A New Model of Light-Powered Chiral Molecular Motor with Higher Speed of Rotation, Part 2 – Dynamics of Motor Rotation

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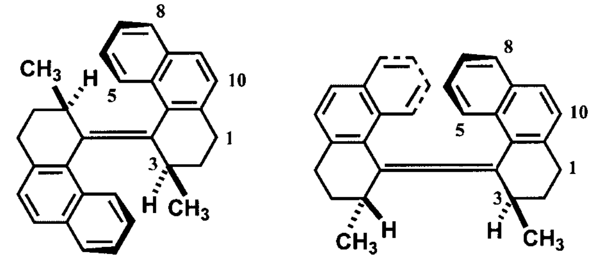
Keywords: Molecular motor / Motor rotation isomer / Circular dichroism / Molecular dynamics

To clarify the mechanism and dynamics of the new model of light-powered chiral molecular motor (**2**) of five-membered ring type, the second motor rotation isomer, the unstable *cis*-olefin **2b**, was isolated and its stereostructure was determined. Similarly, the fourth motor rotation isomer, the unstable *trans*-olefin **2d**, was detected by ^{1}H NMR at low temperature, and its stereostructure was also determined. With the aid of this knowledge of the stereostructures of the motor rotation isomers and their spectroscopic data, the dynamics of the motor rotation **2a** → **2b** → **2c** → **2d** → **2a** were studied by ^{1}H NMR and CD, revealing that the fourth rotation step **2d** → **2a** was much accelerated, as expected from the design of the new motor. Continuous rotation of this motor was achieved by repetition of the operations of photoirradiation and heating.

Introduction

In Part 1 of this series[1] we reported the design and synthesis of a new model of light-powered chiral molecular motor. Our primary goal in the project was to develop a molecular motor capable of rotating more rapidly than the previous motor **1**, of six-membered ring type (Figure 1). In the designed motor model **2**, of five-membered ring type, it was expected that the steric hindrance between the methyl group and the naphthalene moiety should be diminished, and that the motor should hence rotate more speedily (Figure 2). In Part 1[1] the absolute configuration of the motor **2**, of critical importance for controlling the absolute direction of the motor rotation (i.e., clockwise or counterclockwise), was determined by X-ray crystallography and chemical correlation: the absolute stereostructure of the first motor rotation isomer **2a** was [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–) and that of the third motor rotation isomer **2c** was [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*).

Here in Part 2 we report the first isolation and structure determination of the second motor rotation isomer, the unstable *cis*-olefin **2b**, and the ^{1}H-NMR detection at low temperature of the fourth motor rotation isomer, the unstable *trans*-olefin **2d**. From the stereostructures of the motor rotation isomers and their spectroscopic data, the mechanism and dynamics of the motor rotation **2a** → **2b** → **2c** → **2d** → **2a** were clarified by ^{1}H-NMR and CD methods, revealing that the fourth rotation step **2d** → **2a** was, as expected, much accelerated. Furthermore, continuous rotation of this motor was achieved by repeated cycles of photoirradiation and heating. Those studies are described here in detail.



(3*R*,3′*R*)-(*P*,*P*)-(*E*)-(–)-1a **(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-(+)-1c**

Figure 1. The light-powered chiral molecular motor of six-membered ring type.

Results and Discussion

Isolation of the Second Motor Rotation Isomer, the Unstable *cis*-Olefin 2b (Racemic and Chiral), and Its Stereostructure

To clarify the rotation mechanism of a molecular motor it is important to determine the stereostructures of motor rotation isomers. The first motor rotation isomer, the stable *trans*-olefin **2a**, was prepared and its stereostructure was determined as reported in Part 1[1] (Figure 2 and Figure 3). The second motor rotation isomer, the unstable *cis*-olefin **2b**, was formed by photochemical isomerization of **2a** and could be isolated at low temperature as follows. The wavelength dependency of the photochemical conversion of **2a**

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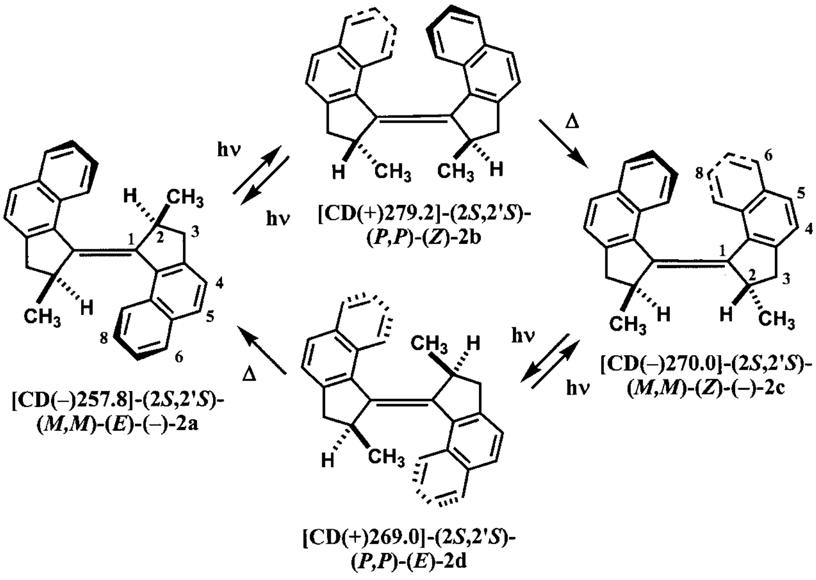

Figure 2. A new model of a light-powered chiral molecular motor of five-membered ring type rotating with a higher speed.

into **2b** was first studied with the aid of the monochromatic UV light apparatus. In the 308–332 nm region, monochromatic light at 312 nm (±12 nm) was the most effective for the conversion of **2a** into **2b**, and so was used hereafter. A solution of the racemic stable *trans*-olefin **2a** in CH_2Cl_2 was irradiated with UV light at 312 nm (±12 nm) for 30 min at –78 °C, and the reaction mixture was then subjected to HPLC on an ODS column (15 ϕ × 300 mm, MeOH) cooled to –40 °C, with the solvent also cooled to –40 °C. The desired unstable *cis*-olefin **2b** was obtained as the fraction eluted second (see Figure 4 for the case of chiral isomers), and this was evaporated in vacuo at –40 to –30 °C to yield the unstable *cis*-olefin **2b** as a yellow powder. This yellow powder (**2b**) was dissolved at –40 °C in CD_2Cl_2 and its ^{1}H-

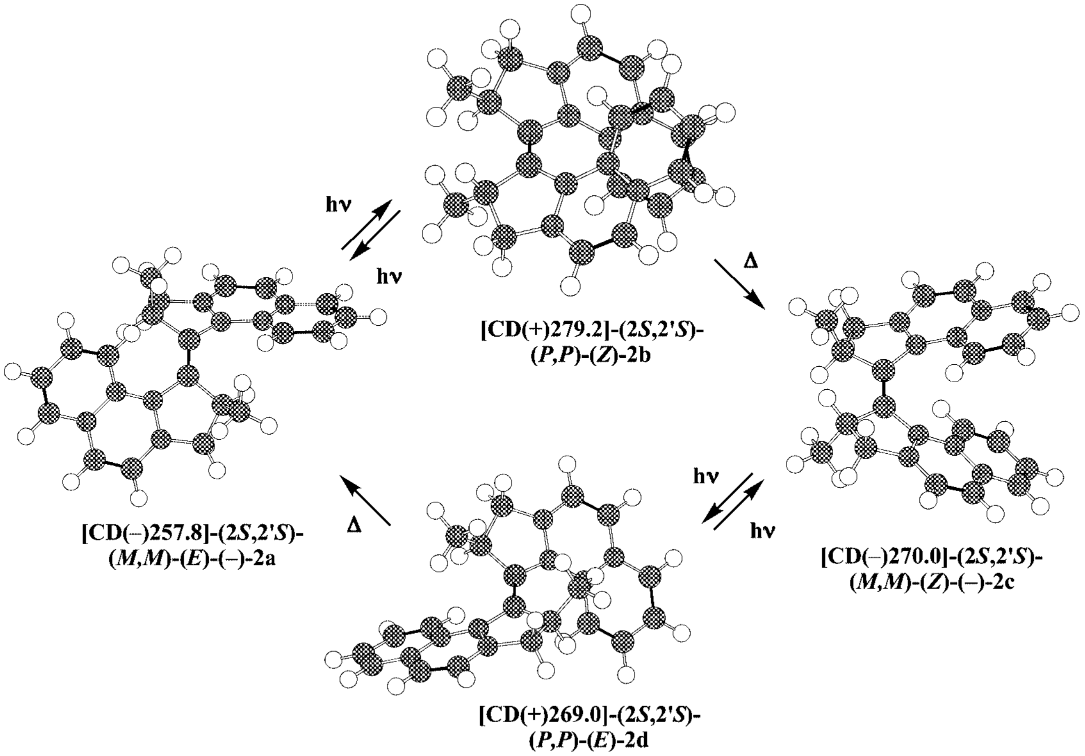

Figure 3. The absolute stereochemistry and the clockwise rotation of the new model of light-powered chiral molecular motor of five-membered ring type.

NMR spectrum was immediately measured at –30 °C, showing that the unstable *cis*-olefin **2b** could be isolated in a pure form (see Table 1 and Supporting Information).

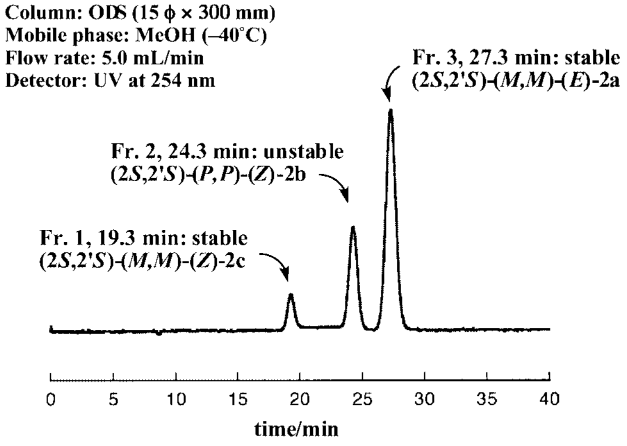

Figure 4. Isolation of the unstable *cis*-olefin (2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** by HPLC (ODS, MeOH) at –40 °C.

Table 1. ^{1}H-NMR data for the unstable *cis*-olefin (±)-**2b** and the unstable *trans*-olefin (±)-**2d** in CD_2Cl_2.[a]

No.	Unstable *cis*-olefin (±)-**2b** at –30 °C	Unstable *trans*-olefin (±)-**2d** at –60 °C
H2ax	3.81 (br. q, J = 6.3 Hz, $W_{1/2}$ = 25.2 Hz, 2 H)	3.59 (br. q, J = 6.1 Hz, $W_{1/2}$ = 25.8 Hz, 2 H)
Me2eq	1.58 (d, J = 6.3 Hz, 6 H)	0.58 (d, J = 6.1 Hz, 6 H)
H3ax	3.42 (dd, J = 15.7, 8.6 Hz, 2 H)	2.91 (dd, J = 15.1, 8.7 Hz, 2 H)
H3eq	3.16 (dd, J = 15.7, 7.4 Hz, 2 H)	3.25 (dd, J = 15.1, 7.6 Hz, 2 H)
H4	7.44 (d, J = 8.3 Hz, 2 H)	7.39–7.47 (m, 2 H)
H5	7.62 (d, J = 8.3 Hz, 2 H)	7.75 (d, J = 8.3 Hz, 2 H)
H6	7.56 (d, J = 8.5 Hz, 2 H)	7.86–7.91 (m, 2 H)
H7	6.94 (m, 2 H)	7.39–7.47 (m, 2 H)
H8	6.48 (ddd, J = 8.8, 6.8, 1.5 Hz, 2 H)	7.39–7.47 (m, 2 H)
H9	6.93 (d, J = 8.8 Hz, 2 H)	7.86–7.91 (m, 2 H)

[a] ^{1}H NMR (400 MHz, ppm).

The stereostructure of the unstable *cis*-olefin **2b** was determined by analysis of ^{1}H-NMR spectroscopic data as follows (Table 1). The aromatic protons appeared in a region of higher magnetic field (δ = 6.48–7.62 ppm) than those of the stable *trans*-olefin **2a** (δ = 7.30–8.25 ppm), but the region was similar to that seen in the case of the stable *cis*-olefin **2c** (δ = 6.36–7.70 ppm). Those data indicate the *cis* configuration of **2b**, in which two naphthalene rings overlap with each other, generating diamagnetic anisotropy effects due to the ring current effect and the aromatic protons hence showing high-field shifts. From analysis of the coupling constants of aliphatic protons and comparison of the data with those relating to the stable *cis*-olefin **2c** with axial methyl groups, especially from the fact that $J_{2ax,3ax}$ = 8.6 Hz in **2b** while $J_{2eq,3eq}$ = 0.0 Hz in **2c**, it was determined that the methyl group of **2b** had adopted an equatorial orientation as illustrated in Figure 3. The relative stereochemistry of the second motor rotation isomer **2b** was therefore assigned as (2*S**,2′*S**)-(*P**,*P**)-(*Z*). In the stereostructure **2b**, two methyl groups conflict with each other, generating severe steric hindrance, and so, to release the steric energy, the central double bond would have to be twisted to some extent, as demonstrated in the X-ray analysis of the unstable *trans*-olefin **1c** of six-membered ring type.[2] This is the reason for the strong yellow color of the unstable *cis*-olefin **2b**.

The chiral unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** was prepared similarly; a solution of the enantiopure stable *trans*-olefin **2a** in CH_2Cl_2 was irradiated with UV light at 312 nm (±12 nm) for 30 min at –78 °C, and the obtained isomers were separated at –40 °C by HPLC on an ODS column (15 ϕ× 300 mm, MeOH). The desired unstable chiral *cis*-olefin **2b** was obtained as the fraction eluted second (Figure 4), its CD spectrum immediately being measured at –32.5 °C (Figure 5). Reflecting the strongly twisted π-electron system of **2b**, its CD spectrum shows very intense Cotton effects around 300–200 nm. Since the unstable *cis*-olefin **2b** shows a positive Cotton effect at 279.2 nm, its chiroptical properties and absolute configuration were designated as [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*). In addition, the unstable *cis*-olefin **2b** exhibits a broad positive CD band around 440–350 nm, the electronic transition of which is responsible for the strong yellow color of **2b**. It is noteworthy that the CD spectrum of [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** is almost opposite in sign to that of [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c**, reflecting the opposite helicity of the π-electron system (compare Figure 5 with Figure 8 in Part 1[1]).

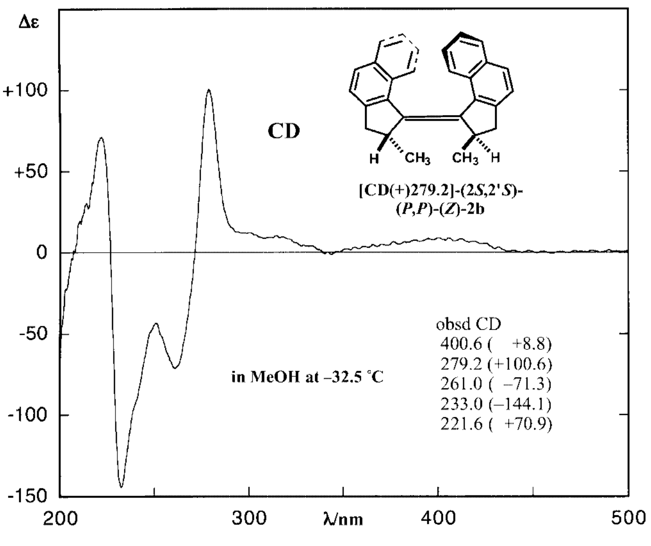

Figure 5. CD spectrum of the unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** in MeOH at –32.5 °C.

^{1}H-NMR Detection of the Fourth Motor Rotation Isomer, the Unstable *trans*-Olefin 2d, and Its CD Spectrum and Absolute Configuration

Unlike in the case of the molecular motor of six-membered ring type, the fourth motor rotation isomer, the *trans-olefin* **2d**, was extremely unstable and was only detected by ^{1}H-NMR spectroscopy at –60 °C. Studies of the wavelength dependency of the conversion of the stable *cis*-olefin **2c** into the unstable *trans*-olefin **2d** revealed that monochromatic 330 nm light (±12 nm) was the most effective for the conversion, so a solution of the racemic stable *cis*-olefin **2c** in CD_2Cl_2 was irradiated with UV light at 330 nm (±12 nm) for 12 min. The ^{1}H-NMR spectrum was first measured at –30 °C, but showed the signals of the stable *trans*-olefin **2a**, indicating that the further thermal isomerization of **2d** to **2a** had occurred even at –30 °C. From then on, ^{1}H-NMR spectra of the unstable *trans*-olefin **2d** were therefore measured at –60 or –50 °C (see Table 1 and Supporting Information). From the peak intensity, the ratio of unstable *trans*-olefin **2d** to stable *cis*-olefin **2c** at photoequilibrium was determined to be 96:4.

As shown in Table 1, the aromatic protons of the unstable *trans*-olefin **2d** appeared in the usual region (δ = 7.39–7.91 ppm), as in the case of the stable *trans*-olefin **2a** (δ = 7.30–8.25 ppm), indicating a *trans* configuration in **2d**. As in the case of the unstable *cis*-olefin **2b**, it was determined through analysis of the coupling constant data of aliphatic protons that the methyl group of the unstable *trans*-olefin **2d** also adopts an equatorial orientation as illustrated in Figure 3: $J_{2ax,3ax}$ = 8.7 Hz in **2d**, while $J_{2eq,3eq}$ = 0.0 Hz in **2a**. In addition, the methyl group signal of **2d** appeared at δ = 0.58 ppm, indicating that the equatorial methyl group is located just above the naphthalene ring, feeling the diamagnetic anisotropy effect. Such an orientation of the methyl group should be accompanied by steric hindrance between the methyl group and the naphthalene ring, and to release the steric energy, the central double bond of **2d** would again be expected to be twisted to some extent, as in the case of the unstable *cis*-olefin **2b**. This is once more the reason for the strong yellow color of the unstable *trans*-olefin **2d**. From those data, the relative configuration of the fourth motor rotation isomer **2d** was assigned as (2*S**,2′*S**)-(*P**,*P**)-(*E*).

A solution of the racemic stable *cis*-olefin **2c** in CD_3OD was similarly irradiated with UV light at 330 nm (±12 nm) at –78 °C for 24 min, and the ratio of the unstable *trans*-olefin **2d** to the stable *cis*-olefin **2c** at photoequilibrium was determined from the ^{1}H-NMR spectral peak intensity to be 93:7.

A solution of the chiral stable *cis*-olefin [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** in MeOH was irradiated with UV light at 330 nm (±12 nm) at –78 °C. The photoreaction was monitored at –60 °C by CD spectroscopy. After irradiation for 18 s, the reaction had reached the photoequilibrium state, at which the ratio of the unstable *trans*-olefin **2d** to the stable *cis*-olefin **2c** was approximately 93:7, as also obtained above by ^{1}H-NMR spectroscopy. The CD spectrum of the products at photoequilibrium was measured at –62 °C and is shown in Figure 6, with intense Cotton effects at 280–200 nm and a broad negative Cotton effect at 440–340 nm. It should be noted that the CD spectral pattern of the unstable *trans*-olefin **2d** is almost the mirror image of that of the stable *trans*-olefin **2a** (compare Figure 6 with Figure 7 in Part 1[1]). Since the CD spectrum of the unstable *trans*-olefin **2d** shows a positive Cotton effect at 269.0 nm, it is hence fully designated as [CD(+)269.0]-(2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d**.

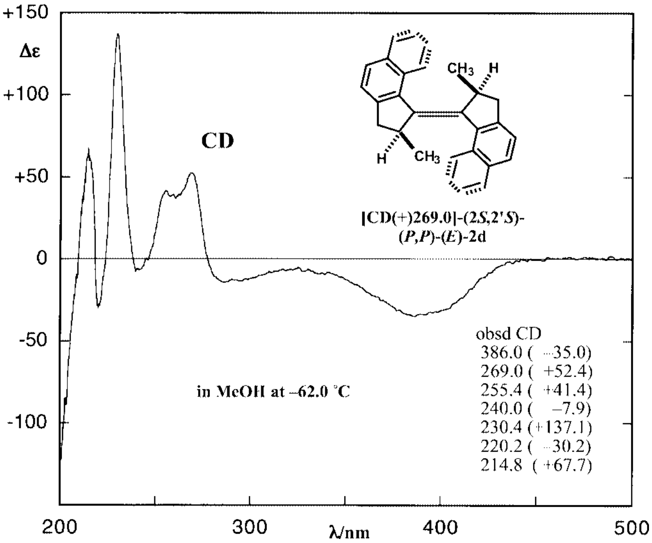

Figure 6. CD spectrum of the unstable *trans*-olefin [CD(+)269.0]-(2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** (93%) in MeOH at –62.0 °C: the sample contained some of the stable *cis*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*Z*)-**2c** (7%); the ratio was estimated by ^{1}H-NMR spectroscopy.

The Dynamics of the Molecular Motor Rotation Studied by ^{1}H-NMR Spectroscopy with a Racemic Sample

1) The Photodynamics of the Transformation of the Stable trans-Olefin 2a into the Unstable trans-Olefin 2d and of the Reverse Reaction

A solution of the stable racemic *trans*-olefin **2a** in CD_2Cl_2 was irradiated with UV light at 330 nm (±12 nm) at –78 °C for a total time of 15 min, during which the photoreaction was monitored by ^{1}H-NMR spectroscopy at –20 °C at intervals of 1–3 min (Figure 7). The ratio of the unstable *cis*-olefin **2b** to the stable *trans*-olefin **2a** was determined from the intensity of the H3eq signals, as shown in Figure 8. After 15 min irradiation, the reaction had reached the photoequilibrium state with the ratio **2b/2a** = 91:9.

The reverse photoreaction **2b** → **2a** was carried out as follows; since studies of the wavelength dependency of the reverse reaction had revealed that monochromatic light at 430 nm (±12 nm) was the most effective, the sample of **2b/2a** (91:9) obtained above was irradiated with 430 nm (±12 nm) visible light at –78 °C. After 4 min irradiation, the unstable *cis*-olefin **2b** had completely reverted to the stable *trans*-olefin **2a**, indicating that the photochemical *trans-cis*

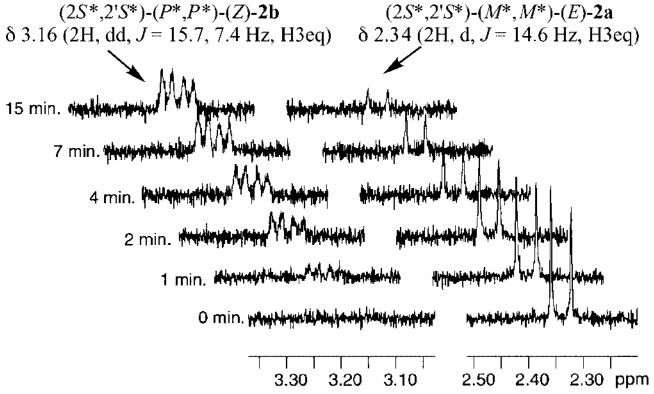

Figure 7. Photochemical isomerization of the stable *trans*-olefin $(2S^*,2'S^*)$-(M^*,M^*)-(E)-**2a** into the unstable *cis*-olefin $(2S^*,2'S^*)$-(P^*,P^*)-(Z)-**2b** at –78 °C, as monitored by ^{1}H NMR (400 MHz, CD_2Cl_2, –20 °C).

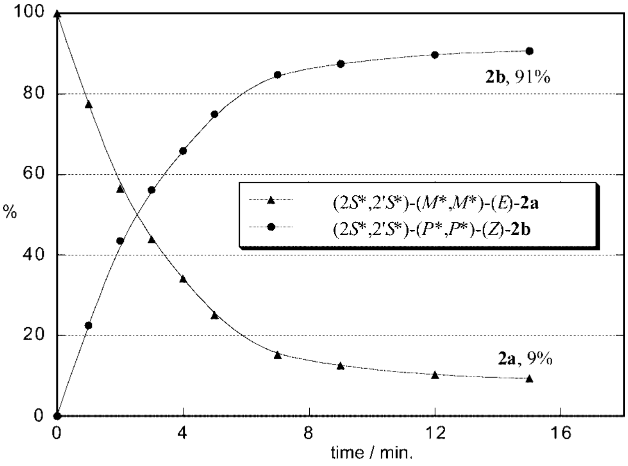

Figure 8. Dynamics of the photoisomerization of the stable *trans*-olefin $(2S^*,2'S^*)$-(M^*,M^*)-(E)-**2a** into the unstable *cis*-olefin $(2S^*,2'S^*)$-(P^*,P^*)-(Z)-**2b** on UV irradiation at 312 nm (±12 nm) at –78 °C as monitored by ^{1}H NMR (400 MHz, CD_2Cl_2, –20 °C).

isomerization between **2a** and **2b** is reversible as expected and that the backward reaction is faster than the forward reaction.

2) The Dynamics of the Thermal Isomerization of the Unstable cis-Olefin 2b into the Stable cis-Olefin 2c

A sample of **2b**/**2a** (ratio 77:23) in CD_2Cl_2 was prepared by photochemical treatment as described above, and its ^{1}H-NMR spectrum was measured at 20 °C at intervals of 5–10 min (Figure 9). The amount of unstable *cis*-olefin **2b** was determined from the peak intensities of the methyl groups of **2b** and **2c**. As can be seen in Figure 9, the peak corresponding to the stable *trans*-olefin **2a** remained unchanged, and did not disturb the observation. The **2b**/**2a** sample mixture can therefore be used with ^{1}H-NMR measurement, and this is the advantage of the ^{1}H-NMR method over others. The rate constants at 15, 20, 25, and 30 °C were obtained from first-order reaction kinetic equations, with the correlation coefficient R = 0.999 in all cases. An activation energy E_a = 20.7 kcal mol^{-1} was obtained from the Arrhenius plot with R = 0.999 (Figure 10), whilst the activation enthalpy ($\Delta H^{\ddagger}$ = 20.7 kcal mol^{-1}) and activation entropy ($\Delta S^{\ddagger}$ = –6.17 cal K^{-1} mol^{-1}) were obtained similarly from the Eyring plot with R = 0.999.

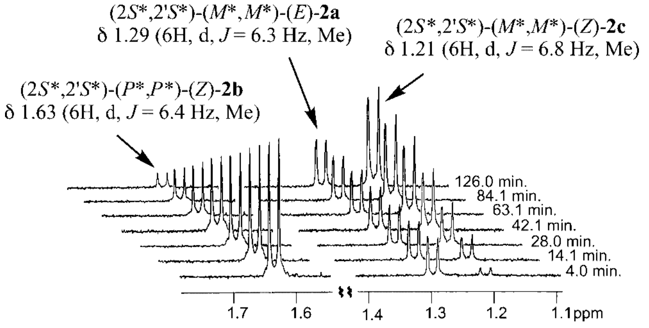

Figure 9. Dynamics of the thermal isomerization of the unstable *cis*-olefin $(2S^*,2'S^*)$-(P^*,P^*)-(Z)-**2b** into the stable *cis*-olefin $(2S^*,2'S^*)$-(M^*,M^*)-(Z)-**2c** at 20 °C as monitored by ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C).

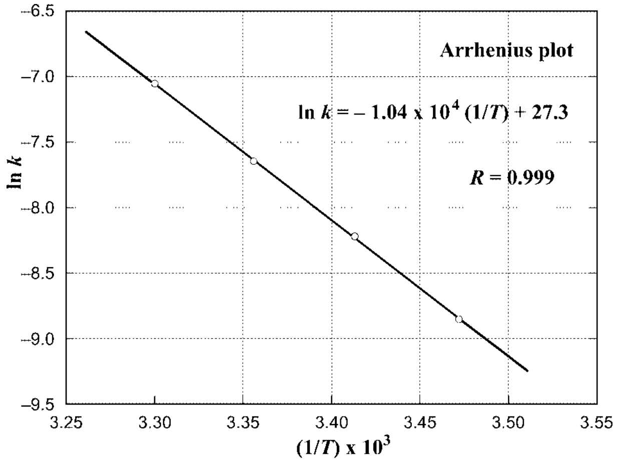

Figure 10. Arrhenius plot for the thermal isomerization of the unstable *cis*-olefin $(2S^*,2'S^*)$-(P^*,P^*)-(Z)-**2b** into the stable *cis*-olefin $(2S^*,2'S^*)$-(M^*,M^*)-(Z)-**2c** as monitored by ^{1}H NMR (400 MHz, CD_2Cl_2).

3) The Photodynamics of the Transformation of the Stable cis-Olefin 2c into the Unstable trans-Olefin 2d and those of the Backward Reaction

A solution of the stable racemic *cis*-olefin **2c** in CD_2Cl_2 was irradiated with 330 nm (±12 nm) UV light at –78 °C for a total time of 12 min, during which the photoreaction was monitored at intervals of 1–2 min by ^{1}H-NMR spectroscopy at –60 °C (Figure 11), the ratio of the unstable *trans*-olefin **2d** to the stable *cis*-olefin **2c** being determined from the peak intensities of the methyl groups of **2d** and **2c**. After 12 min irradiation, the reaction had reached photoequilibrium with the ratio **2d**/**2c** = 96:4 (Figure 12).

The reverse photoreaction **2d** → **2c** was monitored in a similar way; in this case monochromatic light at 430 nm (±12 nm) was the most effective, and so a solution of the sample of **2d**/**2c** (86:14) was irradiated at –78 °C with 430 nm (±12 nm) visible light. At intervals of 1–20 min the

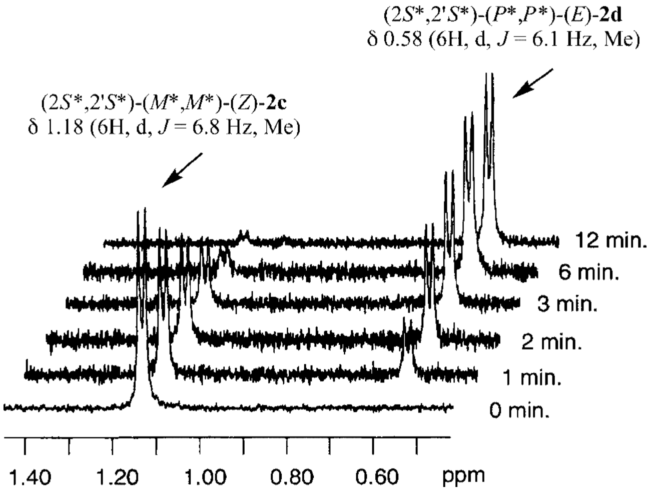

Figure 11. Photochemical isomerization of the stable *cis*-olefin $(2S^*,2'S^*)$-(M^*,M^*)-(Z)-**2c** into the unstable *trans*-olefin $(2S^*,2'S^*)$-(P^*,P^*)-(E)-**2d** at –78 °C as monitored by ^{1}H NMR (400 MHz, CD_2Cl_2, –60 °C).

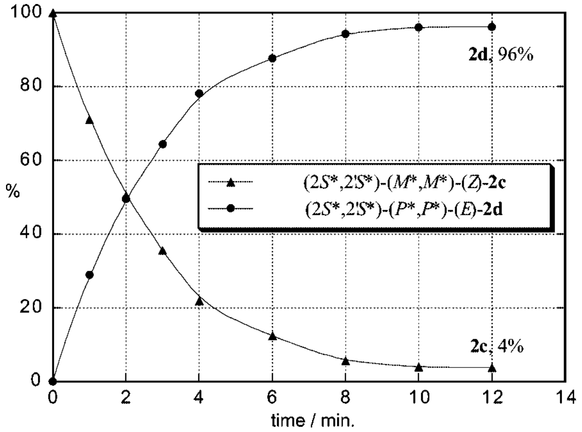

Figure 12. Dynamics of the photoisomerization of the stable *cis*-olefin $(2S^*,2'S^*)$-(M^*,M^*)-(Z)-**2c** into the unstable *trans*-olefin $(2S^*,2'S^*)$-(P^*,P^*)-(E)-**2d** on UV irradiation at 330 nm (±12 nm) and at –78 °C as monitored by ^{1}H NMR (400 MHz, CD_2Cl_2, –60 °C).

reaction was monitored by ^{1}H-NMR spectroscopy (–60 °C), and the ratio was determined. After 60 min irradiation, the final ratio **2d/2c** at photoequilibrium was 25:75. With 430 nm visible light used for the backward reaction, only the unstable *trans*-olefin **2d** absorbed the light to isomerize to **2c**, since the stable *cis*-olefin **2c** has no absorption band in this region, so it is still unclear why the **2d/2c** ratio remained at 25:75. However, as this reaction corresponds to the reverse rotation of the molecular motor, the problem was left unsolved.

4) The Dynamics of Thermal Isomerization of the Unstable trans-Olefin 2d into the Stable trans-Olefin 2a

The thermal isomerization reaction **2d** → **2a** was similarly monitored as follows; a sample of **2d/2c** (80:20) in CD_2Cl_2, for example, was prepared as described above, and ^{1}H-NMR spectra were measured at –9.9 °C at intervals of 3–10 min (Figure 13), the amount of unstable *trans*-olefin **2d** being determined from the peak intensities of the methyl groups of **2d** and **2a**. Rate constants at –9.9, –14.9, –19.9, and –24.9 °C were obtained from first-order reaction kinetic equations, where $R = 0.999$–0.996. An activation energy $E_a = 17.1\ \text{kcal mol}^{-1}$ was obtained from the Arrhenius plot with $R = 0.999$ (Figure 14), whilst an activation enthalpy $\Delta H^{\ddagger} = 16.5\ \text{kcal mol}^{-1}$ and an activation entropy $\Delta S^{\ddagger} = -9.23\ \text{cal K}^{-1}\text{mol}^{-1}$ were obtained from the Eyring plot with $R = 0.999$.

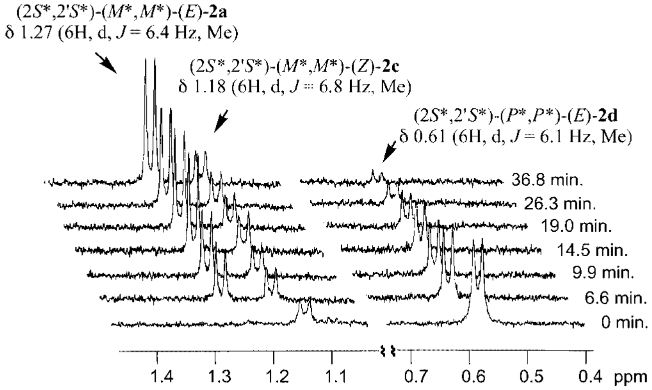

Figure 13. Dynamics of the thermal isomerization of the unstable *trans*-olefin $(2S^*,2'S^*)$-(P^*,P^*)-(E)-**2d** into the stable *trans*-olefin $(2S^*,2'S^*)$-(M^*,M^*)-(E)-**2a** at –9.9 °C as monitored by ^{1}H NMR (400 MHz, CD_2Cl_2).

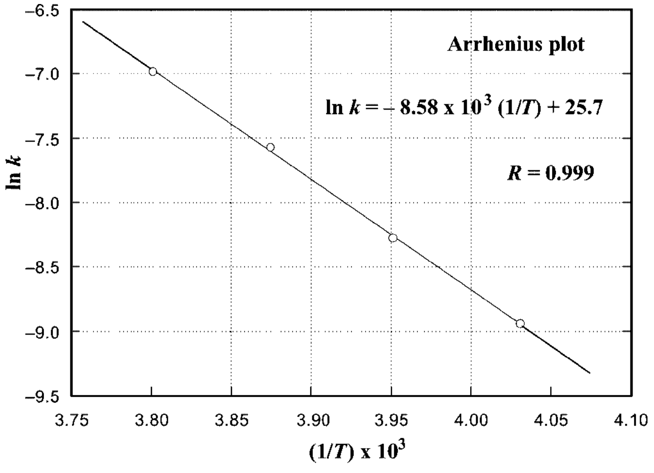

Figure 14. Arrhenius plot for the thermal isomerization of the unstable *trans*-olefin $(2S^*,2'S^*)$-(P^*,P^*)-(E)-**2d** into the stable *trans*-olefin $(2S^*,2'S^*)$-(M^*,M^*)-(E)-**2a** as monitored by ^{1}H NMR (400 MHz, CD_2Cl_2).

The Dynamics of the Molecular Motor Rotation Studied by CD Spectroscopy with a Chiral Sample

1) The Photodynamics of the Transformation of the Stable trans-Olefin 2a into the Unstable cis-Olefin 2b and Those of the Reverse Reaction

A solution of enantiopure [CD(–)257.8]-$(2S,2'S)$-(M,M)-(E)-(–)-**2a** in MeOH was irradiated with 312 nm (±12 nm) UV light for a total of 20.5 s, during which the photoreaction was monitored at intervals of 2–8 s by CD spectroscopy, measured at –25 °C (Figure 15), with the ratio of the unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** to the stable *trans*-olefin **2a** being determined from the CD intensity at 233.0 nm. As can be seen in Figure 16, the reaction had reached photoequilibrium after 20.5 s irradiation, and the **2b**/**2a** ratio at the final stage was 94:6. The photochemical transformation of **2a** into **2b** under the CD measurement conditions is thus much faster than under the ^{1}H-NMR measurement conditions, because of the efficiency of UV irradiation.

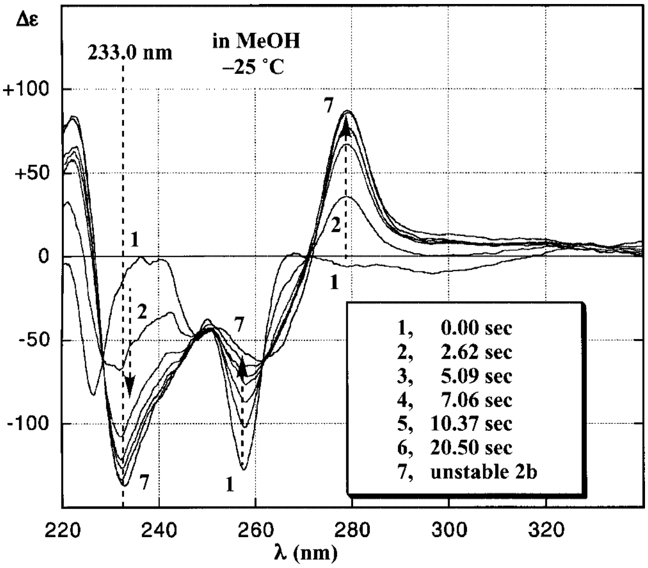

Figure 15. CD spectral changes due to the photoisomerization of the stable *trans*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*E*)-**2a** into the unstable *cis*-olefin (2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** on UV irradiation at 312 nm (±12 nm) at –78 °C, as monitored by CD at –25 °C.

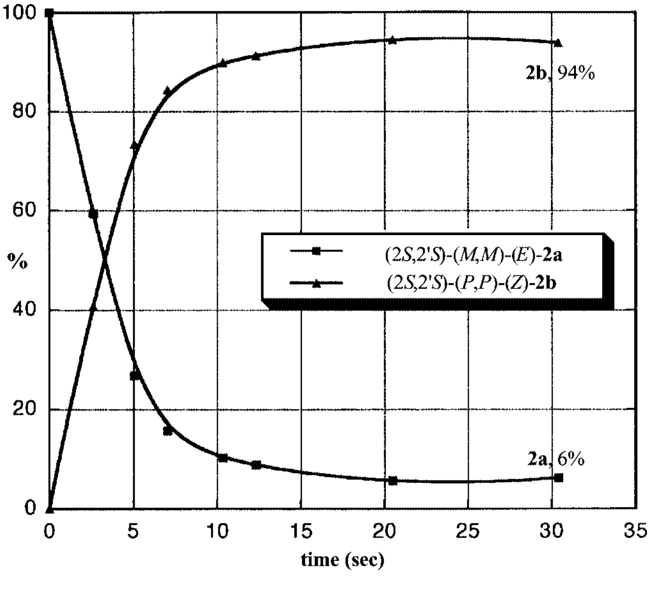

Figure 16. Dynamics of the photoisomerization of the stable *trans*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*E*)-**2a** into the unstable *cis*-olefin (2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** on UV irradiation at 312 nm (±12 nm) and at –78 °C as monitored by CD at –25 °C.

The reverse reaction **2b** → **2a** was carried out similarly; a solution of enantiopure unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** in MeOH was irradiated with 430 nm (±12 nm) visible light at –78 °C. At intervals of 0.8–25 s, the reaction was monitored by CD spectroscopy performed at –33 °C, and the **2b**/**2a** ratio was determined. After 65 s irradiation, the unstable *cis*-olefin **2b** had completely converted into the stable *trans*-olefin **2a**.

2) The Dynamics of the Thermal Isomerization of the Unstable cis-Olefin 2b into the Stable cis-Olefin 2c

The thermal isomerization reaction **2b** → **2c** was monitored by CD spectroscopy as follows: CD spectra of the enantiopure unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** in methanol were measured at 14.8 °C at intervals of 30 min (Figure 17), with the ratio of the unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** to the stable

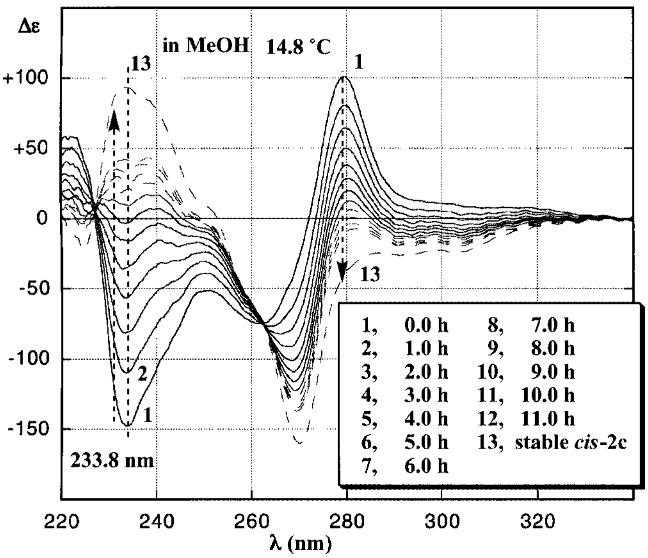

Figure 17. CD spectral changes due to the thermal isomerization of the unstable *cis*-olefin (2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** into the stable *cis*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*Z*)-**2c** at 14.8 °C.

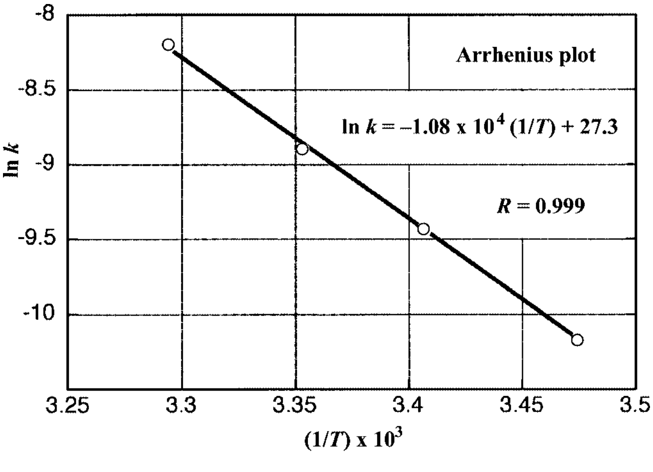

Figure 18. Arrhenius plot for the thermal isomerization of the unstable *cis*-olefin (2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** into the stable *cis*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*Z*)-**2c** as monitored by CD.

cis-olefin [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** being determined from the CD intensity at 233.8 nm. Rate constants were obtained at 14.8, 20.5, 25.2, and 30.5 °C from first-order reaction kinetic equations, where R = 0.999–0.997. An activation energy E_a = 21.4 kcal mol^{-1} was obtained from the Arrhenius plot with R = 0.999 (Figure 18), whilst an activation enthalpy $\Delta H^{\ddagger}$ = 20.8 kcal mol^{-1} and an activation entropy $\Delta S^{\ddagger}$ = –6.30 cal K^{-1}mol^{-1} were obtained similarly from the Eyring plot with R = 0.999. The obtained activation Gibbs energy [$\Delta G^{\ddagger}$(293) = 22.7 kcal mol^{-1}] is similar to that reported by the Feringa group.[3]

3) The Photodynamics of the Transformation of the Stable cis-Olefin 2c into the Unstable trans-Olefin 2d and Those of the Backward Reaction

A solution of the enantiopure stable *cis*-olefin [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** in MeOH was irradiated with UV light at 330 nm (±12 nm) for a total of 23.0 s, during which the photoreaction was monitored at 1–5 s intervals by CD spectroscopy measured at –60 °C (Figure 19), with the ratio of the unstable *trans*-olefin [CD(+)269.0]-(2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** to the stable *cis*-olefin **2c** being determined from the CD intensity at 270.0 nm. As can be seen in Figure 20, the reaction had reached photoequilibrium after 23.0 s irradiation, and the **2d**/**2c** ratio at this stage was 93:7.

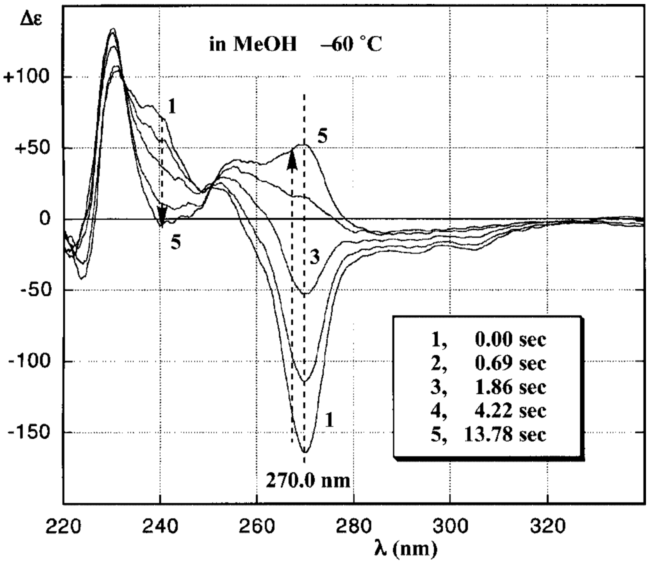

Figure 19. CD spectral changes due to the photoisomerization of the stable *cis*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*Z*)-**2c** into the unstable *trans*-olefin (2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** on UV irradiation at 330 nm (±12 nm) and at –78 °C, as monitored by CD at –60 °C.

The reverse reaction **2d** → **2c** was studied similarly; the sample of **2d**/**2c** (93:7) formed as described above was irradiated with 430 nm (±12 nm) visible light at –78 °C and the reaction was monitored at intervals of 4–20 s by CD spectroscopy performed at –60 °C. After 90 s irradiation, the **2d**/**2c** ratio at photoequilibrium was 20:80. This ratio almost agrees with that (**2d**/**2c** = 25:75) determined by ^{1}H-NMR spectra.

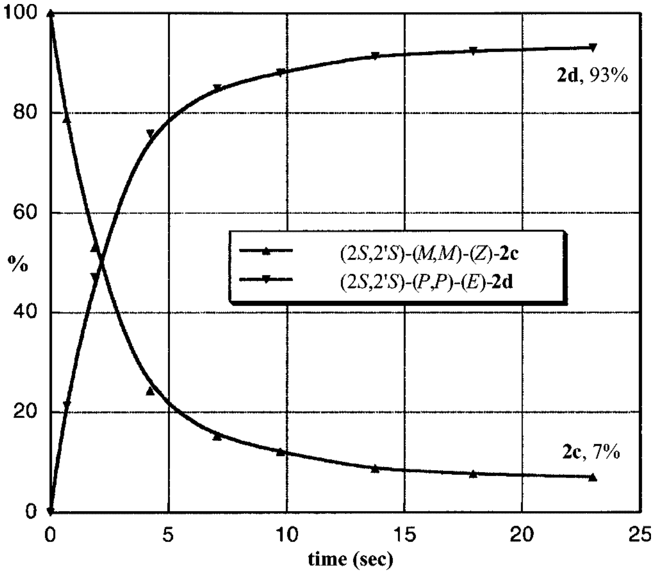

Figure 20. Dynamics of the photoisomerization of the stable *cis*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*Z*)-**2c** into the unstable *trans*-olefin (2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** on UV irradiation at 330 nm (±12 nm) and at –78 °C, as monitored by CD at –60 °C.

4) The Dynamics of the Thermal Isomerization of the Unstable trans-Olefin 2d into the Stable trans-Olefin 2a

The thermal isomerization reaction **2d** → **2a** was monitored as follows; CD spectra of the solution of **2d**/**2c** (93:7) in MeOH were measured at –19.1 °C at intervals of 30 min (Figure 21) and the ratio of the unstable *trans*-olefin [CD(+)269.0]-(2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** to the stable *trans*-olefin [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** was deter-

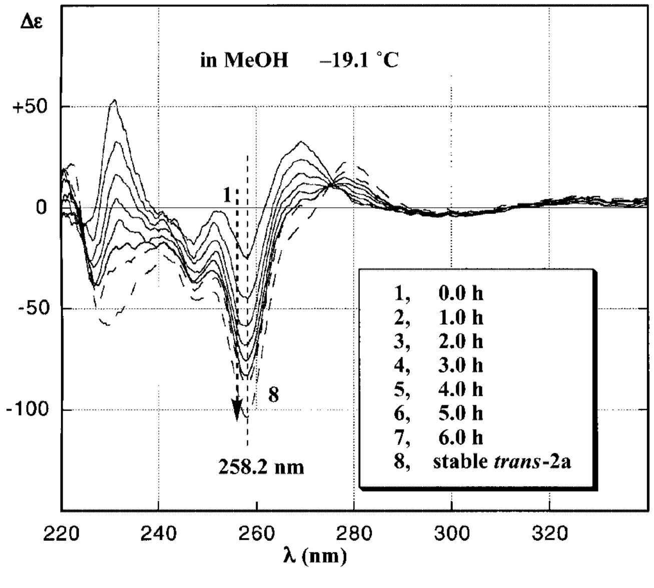

Figure 21. CD spectral changes due to the thermal isomerization of the unstable *trans*-olefin (2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** into the stable *trans*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*E*)-**2a** at –19.1 °C.

mined from the CD intensity at 258.2 nm. Rate constants at –30.8, –28.0, –23.5, –19.1, –16.7, and –14.0 °C were obtained from first-order reaction kinetic equations, where R = 1.000–0.996. An activation energy E_a = 16.8 kcal mol^{-1} was obtained from the Arrhenius plot with R = 0.975 (Figure 22), whilst an activation enthalpy $\Delta H^{\ddagger}$ = 16.3 kcal mol^{-1} and an activation entropy $\Delta S^{\ddagger}$ = –12.6 cal K^{-1} mol^{-1} were similarly obtained from the Eyring plot with R = 0.974. The obtained activation Gibbs energy [$\Delta G^{\ddagger}(293)$ = 20.0 kcal mol^{-1}] is comparable with that reported by the Feringa group.[3]

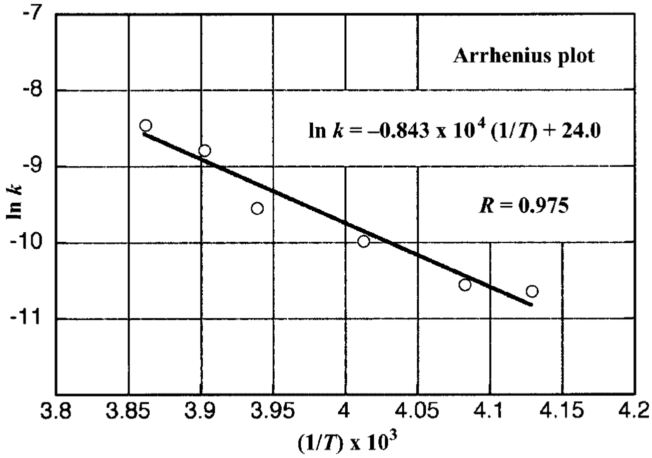

Figure 22. Arrhenius plot for the thermal isomerization of the unstable *trans*-olefin (2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** into the stable *trans*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*E*)-**2a** as monitored by CD.

Comparison of the Molecular Motor Rotation Dynamics Data Obtained by ^{1}H-NMR and CD Spectral Methods

The molecular motor rotation dynamics data are summarized in Table 2. The first rotation step **2a** → **2b** is much faster under the conditions of CD measurement than under the conditions of ^{1}H-NMR measurement because of the photoirradiation efficiency, so the speed of the photochemical rotation step essentially depends on the photoirradiation conditions. As can be seen in Table 2, as the motor can rotate "backwards" (e.g., **2b** → **2a**), the direction of motor rotation has to be controlled by choosing the light wavelength. Namely, the motor rotates "forwards" on UV irradiation at 312 nm, reaching photoequilibrium in 20 s with the **2b**/**2a** ratio = 94:6.

The second rotation step **2b** → **2c** is thermally controlled, and the kinetic data listed in Table 2 were obtained. The data obtained by ^{1}H-NMR and CD methods are a little different from each other, which may be due to experimental errors and/or to the difference in solvent (CD_2Cl_2 and MeOH).

The third step of motor rotation **2c** → **2d** is again faster under the CD measurement conditions, under which the motor rotates forwards on irradiation with 330 nm UV light, reaching the photoequilibrium state in 23 s with the **2d**/**2c** ratio = 93:7.

Table 2. The dynamics data for the molecular motor rotation as monitored by ^{1}H-NMR and CD spectral methods.

Motor rotation	Studied by ^{1}H NMR 400 MHz, in CD_2Cl_2	Studied by CD in MeOH
Forward rotation stable **2a** → unstable olefin **2b**[a]	15 min	20.5 s
$h\nu$, 312 nm[b]	**2b/2a** = 91:9	**2b/2a** = 94:6
Backward rotation unstable **2b** → stable olefin **2a**[a]	4 min	90 s
$h\nu$, 430 nm[b]	**2b/2a** = 0:100	**2b/2a** = 0:100
Forward rotation unstable **2b** → stable olefin **2c**	E_a = 20.7 $\Delta H^{\ddagger}$ = 20.1	E_a = 21.4 $\Delta H^{\ddagger}$ = 20.8
thermal[c]	$\Delta S^{\ddagger}$ = –6.17 R = 0.999, 0.999	$\Delta S^{\ddagger}$ = –6.30 R = 0.999, 0.999
Forward rotation stable **2c** → unstable olefin **2d**[a]	12 min	23 s
$h\nu$, 330 nm[b]	**2d/2c** = 96:4	**2d/2c** = 93:7
Backward rotation unstable **2d** → stable olefin **2c**[a]	60 min	90 s
$h\nu$, 430 nm[b]	**2d/2c** = 25:75	**2d/2c** = 20:80
Forward rotation unstable **2d** → stable olefin **2a**	E_a = 17.1 $\Delta H^{\ddagger}$ = 16.5	E_a = 16.8 $\Delta H^{\ddagger}$ = 16.3
thermal[c]	$\Delta S^{\ddagger}$ = –9.23 R = 0.999, 0.999	$\Delta S^{\ddagger}$ = –12.6 R = 0.975, 0.974

[a] Time to photoequilibrium. [b] Ratio at photoequilibrium. [c] Activation energy E_a and activation enthalpy $\Delta H^{\ddagger}$ in kcal mol^{-1} unit: activation enthalpy $\Delta S^{\ddagger}$ in cal K^{-1} mol^{-1} unit; the values of correlation coefficient R for Arrhenius and Eyring plots, respectively.

Kinetic studies of the fourth step of rotation **2d** → **2a** by CD were difficult because of the instability of **2d**, so the Arrhenius and Eyring plots obtained by CD deviated a little from straight lines, as indicated by the smaller values of the correlation coefficient (R = 0.975–0.973). However, the ^{1}H-NMR method was very useful for a case such as the extremely unstable *trans*-olefin **2d**, because the ^{1}H-NMR peaks of **2d** and **2a** were separately observable, and their peak intensities could be clearly evaluated, kinetic parameters therefore being exactly determined with R = 0.999. It should be noted that both methods gave almost similar values of kinetic parameters, as shown in Table 2. The activation energy E_a = 17.1–16.8 kcal mol^{-1} was much lower than that found with the motor of six-membered ring type (E_a = 24.8 kcal mol^{-1}), so the new motor rotates much more rapidly at the fourth thermal step.

Continuous Rotation of the New Model of Molecular Motor as Monitored by the CD Method

Continuous rotation experiments were carried out as follows: 1) for the first rotation step, a solution of the enantiopure stable *trans*-olefin **2a** in *n*-pentanol was irradiated with UV light at 312 nm (±12 nm) at –78 °C for 30 s and its CD spectrum was measured at –50 °C, 2) for the second rotation step, the solution was next heated at 120 °C for 20 s, and its CD spectrum was measured at –50 °C, 3) for the third rotation step, the solution was irradiated with UV light at 330 nm (±12 nm) at –78 °C for 30 s and its CD spectrum was measured at –50 °C, and 4) for the fourth rotation step, the solution was heated at 120 °C for 10 s, and its CD spectrum was measured at –50 °C. Those operations were repeated ten times as shown in Figure 23, with the CD intensity at 275 nm plotted after each operation. One cycle of operations (i. e., 360° rotation of the motor) took 90 s under these condition, and the CD still keeps intensities of similar levels even after ten rotations, indicating that the molecular motor rotates continuously and is durable for such operations.

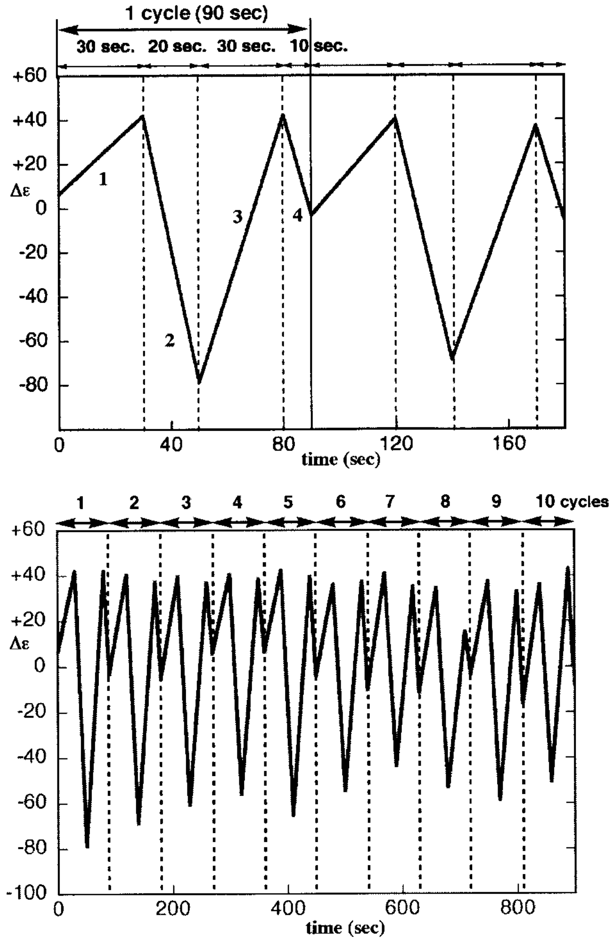

Figure 23. Continuous rotation of the new molecular motor **2** as monitored by CD.

Conclusions

The mechanism and dynamics of the light-powered chiral molecular motor **2** of five-membered ring type have been studied by the ^{1}H-NMR method with a racemic sample and also by the CD method with an enantiopure sample, with the absolute stereostructures of the unstable motor rotation isomers having been unambiguously determined. Through those studies, the mechanism of the photochemical rotation steps was clarified, and kinetic data for the thermal one-directional rotation steps were obtained. As expected in the design of this new model, the fourth thermal rotation step was much accelerated, in relation to the motor of six-membered ring type. In the case of the molecular motor starting from [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a**, it was established that the chiral motor rotates clockwise as illustrated in Figure 3, because the direction of motor rotation is controlled by the molecular chirality of the motor. It is therefore natural that the motor with the opposite chirality should rotate counterclockwise. Furthermore, it was demonstrated that the motor **2** rotates continuously on repetition of the operations of UV irradiation and heating, and is durable for such continuous rotation.

Experimental Section

General Methods: UV irradiation of olefin compounds was performed with a Bunkoukeiki SM-25 Hypermonolight apparatus with a 300 W Xenon lamp: wavelength variable in the region of 250–1000 nm, light bandwidth ±12 nm. The HPLC separation of unstable compounds was carried out at –40 °C with a prepacked glass column (15 φ × 300 mm) of ODS (particle size 20 µm) from Kusano Co., Ltd., and a Shimamura YRU-880UV/RI detector, with the solvent, column, and receiver cooled to –40 °C with an Eyela PSL-1800 low-temp. bath. ^{1}H-NMR spectra were recorded on Jeol JNM-LA400 (400 MHz) and/or Jeol JNM-LA600 (600 MHz) spectrometers. All NMR spectroscopic data for $CDCl_3$ or CD_3OD solutions are reported as δ values (ppm) downfield from TMS. In the case of CD_2Cl_2 solutions, the signal of $CHDCl_2$ was used as the internal standard of chemical shift.

Correction of the CD Intensity Data Measured at Low Temperature:[4] The $\Delta\varepsilon$ values were corrected for volume contraction by the following equations and parameters:

$$\Delta\varepsilon(\text{corrected}) = \Delta\varepsilon(\text{uncorrected})V^t_{20}$$

$$V^t_{20} = 1 + \alpha\{(T-20)/1000\} + \beta\{(T-20)/1000\}^2$$

With use of the values of $\alpha = 1.233$, $\beta = 1.11$ reported for MeOH.

Isolation of Racemic and Chiral Unstable *cis*-Olefin 2b – [CD(+)-279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-2,2'-Dimethyl-2,2',3,3'-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene]: A small Pyrex vial containing a solution of the racemic stable *trans*-olefin **2a** (2.5 mg) in CH_2Cl_2 (0.2 mL) was immersed in methanol cooled to –78 °C in a quartz Dewar vessel fitted with windows. The solution was irradiated with UV light at 312 nm (±12 nm) for 30 min, and was then injected by cold pipette into the HPLC column, cooled to –40 °C. The HPLC separation of unstable and stable olefins was carried out at –40 °C on an ODS column (15 φ × 300 mm, MeOH), with solvent and the column cooled to –40 °C. The desired unstable *cis*-olefin **2b** was obtained as the fraction eluted second, and was collected in a flask cooled to –78 °C. The solution was evaporated in vacuo at –40 to –30 °C, the evaporated solvent being collected in a trap cooled with liquid nitrogen. The unstable *cis*-olefin **2b** was obtained as yellow powder, which was dissolved in CD_2Cl_2 cooled to –40 °C, and its ^{1}H-NMR spectrum was immediately measured at –30 °C.

The chiral stable *trans*-olefin [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** was treated similarly, yielding the chiral unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b**, the CD spectrum of which was measured at –32.5 °C. The concentration of the chiral unstable *cis*-olefin **2b**, necessary for the calculation of CD $\Delta\varepsilon$ values, was determined as follows; after the CD measurement, the solution was allowed to stand at room temperature overnight, during which time the unstable chiral *cis*-olefin **2b** completely converted into the stable chiral *cis*-olefin **2c**. The concentration of **2c** (i.e., that of **2b**) was determined from the UV spectrum of the solution, as the UV ε values of the stable *cis*-olefin **2c** are already known.

^{1}H-NMR Detection of the Unstable Racemic *trans*-Olefin 2d and the CD Spectrum of the Unstable Chiral *trans*-Olefin 2d – [CD(+)-269.0]-(2*S*,2′*S*)-(*P*,*P*)-(*E*)-2,2’-Dimethyl-2,2’,3,3’-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene]: A quartz NMR tube containing a solution of the stable racemic *cis*-olefin **2c** (0.793 mg) in CD_2Cl_2 (0.5 mL) was immersed in methanol cooled to –78 °C in a quartz Dewar vessel fitted with windows. The solution was irradiated with UV light at 330 nm (±12 nm) for 12 min, during which the photoreaction was monitored by ^{1}H-NMR spectroscopy performed at –60 °C. The formation of the unstable *trans*-olefin **2d** was followed by ^{1}H-NMR spectroscopy, giving the data listed in Table 1, from which the structure was determined. After 12 min, the ratio of the unstable *trans*-olefin **2d** to the stable *cis*-olefin **2c** had reached 96:4.

A solution of the stable racemic *cis*-olefin **2c** (0.30 mg) in CD_3OD (0.5 mL) in a quartz NMR tube was similarly irradiated with UV light at 330 nm (±12 nm) and at –78 °C. After irradiation for 24 min, the ratio of the unstable *trans*-olefin **2d** to the stable *cis*-olefin **2c** had reached 93:7.

A proportion of the solution of the stable chiral *cis*-olefin [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** (0.1707 mg) in MeOH (5.0 mL) was placed in a quartz CD cell (1.0 mm) and was irradiated at –78 °C with UV light at 330 nm (±12 nm). The photoreaction was monitored by CD spectroscopy performed at –60 °C. After irradiation for 18 s, the reaction had reached the equilibrium state; the ratio of the unstable *trans*-olefin **2d** to the stable *cis*-olefin **2c** was estimated as 93:7.

The Photodynamics of the Transformation of the Stable *trans*-Olefin 2a into the Unstable *cis*-Olefin 2b and those of the Reverse Reaction as Monitored by ^{1}H-NMR Spectroscopy with a Racemic Sample: A quartz NMR tube containing a solution of the stable racemic *trans*-olefin **2a** (0.533 mg) in CD_2Cl_2 (0.5 mL) was immersed in methanol cooled to –78 °C in a quartz Dewar vessel containing windows. The solution was irradiated with UV light at 330 nm (±12 nm) for 15 min in total, during which the photoreaction was monitored at intervals of 1–3 min by ^{1}H-NMR spectroscopy performed at –20 °C. The ratio of the unstable *cis*-olefin **2b** to the stable *trans*-olefin **2a** was calculated from the peak intensities of H3eq of **2b** (δ = 3.16 ppm) and **2a** (δ = 2.33 ppm). After 15 min irradiation, the **2b/2a** ratio at photoequilibrium was 91:9.

The reverse photoreaction **2b** → **2a** was carried out as follows; the sample of **2b/2a** (91:9) was irradiated with 430 nm (±12 nm) visible light at –78 °C. The reaction was monitored at intervals of 0.5–1 min by ^{1}H-NMR spectroscopy performed at –20 °C, and the ratio was determined. After 4 min irradiation, the **2b/2a** ratio was 0:100.

Dynamics of the Thermal Isomerization of the Unstable *cis*-Olefin 2b into the Stable *cis*-Olefin 2c as Monitored by ^{1}H-NMR Spectroscopy with a Racemic Sample: The thermal isomerization reaction **2b** → **2c** was monitored as follows; the sample of **2b/2a** (77:23) in CD_2Cl_2 (0.5 mL) was prepared as described above, and ^{1}H-NMR spectra were measured at 20 °C at intervals of 5–10 min, with the amount of unstable *cis*-olefin **2b** being determined from the peak intensities of the methyl groups of **2b** (δ = 1.63 ppm) and **2c** (δ = 1.21 ppm). Rate constants were obtained from first-order reaction kinetic equations: at 20 °C, ln[*cis*-**2b**] = (-1.62×10^{-2})t – 5.30, R = 0.999. Similar studies were carried out at 15 °C, 25 °C, and 30 °C, giving good linear equations: in all cases, R = 0.999. Rate constants were obtained from those data: at 15 °C, $k = 1.43\times10^{-4}\,\text{s}^{-1}$; at 20 °C, $k = 2.69\times10^{-4}\,\text{s}^{-1}$; at 25 °C, $k = 4.78\times10^{-4}\,\text{s}^{-1}$; at 30 °C, $k = 8.64\times10^{-4}\,\text{s}^{-1}$. The activation energy E_a = 20.7 kcal mol^{-1} was obtained from the Arrhenius plot with R = 0.999. Similarly the following kinetic data were obtained from the Eyring plot with R = 0.999: activation enthalpy $\Delta H^{\ddagger}$ = 20.7 kcal mol^{-1} and activation entropy $\Delta S^{\ddagger}$ = –6.17 cal K^{-1} mol^{-1}.

The Photodynamics of the Transformation of the Stable *cis*-Olefin 2c into the Unstable *trans*-Olefin 2d and those of the Reverse Reaction as Monitored by ^{1}H-NMR Spectroscopy with a Racemic Sample: A quartz NMR tube containing a solution of the stable racemic *cis*-olefin **2c** (0.793 mg) in CD_2Cl_2 (0.5 mL) was immersed in methanol cooled to –78 °C in a quartz Dewar vessel fitted with windows. The solution was irradiated with UV light at 330 nm (±12 nm) for 12 min in total, during which the photoreaction was monitored at intervals of 1–2 min by ^{1}H-NMR spectroscopy performed at –60 °C. The ratio of unstable *trans*-olefin **2d** to stable *cis*-olefin **2c** was calculated from the peak intensities of the methyl groups of **2d** (δ = 0.58 ppm) and **2c** (δ = 1.21 ppm). After 12 min irradiation, the **2d/2c** ratio at photoequilibrium was 96:4. When the ^{1}H-NMR spectra were measured at –30 °C, the formation of the stable *trans*-olefin **2a** and the unstable *cis*-olefin **2b** was observed.

The reverse photoreaction **2d** → **2c** was monitored as follows; the sample of **2d/2c** (86:14) was irradiated with 430 nm (±12 nm) visible light at –78 °C. At intervals of 1–20 min, the reaction was monitored by ^{1}H-NMR spectroscopy performed at –60 °C, and the ratio was determined. After 60 min irradiation, the final **2d/2c** ratio at photoequilibrium was 25:75.

The Dynamics of the Thermal Isomerization of the Unstable *trans*-Olefin 2d into the Stable *trans*-Olefin 2a as Monitored by ^{1}H-NMR Spectroscopy with a Racemic Sample: The thermal isomerization reaction **2d** → **2a** was monitored as follows; as an example, a sample of **2d/2c** (80:20) in CD_2Cl_2 (0.5 mL) was prepared as described above, and ^{1}H-NMR spectra were measured at –9.9 °C at intervals of 3–10 min. The amount of the unstable *trans*-olefin **2d** was determined from the peak intensities of the methyl groups of **2d** (δ = 0.58 ppm) and **2a** (δ = 1.30 ppm). The rate constant was obtained from first-order reaction kinetic equations: at –9.9 °C, ln[*trans*-**2d**] = (-5.56×10^{-2})t – 5.31, R = 0.996. Similar studies were carried out at –14.9 °C, –19.9 °C, and –24.9 °C, giving good linear equations: in those cases, R = 0.999–0.997. Rate constants were obtained from those data: at –24.9 °C, $k = 1.31\times10^{-4}\,\text{s}^{-1}$; at –19.9 °C, $k = 2.55\times10^{-4}\,\text{s}^{-1}$; at –14.9 °C, $k = 5.15\times10^{-4}\,\text{s}^{-1}$; at –9.9 °C, $k = 9.27\times10^{-4}\,\text{s}^{-1}$. The activation energy (E_a = 17.1 kcal mol^{-1}) was obtained from the Arrhenius plot with R = 0.999. The following kinetic data were obtained similarly from the Eyring plot with R = 0.999: activation enthalpy $\Delta H^{\ddagger}$ = 16.5 kcal mol^{-1} and activation entropy $\Delta S^{\ddagger}$ = –9.23 cal K^{-1} mol^{-1}.

The Photodynamics of the Transformation of the Stable *trans*-Olefin 2a into the Unstable *cis*-Olefin 2b and those of the Reverse Reaction as Monitored by CD Spectroscopy with an Enantiopure Sample: A proportion of the solution of [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** (0.181 mg) in MeOH (5 mL) was placed in a quartz CD cell (1.0 mm), which was immersed in methanol cooled to –78 °C in a quartz Dewar vessel fitted with windows. The solution was irradiated with UV light at 312 nm (±12 nm) for 20.5 s in total, during which the photoreaction was monitored at intervals of 2–8 s by CD spectroscopy performed at –25 °C. The ratio of unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** to stable *trans*-olefin **2a** was calculated from the CD intensity at 233.0 nm, with use of the $\Delta\varepsilon$ values of enantiopure **2a** and **2b** as standards. After 20.5 s irradiation, the **2b/2a** ratio at photoequilibrium was 94:6.

The reverse photoreaction **2b** → **2a** was carried out as follows; the sample of **2b/2a** (94:6) was irradiated with 430 nm (±12 nm) visible light at –78 °C. At intervals of 0.8–25 s, the reaction was monitored by CD spectroscopy performed at –33 °C, and the **2b/2a** ratio was determined. After irradiation for 65 s, the **2b/2a** ratio was 0:100.

Dynamics of the Thermal Isomerization of the Unstable *cis*-Olefin 2b into the Stable *cis*-Olefin 2c as Monitored by CD Spectroscopy with an Enantiopure Sample: The thermal isomerization reaction **2b** → **2c** was monitored as follows; as an example, a proportion of the methanol solution of the enantiopure unstable *cis*-olefin **2b** isolated by HPLC at –40 °C as described above was placed in a CD cell (1.0 mm) and its CD spectra was measured at 14.8 °C at intervals of 30 min. The ratio of the unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** to the stable *cis*-olefin [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** was calculated from the CD intensity at 233.8 nm, with use of the $\Delta\varepsilon$ values of enantiopure **2b** and **2b** as standards and $\Delta\varepsilon$ values were corrected for volume contraction. The rate constant was obtained from first-order reaction kinetic equations: at 14.8 °C, $\ln[cis\text{-}\mathbf{2b}] = (-2.33\times10^{-3})t - 8.78$, $R = 0.998$. Similar measurements were carried out at 20.5 °C, 25.2 °C, and 30.5 °C, giving good linear equations with R = 0.999–0.997. Rate constants were obtained from those data: at 14.8 °C, $k = 3.88\times10^{-5}\,\mathrm{s}^{-1}$; at 20.5 °C, $k = 8.06\times10^{-5}\,\mathrm{s}^{-1}$; at 25 °C, $k = 1.37\times10^{-4}\,\mathrm{s}^{-1}$; at 30.5 °C, $k = 2.74\times10^{-4}\,\mathrm{s}^{-1}$. The activation energy (E_a = 21.4 kcal mol^{-1}) was obtained from the Arrhenius plot with $R = 0.999$. The following kinetic data were similarly obtained from the Eyring plot with $R = 0.999$: activation enthalpy $\Delta H^{\ddagger}$ = 20.8 kcal mol^{-1} and activation entropy $\Delta S^{\ddagger}$ = –6.30 cal K^{-1} mol^{-1}.

Photodynamics of the Transformation of the Stable *cis*-Olefin 2c into the Unstable *trans*-Olefin 2d and those of the Reverse Reaction as Monitored by CD Spectroscopy with an Enantiopure Sample: A proportion of the solution of the enantiopure stable *cis*-olefin [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** (0.171 mg) in MeOH (5 mL) was placed in a quartz CD cell (1.0 mm), which was immersed in methanol cooled to –78 °C in a quartz Dewar vessel fitted with windows. The solution was irradiated with UV light at 330 nm (±12 nm) for 23.0 s in total, during which the photoreaction was monitored at intervals of 1–5 s by CD spectroscopy performed at –60 °C. The ratio of the unstable *trans*-olefin [CD(+)269.0]-(2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** to the stable *cis*-olefin **2c** was calculated from the CD intensity at 270.0 nm, with use of the $\Delta\varepsilon$ value of enantiopure **2c** as the standard and with correction of the $\Delta\varepsilon$ values for volume contraction, and the final **2d/2c** ratio at photoequilibrium was estimated as 93:7, as had been obtained from the ^{1}H-NMR (400 MHz, CD_3OD) spectrum of another sample measured at –50 °C.

The reverse photoreaction **2d** → **2c** was monitored as follows; the sample of **2d/2c** (93:7) was irradiated with 430 nm (±12 nm) visible light at –78 °C. The reaction was monitored at intervals of 4–20 s by CD spectroscopy performed at –60 °C, and the **2d/2c** ratios were determined. After 90 s irradiation, the **2d/2c** ratio at photoequilibrium was 20:80.

Dynamics of the Thermal Isomerization of the Unstable *trans*-Olefin 2d into the Stable *trans*-Olefin 2a as Monitored by CD Spectroscopy with an Enantiopure Sample: The thermal isomerization reaction **2d** → **2a** was monitored as follows; as an example, a sample of **2d/2c** (93:7) in MeOH was prepared as described above, and its CD spectra were measured at –19.1 °C at intervals of 30 min. The ratio of the unstable *trans*-olefin [CD(+)269.0]-(2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** to the stable *trans*-olefin [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** was calculated from the CD intensity at 258.2 nm, with use of the $\Delta\varepsilon$ value of enantiopure **2a** as the standard and correction of $\Delta\varepsilon$ values for volume contraction. The rate constant was obtained from first-order reaction kinetic equations: at –19.1 °C, $\ln[trans\text{-}\mathbf{2d}] = (-4.34\times10^{-3})t - 9.25$, $R = 1.000$. Similar measurements were carried out at –30.8 °C, –28.0 °C, –23.5 °C, –16.7 °C, and –14.0 °C giving good linear equations with R = 1.000–0.996. Rate constants were obtained from those data: at –30.8 °C, $k = 2.43\times10^{-5}\,\mathrm{s}^{-1}$; at –28.0 °C, $k = 2.64\times10^{-5}\,\mathrm{s}^{-1}$; at –23.5 °C, $k = 4.81\times10^{-5}\,\mathrm{s}^{-1}$; at –19.1 °C, $k = 7.23\times10^{-5}\,\mathrm{s}^{-1}$; at –16.7 °C, $k = 1.57\times10^{-4}\,\mathrm{s}^{-1}$; at –14.0 °C, $k = 2.18\times10^{-4}\,\mathrm{s}^{-1}$. The activation energy (E_a = 16.8 kcal mol^{-1}) was obtained from the Arrhenius plot with R = 0.975. The following kinetic data were obtained similarly from the Eyring plot with R = 0.974: activation enthalpy $\Delta H^{\ddagger}$ = 16.3 kcal mol^{-1} and activation entropy $\Delta S^{\ddagger}$ = –12.6 cal K^{-1} mol^{-1}.

Continuous Rotation of the New Model Molecular Motor

Step 1) Photochemical Rotation: A proportion of the solution of the enantiopure stable *trans*-olefin [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** (0.260 mg) in *n*-pentanol (5 mL) was placed in a quartz CD cell (1.0 mm), which was immersed in methanol cooled to –78 °C in a quartz Dewar vessel fitted with windows. The solution was irradiated with UV light at 312 nm (±12 nm) for 30 s, and its CD spectrum was then measured at –50 °C.

Step 2) Thermal Rotation: The above solution containing the unstable *cis*-olefin [CD(+)279.2]-(2*S*,2′*S*)-(*P*,*P*)-(*Z*)-**2b** as a major component was heated at 120 °C for 20 s by immersion in an oil bath, and its CD spectrum was then measured at –50 °C.

Step 3) Photochemical Rotation: The above solution containing the stable *cis*-olefin [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** as a major component was irradiated with UV light at 330 nm (±12 nm) for 30 s, and its CD spectrum was then measured at –50 °C.

Step 4) Thermal Rotation: The above solution containing the unstable *trans*-olefin [CD(+)269.0]-(2*S*,2′*S*)-(*P*,*P*)-(*E*)-**2d** as a major component was heated at 120 °C for 10 s by immersion in an oil bath, and its CD spectrum was then measured at –50 °C.

The one-cycle rotation of the molecular motor **2** consists of the operations step 1) → step 2) → step 3) → step 4), and each rotation step was monitored by CD spectra. By repetition of those operations, a continuous rotation of 10 cycles was achieved, with changes of CD intensity at 275 nm being plotted.

Supporting Information: Supporting Information for this article is available on the WWW under http://www.eurjoc.org or from the authors: Figure S01, ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2, –30 °C) of molecular motor rotation isomer, unstable *cis*-olefin (2*S**,2′*S**)-(*P**,*P**)-(*Z*)-**2b**. Figure S02, ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2, –50 °C) of molecular motor rotation isomer, unstable *trans*-olefin (2*S**,2′*S**)-(*P**,*P**)-(*E*)-**2d** (96%). The sample contained 4% of stable *cis*-olefin (2*S**,2′*S**)-(*M**,*M**)-(*Z*)-**2c**.

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[1] T. Fujita, S. Kuwahara, N. Harada, *Eur. J. Org. Chem.* **2005**, 0000–0000; see the preceding paper in this issue.
[2] N. Koumura, N. Harada, *Chem. Lett.* **1998**, 1151–1152.
[3] M. K. J. ter Wiel, R. A. van Delden, A. Meetsma, B. L. Feringa, *J. Am. Chem. Soc.* **2003**, *125*, 15076–15086.
[4] R. Passerini, I. G. Ross, *J. Sci. Instr.* **1953**, *30*, 274–276.

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