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A Pentiptycene-Derived Light-Driven Molecular Brake

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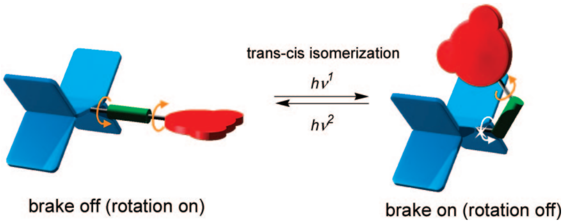
ABSTRACT



A room-temperature light-driven molecular brake (1), consisting of a pentiptycene rotator, a 3,5-dinitrophenyl brake, and a photoisomerizable ethenyl spacer, is reported. The rotation rates of the rotator differ by about 9 orders of magnitude between the brake-on (*cis*-1) and brake-off (*trans*-1) states.

The ability to control specific motions of subunits in molecules or supramolecular ensembles is essential for the development of molecular machines.[1] As photons are cleaner, faster, and longer-range control elements (stimuli) compared to chemicals and electrons,[2] many efforts have been devoted to constructing prototypes of light-driven or photocontrollable linear and rotary motions.[1–3] However, the progress in some aspects falls behind the corresponding chemical-controlled systems. One particular example is “molecular brakes”, in which the Brownian rotary motion of a rigid wheel component about a single bond can be slowed down by a brake unit. Since the first chemical-driven molecular brake reported by Kelly and co-workers in 1994,[4] several others have also been developed.[5] The first approach toward a light-driven counterpart was reported by Feringa and co-workers in 1997 using a *cis*−*trans* interconvertable sterically overcrowded alkene.[6] However, the desired rotary motion is restricted for both the trans and cis isomers at room temperature because of unexpectedly high and similar rotational barriers (19.7 and 19.0 kcal mol^{-1}, respectively, at 303 K). In a later report on a similar system, the rate of rotation (k_{rot}) was determined to be less than 0.1 s^{-1} for all the stable and unstable states at 298 K. [7] To date, an effective room-temperature photocontrollable molecular brake has yet to be demonstrated.

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‡ Academia Sinica.

[1] Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines−A Journey into the Nano World*; Wiley-VCH: Weinheim, 2003.

[2] (a) Raymo, F. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 5249–5251. (b) Credi, A. *Aust. J. Chem.* **2006**, *59*, 157–169. (c) Saha, S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 77–92.

[3] (a) Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. *Chem. Rev.* **2005**, *105*, 1281–1376. (b) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191. (c) Feringa, B. L. *J. Org. Chem.* **2007**, *72*, 6635–6652.

[4] Kelly, T. R.; Bowyer, M. C.; Bhaskar, K. V.; Bebbington, D.; Garcia, A.; Lang, F.; Kim, M. H.; Jette, M. P. *J. Am. Chem. Soc.* **1994**, *116*, 3657–3658.

[5] (a) Jog, P. V.; Brown, R. E.; Bates, D. K. *J. Org. Chem.* **2003**, *68*, 8240–8243. (b) Annunziata, R.; Benaglia, M.; Cinquini, M.; Raimondi, L.; Cozzi, F. *J. Phys. Org. Chem.* **2004**, *17*, 749–751. (c) Alfonso, I.; Burguete, M. I.; Luis, S. V. *J. Org. Chem.* **2006**, *71*, 2242–2250.

[6] Schoevaars, A. M.; Kruizinga, W.; Zijlstra, R. W. J.; Veldman, N.; Spek, A. L.; Feringa, B. L. *J. Org. Chem.* **1997**, *62*, 4943–4948.

[7] ter Wiel, M. K. J.; van Delden, R. A.; Meetsma, A.; Feringa, B. L. *Org. Biomol. Chem.* **2005**, *3*, 4071–4076.

10.1021/ol800689a CCC: $40.75

We report herein the first example of a room-temperature light-driven molecular brake (**1**) that displays distinct rates of rotation in the brake-on versus brake-off states. The rigid pentiptycene group[8] in **1** serves as a four-bladed wheel, and the trans−cis photoisomerizable dinitrostyryl group behaves as a photoresponsive brake component (Figure 1). In the trans form (*trans*-**1**, the brake-off state), the pentiptycene rotator undergoes free rotation ($k_{\mathrm{rot}} \approx 10^9\ \mathrm{s}^{-1}$) due to a small rotational barrier ($\Delta G^{\ddagger} \approx 4.5$ kcal/mol at 298 K). However, such a rotation is nearly blocked ($k_{\mathrm{rot}} = 3\ \mathrm{s}^{-1}$, $\Delta G^{\ddagger} \approx 16.4$ kcal mol^{-1} at 298 K) in the cis form (*cis*-**1**, the brake-on state) as the result of an intercalation of the dinitrophenyl group into the U-shaped cavities of the rotator. As a result, the rate of rotation in the brake-on and brake-off states differs by nearly 9 orders of magnitude at 298 K.

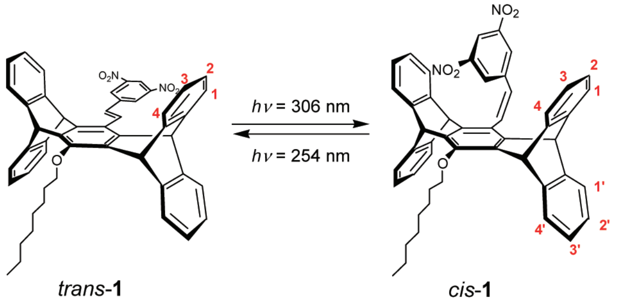

Figure 1. Molecular structures of a light-driven molecular brake (**1**) corresponding to the schematic illustrations shown in the Abstract graphic. The trans (*trans*-**1**) and cis (*cis*-**1**) isomers correspond to the brake-off and brake-on states. The numerical labels for protons and carbons are for discussion of the VT NMR spectra.

The synthesis of molecular brake **1** is outlined in Scheme 1. The commercially available 3,5-dinitrobenzyl alcohol **2** was first converted with thionyl chloride to 3,5-dinitrobenzyl chloride **3**, which then reacted with triphenylphosphine to form the phosphonium salt **4**. The latter reaction was kept under 60 °C, because the salt decomposes at higher temperatures. The stilbene backbone was finally constructed by the Wittig reaction of **4** and formylpentiptycene **5**, the synthesis of which has recently been reported.[9] The resulting trans and cis isomers of **1** (2: 1) can be readily separated by column chromatography.

Scheme 1

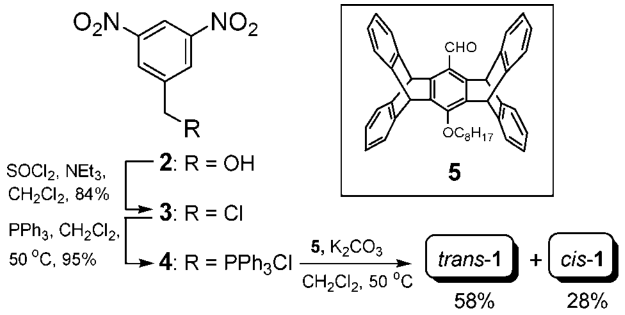

Figure 2 shows the aromatic region of ^{1}H and ^{13}C NMR spectra of *trans*-**1** and *cis*-**1** in DMSO-d_6 at 298 K. The presence of only one set of signals for *trans*-**1** suggests that both the pentiptycene rotator and the dinitrophenyl brake can undergo free rotation about the $\mathrm{C_{vinyl}}{-}\mathrm{C_{aryl}}$ single bonds. In contrast, the observation of two sets of signals for the pentiptycene methine nuclei but not for the dinitrophenyl nuclei indicates that rotation of the rotator but not the brake component is slower than the NMR time scale. Except for some quaternary carbons, the signals can be unambiguously assigned on the basis of a series of 2D NMR experiments, including COSY, HSQC, NOESY, and ROESY (Supporting Information, Figures S5−S11), and the numerical labels in Figure 2 correspond to the labeled protons and carbons in Figure 1.

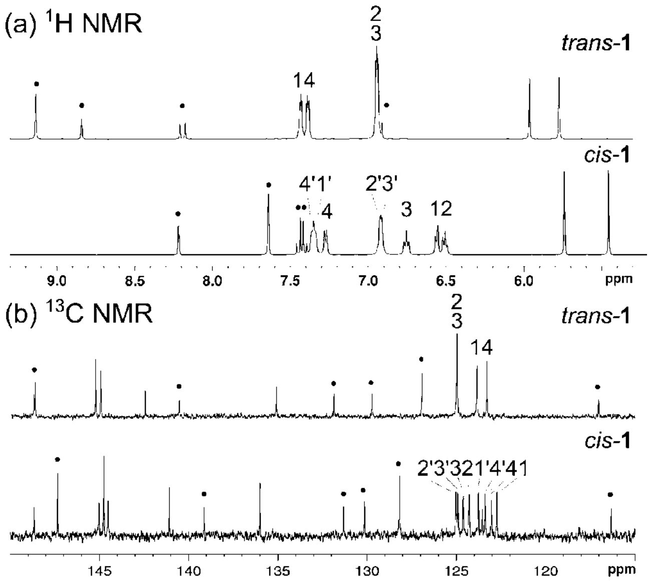

Figure 2. Aromatic region of (a) ^{1}H and (b) ^{13}C NMR spectra of *trans*-**1** and *cis*-**1** in DMSO-d_6 at 298 K. The solid circles denote peaks due to the dinitrostyryl group and the Arabic numerals denote the corresponding protons and carbons labeled in Figure 1.

The information about rotational barriers and rates for the pentiptycene rotator in *cis*-**1** can be obtained from variable-temperature (VT) NMR studies and spectral simulations. As shown in Figure 3a, some of the proton peaks at 298 K coalesce at higher temperatures. For example, a coalescence temperature (T_c) near 348 K is found for protons H_3 and $H_{3'}$, corresponding to an energy barrier of $\Delta G^{\ddagger}_{(348\mathrm{K})} = 16.9 \pm 0.2$ kcal mol^{-1}. However, the multiplicity of proton signals and the presence of more than one type of spin systems in

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(8) For a recent review on pentiptycene chemistry, see: Yang, J.-S.; Yan, J.-L. *Chem. Commun.* **2008**, 1501–1512.

(9) Yang, J.-S.; Ko, C.-W. *J. Org. Chem.* **2006**, *71*, 844–847.

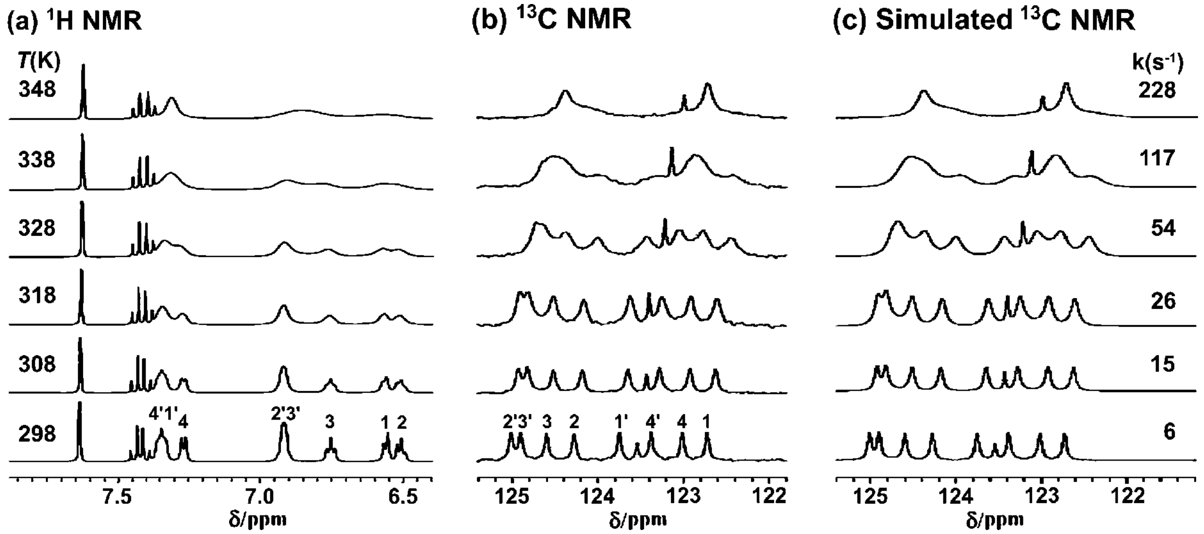

Figure 3. Pentiptycene peripheral phenylene (blade) region of the (a) experimental proton and (b) carbon and (c) simulated carbon VT NMR spectra of *cis*-**1** (9 and 60 mM for proton and carbon, respectively, DMSO-d_6, 500 MHz). Values of temperature (*T*, K) and interconversion rate (*k*, s^{-1}) between the two isoenergetic states are also given for every trace. Simulated spectra were obtained with the Topspin 2.0 program.[10]

the phenylene blades of the pentiptycene rotator prevent a direct spectral simulation. Thus, a VT ^{13}C NMR experiment was carried out, and the resulting spectra (Figure 3b) were simulated (Figure 3c).[10] The results suggest that the rotation is nearly blocked at 298 K, and the rate constant (*k*) for interconversion between the two isoenergetic conformers of *cis*-**1** is only 6 s^{-1}. In other words, it takes ca. 0.33 s for a 360° rotation (i.e., $k_{rot} = k/2$). The activation energy (E_a = 14.8 ± 0.5 kcal mol^{-1}) and enthalpic ($\Delta H^{\ddagger}$ = 14.1 ± 0.5 kcal mol^{-1}) and entropic ($\Delta S^{\ddagger} = -7.6 \pm 1.4$ cal K^{-1} mol^{-1}) contributions to the free energy of activation ($\Delta G^{\ddagger}$ = 16.4 and 16.8 kcal mol^{-1} at 298 and 348 K, respectively) were obtained by Arrhenius and Eyring plots (Supporting Information, Figures S12 and S13). Since the rotational barrier is mainly due to an enthalpic factor, the transition state is destabilized mainly due to steric effect. It should also be noted that the values of $\Delta G^{\ddagger}$ at 348 K deduced from ^{1}H and ^{13}C VT NMR are essentially the same.

To obtain structural information about the transition structure and the optimized conformation of *cis*-**1** along the pentiptycene rotation coordinates, we have carried out DFT (BMK/6-311+G**//B3LYP/6-31G*) calculations.[11] The calculation results are justified by the good agreement of the calculated (16.75 kcal mol^{-1}) and the NMR-determined $\Delta G^{\ddagger}$ value (16.4 kcal mol^{-1}) at 298 K. The brake moiety in the structurally optimized *cis*-**1** (Figure 4a) is, as expected, located at the U-shaped cavities, although the protruding pentiptycene blades create two types of cavities (U- vs V-shaped). The V-shaped cavities are in fact inaccessible to the dinitrophenyl group as a result of severe steric interactions with H_1, $H_{1'}$, and the bridgehead hydrogen atom, as revealed by the transition structure (Figure 4b). Strains in bond angles and bond lengths also account in part for the high energy of the transition state. The structural coordinates are supplied as Supporting Information.

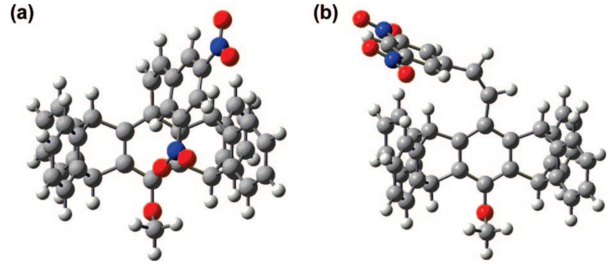

Figure 4. DFT-derived structures for *cis*-**1**: (a) the optimized conformation and (b) the transition structure along the pentiptycene rotation coordinate.

An attempt to evaluate the rotational barriers for the pentiptycene rotator in *trans*-**1** and the dinitrophenyl brake in *cis*-**1** with VT ^{1}H NMR was hampered by their low energy barriers, as we could not observe decoalescence of the signals even at a temperature as low as 183 K (in CD_2Cl_2). In view of the good agreement of DFT calculations and NMR experiments in the pentiptycene rotation barrier of *cis*-**1**, DFT calculations have been applied to retrieve the corresponding information for that in *trans*-**1** (4.45 kcal mol^{-1})[12] and the brake rotation in *cis*-**1** (6.85 kcal mol^{-1}). With a calculated $\Delta G^{\ddagger}$ value differing by 12.3 kcal mol^{-1} for the pentiptycene

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[10] All line shape simulations were performed using the Bruker Topspin 2.0 program.

[11] To expedite the calculations, the octyl group was replaced by a methyl group. The BMK functional has been shown to be a good functional in terms of thermochemistry and kinetics for main-group elements. Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.

rotation in *trans*-**1** versus *cis*-**1** at 298 K, the difference in rotation rate is in the order of 10^9.[13]

Photoswitching between *trans*-**1** and *cis*-**1** has been investigated in dichloromethane solutions.[14,15] On the basis of their relative molar absorptivity (ε), the wavelengths of 306 ($\varepsilon_{trans\text{-}\mathbf{1}}/\varepsilon_{cis\text{-}\mathbf{1}} = 3.35$) and 254 nm ($\varepsilon_{trans\text{-}\mathbf{1}}/\varepsilon_{cis\text{-}\mathbf{1}} = 1.20$) were adopted for the *trans*-**1** → *cis*-**1** and the *cis*-**1** → *trans*-**1** conversion, respectively. The corresponding ratio of [*trans*-**1**]/[*cis*-**1**] determined by ^{1}H NMR is 25/75 and 45/55 in the photostationary states. As monitored by absorption spectra (Figure 5), photoswitching between the two photostationary states is quite robust (Figure 5, inset).

In summary, the pentiptycene-derived stilbene **1** has been prepared and investigated as a photocontrollable molecular brake that functions at room temperature. Both experimental and computational results reveal that at 298 K rotation of the four-bladed pentiptycene (the rotator) is "free" in *trans*-**1** but is nearly blocked in *cis*-**1**. The brake-on (*cis*-**1**) and brake-off (*trans*-**1**) states differ by a rotation rate of ~10^9-fold and can be interconverted through the ethylene trans−cis photoisomerization reactions. Studies on the related systems are in progress in our laboratory in order to gain insights into substituent effects on the brake performance.

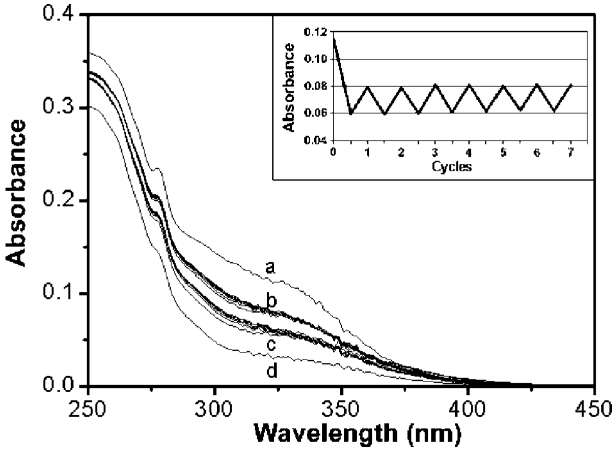

Figure 5. Absorption spectra of *trans*-**1** (curve a) and *cis*-**1** (curve d) and their photostationary states irradiated with alternating 306- (curves c) and 254-nm (curves b) UV light irradiation in dichloromethane. Inset shows the changes in absorbance at 322 nm starting from *trans*-**1** (10 μM) for 7 switching cycles.

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Supporting Information Available: Experimental methods, synthesis of intermediates **3** and **4**, 1D and 2D NMR spectra and DFT-derived structural coordinates for *trans*-**1** and *cis*-**1**, and the Arrhenius and Eyring plots for *cis*-**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) A barrier of ~1000 cm^{-1} (2.86 kcal mol^{-1}) was found for the rotation of a single phenyl ring in *trans*-stilbene and its 4,4′-disubstituted derivatives. Arp, Z.; Chiang, W.-Y.; Laane, J.; Sakamoto, A.; Tasumi, M. *J. Phys. Chem. A* **2002**, *106*, 3479–3484.

(13) Even with a consideration of 1−2 kcal/mol uncertainty in calculated $\Delta G^{\ddagger}$ value for pentiptycene rotation in *trans*-**1**, the ratio of the on-off rotation rate is still around 10^7−10^8.

(14) The quantum yields for the *trans*-**1** → *cis*-**1** and *cis*-**1** → *trans*-**1** photoisomerization in dichloromethane are 0.17 and 0.21, respectively.

(15) Thermal isomerization of the double bond in **1** has been evaluated by DFT (UBMK/6-311+G**//UB3LYP/6-31G*) modeling. The calculated free energy barrier was 45.22 kcal mol^{-1} relative to *cis*-**1**, and the free energy difference between *cis*-**1** and *trans*-**1** was 0.76 kcal mol^{-1}. These values are similar to the computational and experimental data reported for the parent stilbene (41−46 kcal mol^{-1} for the thermal isomerization barrier and 2.3−5.7 kcal mol^{-1} for the energy difference between the cis and trans isomers), see: (a) Meier, H. *Angew. Chem., Int. Ed.* **1992**, *31*, 1399–1420. (b) Han, W.-G.; Lovell, T.; Liu, T.; Noodleman, L. *ChemPhysChem* **2002**, *3*, 167–178.