is on the way to explain sufficiently the thermal stability of **3cc**.

To observe the short-lived species, **3tc**, we measured absorption spectra immediately after irradiation of a chloroform solution of **3tt** at 366 nm. A photodiode array detector was used to observe any spectral changes that occur within seconds. Figure 3 displays the recovery of the absorption
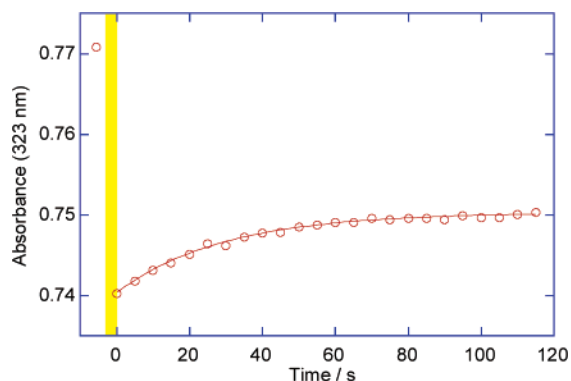
Figure 3. Time profile of the transient absorption of a chloroform solution of **3** observed at 323 nm after irradiation at 366 nm. The irradiation time was 3 s (yellow area). "Time" indicates the delay time after the irradiation with light. The first point at $t =$ ca. -5 s is the absorption before irradiation.

after irradiation. Bleaching (i.e., a decrease of the absorption band) was observed just after irradiation; its recovery occurred with a rate constant $k = 0.035$ s^{-1} at 23 °C. The recovery of the absorption band corresponds to the reformation of **3tt**. The fact that the absorption intensity did not

recover to the initial intensity it had before irradiation suggests the formation of another photoproduct, namely, **3cc**. From these results, we propose in Scheme 2 a reaction scheme for the photochemical and thermal isomerizations of **3**.

Scheme 2. Photochemical and Thermal Isomerizations of **3**

$$\textbf{3tt} \underset{\text{436 nm, }\Delta}{\overset{\text{366 nm}}{\rightleftharpoons}} \textbf{3tc} \underset{\text{436 nm}}{\overset{\text{366 nm}}{\rightleftharpoons}} \textbf{3cc}$$

Generally, in a system such as that presented in Scheme 2, where the reaction intermediate (in this case, **3tc**) has a short lifetime and the final product (**3cc**) is fairly stable, the photochemical formation (yield) of the final product (**3cc**) is dependent on the intensity of the light.[10] To verify that the observed intermediate is **3tc**, we investigated the effect of light intensity on the isomerization processes of **3** in chloroform (Figure 4). The curves obtained at intensities of
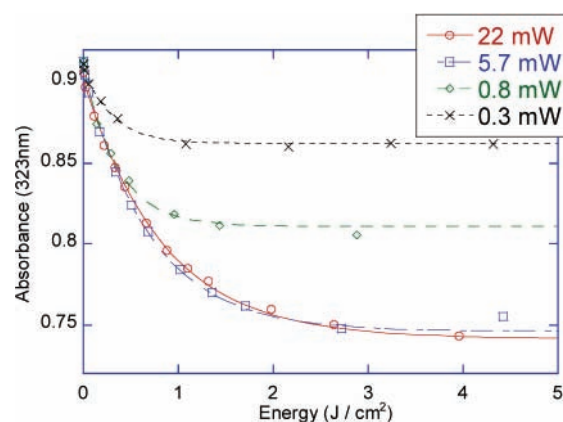
Figure 4. Absorption change of **3** in chloroform at 323 nm, with respect to the total energy of light, upon irradiation at 366 nm using various intensities of light.

5.7 and 22 mW cm^{-2} are nearly identical, and no dependency was observed. At weaker intensities of light (0.8 and 0.3

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mW cm^{-2}), the isomerization of **3** depends on the irradiating light intensity, although the total energy of light was maintained. The observed intermediate, therefore, is most reasonably assigned to **3**tc, and its lifetime at 23 °C in chloroform is 28 s.

Recently, we have studied the correlation between the structure and the photo and thermal isomerization reaction of cyclic azobenzene dimer, where two azobenzene units are connected by methylene linkers at the meta position.[11] In that molecule, the trans/cis isomer was fairly stable ($t \sim 6.1$ days at 298 K) because the ring has flexibility to form a stabilized conformation. As for **3**tc, in contrast, the rigid structure of xanthene moieties prevents the molecule from forming a stable conformer.

In conclusion, we have demonstrated a new type of light-driven molecular motion that is similar to the function of a hinge. This motion can be controlled by the irradiation wavelength, and the yield depends on the light intensity. The change in molecular shape is large, and therefore we believe that such systems might be of use in various fields, e.g., as storage devices or other switching devices. The highly regulated motion of the hinge has a potential to display drastic switching behavior, especially for anisotropic media such as liquid crystals.

Supporting Information Available: Detailed synthetic procedures and characterizations of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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