Chemistry of Unique Chiral Olefins. 2. Unexpected Thermal Racemization of *cis*-1,1′,2,2′,3,3′,4,4′-Octahydro-4,4′-biphenanthrylidene

Nobuyuki Harada,*[,1a,1b] Akira Saito,[1a] Nagatoshi Koumura,[1a] D. Christopher Roe,[1b] Wolter F. Jager,[1c] Robert W. J. Zijlstra,[1c] Ben de Lange,[1c] and Ben L. Feringa*[,1c]

Contribution from the Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980-77, Japan, Central Research & Development Department, Experimental Station, E. I. DuPont de Nemours and Company, Wilmington, Delaware 19880, and Department of Organic and Molecular Inorganic Chemistry, Groningen Centre for Catalysis and Synthesis, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

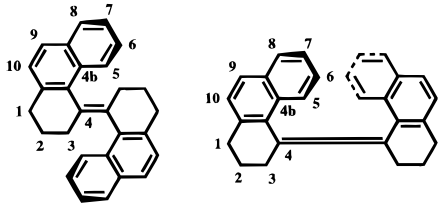
Received March 3, 1997[⊗]

Abstract: During the studies of the unique chiral olefins, (*E*)-1,1′,2,2′,3,3′,4,4′-octahydro-4,4′-biphenanthrylidene (**1**) and its (*Z*)-isomer (**2**), we found the unexpected thermal racemization of *cis*-olefin **2** at room temperature. The CD spectrum of optically active **2** shows rapid decrease of intensity with the half-life time $t_{1/2} = 1.2$ h at room temperature. After the CD Cotton effects vanish, the sample of *cis*-olefin **2** was checked by HPLC with a chiral stationary phase, and two enantiomers of *cis*-olefin **2** were detected, but *trans*-olefin **1** was never detected. The racemization of sterically more-hindered *cis*-olefin **2** occurs by the direct interconversion between the two enantiomers (*M,M*)-(*Z*)-**2** and (*P,P*)-(*Z*)-**2** without formation of *trans*-olefin **1** as an intermediate. The enantiomeric interconversion between the two enantiomers of **2** was also studied by the ^{1}H NMR magnetization transfer technique. The kinetic values of the enantiomeric interconversion of **2** were obtained by CD and NMR spectroscopic studies and lead to an activation energy $E_a = 21.5$ kcal mol^{-1}, activation enthalpy $\Delta H^{\ddagger} = 20.8$ kcal mol^{-1}, and activation entropy $\Delta S^{\ddagger} = -8.5$ cal K^{-1} mol^{-1}. The stereostructure of *cis*-olefin **2** was established by the X-ray crystallographic analysis. On the other hand, *trans*-olefin **1** does not racemize at room temperature, but can be observed to racemize at 55−95 °C. The kinetic values of the enantiomeric interconversion of **1** were obtained by polarimetric studies: activation energy $E_a = 25.2$ kcal mol^{-1}, activation enthalpy $\Delta H^{\ddagger} = 24.6$ kcal mol^{-1}, and activation entropy $\Delta S^{\ddagger} = -9.1$ cal K^{-1} mol^{-1}.

Introduction

In the preceding paper,[2,3] we reported the synthesis, enantioresolution, circular dichroism spectra, and theoretical determination of absolute stereochemistry of the unique chiral olefins, (*E*)-1,1′,2,2′,3,3′,4,4′-octahydro-4,4′-biphenanthrylidene (**1**) and its (*Z*)-isomer (**2**) (Chart 1).[4,5] During these studies, we found the strange phenomenon that the sterically more-hindered *cis*-olefin **2** with two overlapping naphthalene moieties racemizes at room temperature without formation of *trans*-olefin **1** as an intermediate. On the other hand, *trans*-olefin **1** does not racemize at room temperature. It is known that the sterically hindered hexahelicene and higher analogs racemize at elevated temperature.[6] Therefore, it is accepted that aromatic benzene rings are flexible to some extent. The racemization of chiral *cis*-olefin **2** is similar to that of heptahelicene in this sense. However, the remarkable difference is the fact that *trans*-olefin **1**, which seems sterically less-hindered, does not racemize at room temperature, while *cis*-olefin **2**, which seems sterically more-hindered, easily racemizes at room temperature. The racemization of chiral *trans*-olefin **1** needs a higher temperature. To confirm such easy racemization of *cis*-olefin **2** and to clarify its reaction mechanism, we studied the kinetics of enantiomeric interconversion between the two enantiomers of **2** by HPLC, CD, and NMR methods and established the stereochemistry of **2** by X-ray crystallography. *Trans*-olefin **1** was studied by HPLC and optical rotation methods.

Chart 1



Results and Discussion

Stability of Optically Pure *trans*-Olefin 1 Kept at Room Temperature Checked by HPLC Method. As discussed in the first paper of this series,[2] (±)-*trans*-olefin **1** was base-

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

(1) (a) Tohoku University. (b) E. I. DuPont de Nemours and Company. (c) University of Groningen.

(2) See papers of this series: (a) (part 1), Harada, N.; Saito, A.; Koumura, N.; Uda, H.; de Lange, B.; Jager, W. F.; Wynberg, H.; Feringa, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 7241. (b) (part 3), Harada, N.; Koumura, N.; Feringa, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 7256.

(3) See: Feringa, B.; Wynberg, H. *J. Am. Chem. Soc.* **1977**, *99*, 602.

(4) See also other chiral olefins: Feringa, B. L.; Jager, W. F.; de Lange, B.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5468. Jager, W. F.; de Jong, J. C.; de Lange, B.; Huck, N. P. M.; Meetsma, A.; Feringa, B. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 348 and references cited therein.

(5) See also: Huck, N. P. M.; Jager, W. F.; de Lange, B.; Feringa, B. L. *Science* **1996**, *273*, 1686. Feringa, B. L.; Huck, N. P. M.; van Doren, H. A. *J. Am. Chem. Soc.* **1995**, *117*, 9929 and references cited therein.

(6) For a review about (hetero)helicenes, see: (a) Prinsen, W. J. C.; Laarhoven, W. H. In *Topics in Current Chemistry 125*; Vögtle, F., Weber, E., Eds.; Springer-Verlag: Berlin, Heidelberg, 1984. (b) Martin, R. H. *Angew. Chem.* **1974**, *86*, 727. Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649. (c) Wynberg, H. *Acc. Chem. Res.* **1971,** *4*, 65.

S0002-7863(97)00668-9 CCC: $14.00

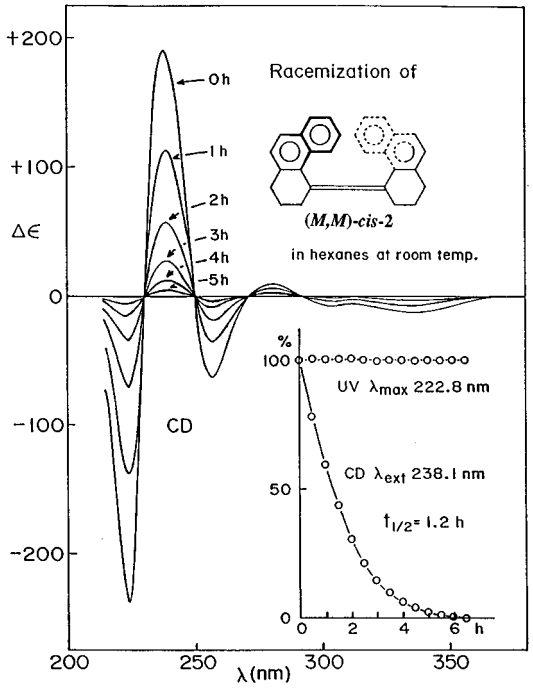


Figure 1. Decrease of CD intensity of the first-eluted *cis*-olefin [CD(+)238.1]-(*M,M*)-(*Z*)-**2** in hexane due to thermal racemization at room temperature.

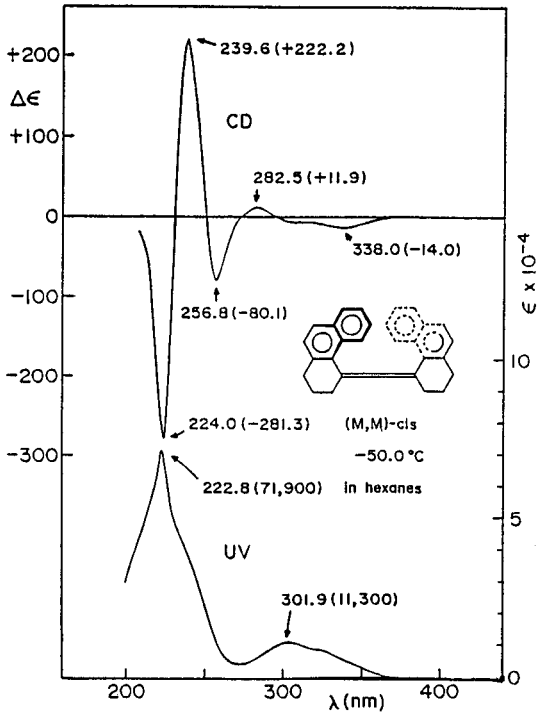


Figure 2. Observed CD and UV spectra of the first-eluted *cis*-olefin [CD(+)238.1]-(*M,M*)-(*Z*)-**2** in hexane −50 °C.

line-separated under the reverse phase condition of HPLC using a column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate) and methanol. It was found that the obtained optically pure enantiomers of *trans*-olefin were stable toward racemization at room temperature; after the optically pure first-eluted enantiomer (*M,M*)-*trans*-**1** was kept at room temperature for 2 days, the sample was subjected to HPLC under the same condition of the enantioresolution. The HPLC of the sample showed no peak corresponding to the other enantiomer (*P,P*)-*trans*-**1** (see the Supporting Information). It is thus obvious that *trans*-olefin **1** does not racemize at room temperature.

CD Spectra of *trans*-Olefin [CD(+)239.0]-(*M,M*)-(*E*)-1 Measured at −50 °C. The CD spectrum of the first-eluted enantiomer (*M,M*)-(*E*)-**1** was measured at −50 °C (223 K) using a cryostat (see the Supporting Information). The observed CD values were corrected for volume contraction by using the parameters of EtOH, $V^t_{20} = 0.929$ as described in the Experimental Section, because the parameter values for MeOH was not available from the literature:[7] CD (corrected, MeOH) λ_{ext} 330.3 nm ($\Delta\epsilon$ +23.2), 253.0 (−20.8), 238.5 (+55.6), 221.6 (−76.2), 213.9 (−150.5), where the concentration of the sample was determined from the UV absorption intensity. For *trans*-olefin [CD(+)239.0]-(*M,M*)-(*E*)-**1**, the CD spectra measured at room temperature and −50 °C are almost identical to each other in intensity indicating that compound **1** retains the same stable conformation at room temperature as that at −50 °C.

Unexpected Racemization of *cis*-Olefin [CD(+)238.1]-(*M,M*)-(*Z*)-2 Detected by CD Spectra. During our studies of enantioresolution and CD spectra of *cis*-olefin **2**, we found the surprising phenomenon that the CD intensity of *cis*-olefin **2** is dependent on time. When the CD spectra of the first-eluted enantiomer (*M,M*)-*cis*-**2** were measured consecutively at room temperature, the CD spectra decreased rapidly as shown in Figure 1 and the CD curve became totally flat after 6 h, while the UV spectrum kept its original pattern and intensity. The half-life time of CD intensity was ca. 1.2 h at room temperature.

(7) Passerini, R.; Ross, I. G. *J. Sci. Instr.* **1953**, *30*, 274.

These observations indicate that unlike *trans*-olefin **1**, *cis*-olefin **2** easily racemizes at room temperature. Therefore, the enantiomer of *cis*-olefin **2** resolved by HPLC at 3 °C as described in the first paper of this series may not have been enantiopure.[2a]

Enantioresolution of (±)-*cis*-Olefin 2 by HPLC at Low Temperature. To obtain the enantiopure *cis*-olefin **2**, the HPLC column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate) was connected in series with a short HPLC column of silica gel. The column system was cooled at −30 °C by circulating cold methanol in the column jacket and equilibrated with hexane as eluent. Receiver flasks for collecting eluate were placed in a dry ice/methanol bath (−70 °C). The sample of (±)-*cis*-**2** was injected as a hexane solution, and separation of enantiomers was monitored by a UV detector. The first-eluted fraction was collected, and its CD spectrum was immediately measured. As will be discussed later, since the decrease of CD intensity is less than 2% when a solution of the first-eluted enantiomer was kept at 0 °C for 40 min, the first-eluted enantiomer separated at −30 °C would be enantiopure.

CD Spectra of *cis*-Olefin [CD(+)238.1]-(*M,M*)-(*Z*)-2 Measured at −50 °C. The CD spectrum of the first-eluted enantiomer (*M,M*)-(*Z*)-**2** was measured at −50 °C (223 K) using a cryostat, and the observed CD values were corrected for volume contraction, $V^t_{20} = 0.906$ as described in the Experimental Section:[7] CD (corrected, hexane) λ_{ext} 338.0 nm ($\Delta\epsilon$ −14.0), 282.5 (+11.9), 256.8 (−80.1), 239.6 (+222.2), 224.0 (−281.3), where the concentration of the sample was determined from the UV absorption intensity (Figure 2). In comparison with the previous CD spectrum of (*M,M*)-(*Z*)-**2** illustrated in Figure 4 of the first paper of this series,[2a] the CD Cotton effects observed here were larger in their intensity by the factor of ca. 117%. From these CD data, the sample was considered to be almost enantiopure *cis*-olefin (*M,M*)-(*Z*)-**2**.

HPLC and CD Check of the First-Eluted Enantiomer of *cis*-Olefin 2 Kept at Room Temperature. The first-eluted enantiomer of *cis*-olefin **2** obtained by HPLC separation at −30 °C was kept in the dark at room temperature for 24 h, and then the sample was checked by HPLC under the same condition

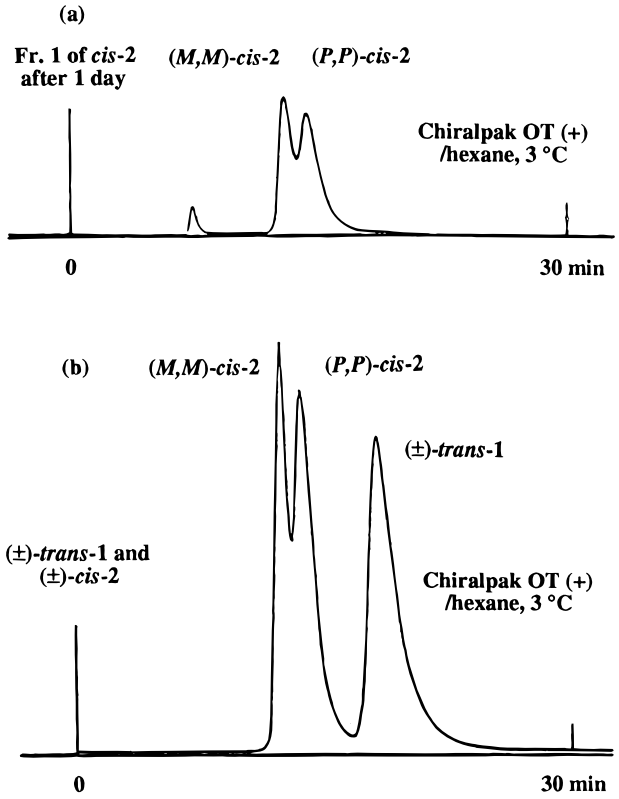


Figure 3. (a) Normal phase HPLC of the sample of (*M*,*M*)-(*Z*)-**2** kept at room temperature for 1 day. The Okamoto column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate) and hexane were used. (b) HPLC of a mixture of (±)-**1** and (±)-**2** under the same conditions.

used for separation. As shown in Figure 3, two peaks corresponding to (*M*,*M*)-*cis*-**2** and (*P*,*P*)-*cis*-**2** were observed. However, it is interesting that no peak corresponding to *trans*-olefin **1** was found. The CD spectra of the first- and second-eluted fractions obtained were identical with those of [CD(+)-238.1]-(*M*,*M*)-(*Z*)-**2** and [CD(−)238.1]-(*P*,*P*)-(*Z*)-**2**, respectively.

Racemization of *cis*-Olefin 2 through Diradical or Ionic Intermediates? As discussed above, it is very interesting that the sterically much-hindered *cis*-olefin **2** does undergo easy racemization at room temperature, while the less-hindered *trans*-olefin **1** does not racemize at room temperature. What reaction mechanism is applicable to the racemization of *cis*-olefin? One of the possible mechanisms of the racemization is the rotation around the central double bond. As the intermediate of racemization, photochemically excited diradical **3**[8] or cationic intermediate **4** are possible (Figure 4). However, these mechanisms can be ruled out because if these intermediates are involved, they should give rise to *trans*-olefin **1** in addition to *cis*-olefin **2**. As shown in Figure 3, the racemization of *cis*-olefin **2** is not accompanied by formation of *trans*-olefin **1**. It is clear that the racemization of *cis*-olefin occurs without the contribution of photochemistry and/or acid catalyzed reaction.

Kinetics of Racemization of *cis*-Olefin 2 Studied by CD Spectra.[9] To clarify the reaction mechanism, we measured the CD spectra of the first-eluted enantiomer [CD(+)238.1]-(*M*,*M*)-*cis*-**2** at various temperatures. To obtain the kinetic parameters of the racemization of *cis*-olefin **2**, the decrease of CD intensity at 238.1 nm was followed at various temperatures (0−24.9 °C). The sample was placed in a cryostat whose temperature was controlled within ±0.1−0.2 °C. The decrease of CD intensity

(8) Schuddeboom, W.; Jonker, S. A.; Warman, J. M.; de Haas, M. P.; Vermeulen, M. J. W.; Jager, W. F.; de Lange, B.; Feringa, B. L.; Fessenden, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 3286.

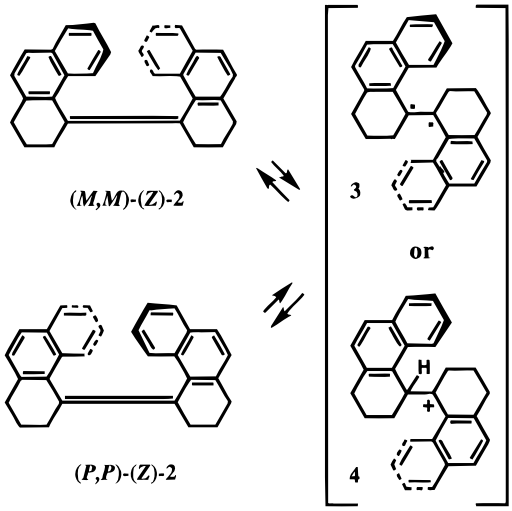


Figure 4. One of the possible reaction pathways of the racemization of *cis*-olefin **2**.

Table 1. Temperature Dependence of the Rate Constant of Enantiomeric Isomerization of (*Z*)-1,1′,2,2′,3,3′,4,4′-Octahydro-4,4′-biphenanthrylidene (**2**) Studied by CD and NMR Spectroscopic Methods

T (°C)	*k* (s^{-1})
CD in Hexane	
0.0	2.243×10^{-6}
9.8	6.747×10^{-6}
15.1	13.672×10^{-6}
19.9	22.142×10^{-6}
24.9	47.511×10^{-6}
^{1}H NMR in *o*-Xylene-d_{10}	
101.1	0.0845
111.2	0.1645
121.7	0.3310
130.2	0.6365
140.2	1.2090
150.2	2.1205

at 238.1 nm was recorded for 150 min and analyzed using the equations of first-order reaction. The rate constant (k') of the racemization and the rate constant of enantiomeric isomerization ($k = k'/2$) were determined (Table 1). By direct nonlinear least-squares fitting of the Eyring equation, the activation energy (E_a), activation enthalpy ($\Delta H^{\ddagger}$), and activation entropy ($\Delta S^{\ddagger}$) of enantiomeric isomerization were determined: $E_a = 19.7$ kcal mol^{-1}; $\Delta H^{\ddagger} = 19.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -14.4$ cal K^{-1} mol^{-1} (see the Supporting Information and Figure 7 for the Arrhenius plot). These results indicate that the racemization of *cis*-olefin **2** is thermally accelerated.

In general, it is recognized that enantioresolution cannot be achieved unless the activation energy of racemization is larger than 15−18 kcal mol^{-1}. Therefore, the present resolution of *cis*-olefin **2** is one of such cases at the limit with respect to the activation energy of racemization.

Chemical Dynamics of Racemization of *cis*-Olefin 2 Studied by ^{1}H NMR Spectroscopy: Attempt To Detect

(9) For the racemization of first-order reaction, the decrease of enantiomeric excess is formulated as $-d([S] - [R])/dt = k'([S] - [R])$ where [*S*] and [*R*] are the concentration of enantiomers *S* and *R*, respectively, and k' is the apparent rate constant of racemization obtained from CD or NMR data. The equation is expressed as $-d[S]/dt + d[R]/dt = k'([S] - [R])$. On the other hand, the increase of *S* enantiomer in an enantiomeric interconversion system is formulated as $d[S]/dt = -k[S] + k[R]$ where k is the actual rate constant of enantiomeric isomerization. Similarly, $d[R]/dt = k[S] - k[R]$. Subtraction of $d[S]/dt = -k[S] + k[R]$ from $d[R]/dt = k[S] - k[R]$ gives $-d[S]/dt + d[R]/dt = 2k([S] - [R])$. From this equation and $-d[S]/dt + d[R]/dt = k'([S] - [R])$, $k = k'/2$. Namely, the rate constant of enantiomeric interconversion is half of the rate constant of racemization.

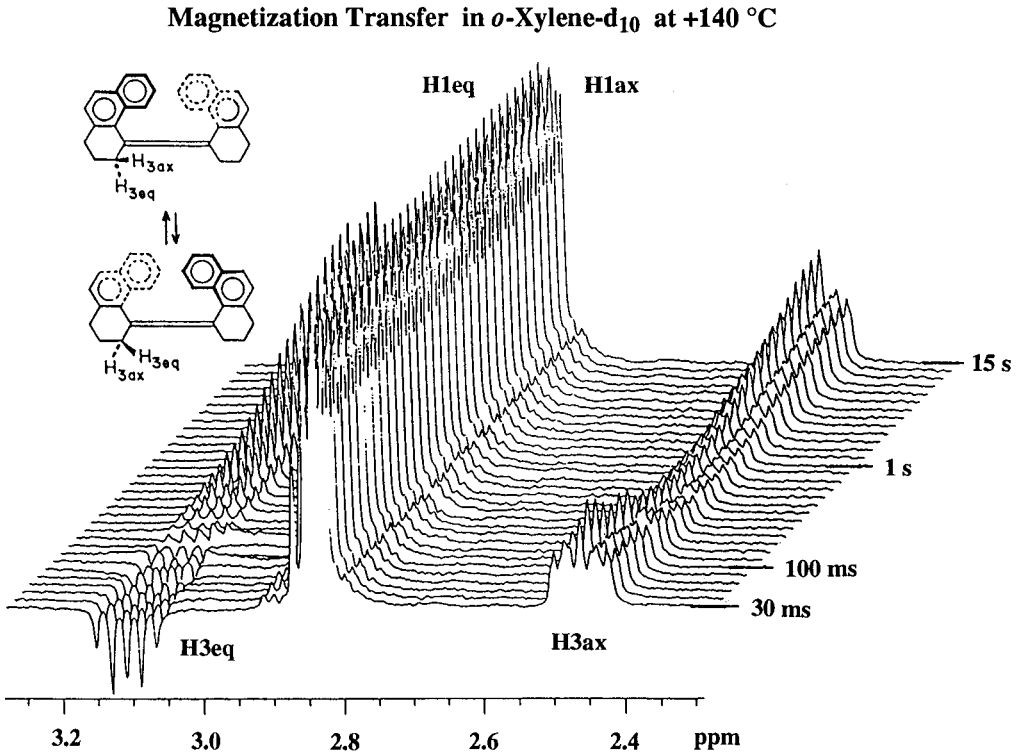


Figure 5. Magnetization transfer due to the enantiomeric interconversion of *cis*-olefin (±)-**2** in *o*-xylene-d_{10} at 140.2 °C: decrease and recovery of the H3ax signal at 2.46 ppm when the spin of H3eq proton at 3.10 ppm was inverted.

Coalescence Phenomena. The unique racemization of *cis*-olefin **2** was next investigated by ^{1}H NMR spectroscopy. The NMR signals of **2** were fully assigned at 24 °C as described in the first paper of this series.[2a] The racemization of *cis*-olefin **2** is based on the isomerization of (*M*,*M*)-*cis* to (*P*,*P*)-*cis* and its reverse isomerization from (*P*,*P*)-*cis* to (*M*,*M*)-*cis*. During the interconversion between enantiomers, the H3ax (ax = axial) proton of **2** exchanges its chemical position with that of the H3eq (eq = equatorial) proton, and inversely, the H3eq proton changes to the H3ax proton. Therefore, it may be possible that if the ^{1}H NMR spectra of racemic *cis*-olefin is measured at elevated temperature, the coalescence phenomenon between the two signals of H3ax and H3eq protons would be observed.

The ^{1}H NMR (300 MHz) spectrum of *cis*-olefin (±)-**2** was measured in toluene-d_8 at 140 °C, but even at 140 °C the coalescence between signals of H3ax and H3eq protons was not observed. The same was true for the H2eq and H2ax proton signals. If a 60 MHz instrument is used, the coalescence may be observed. Therefore, the ^{1}H NMR coalescence technique[10] was not used in this case.

Chemical Dynamics of Racemization of *cis*-Olefin 2 Studied by the Time-Resolved ^{1}H NMR Spectroscopy of Magnetization Transfer. ^{1}H NMR magnetization transfer[11,12] was then investigated to study the racemization dynamics of *cis*-olefin **2**. The sample of racemic *cis*-olefin (±)-**2** in *o*-xylene-d_{10} was heated at 140 °C in a NMR probe. A selective 180° inversion pulse was applied to the H3eq proton signal at 3.10 ppm, and NMR spectra were acquired as a function of time consistent with T_1 relaxation of these protons. Selective inversion of the spin of H3eq proton at 3.10 ppm resulted in the sharp decrease and gradual recovery of the intensity of H3ax proton signal at 2.46 ppm as shown in Figures 5 and 6. On the other hand, the H1eq and H1ax proton signals remained unchanged. When the spin of H3ax proton at 2.46 ppm was inverted, the H3eq proton signal at 3.10 ppm exhibited similar behavior in the time-resolved spectra. These phenomena are characteristic for exchange between H3ax and H3eq protons; the negative signal intensity of H3eq proton at 3.10 ppm formed by the spin inversion was transferred to the signal of H3ax proton at 2.46 ppm because the H3eq proton in (*M*,*M*)-*cis* **2** becomes the H3ax proton in (*P*,*P*)-*cis* **2** and the H3eq proton of (*P*,*P*)-*cis* **2** becomes the H3ax proton of (*M*,*M*)-*cis* **2** by the enantiomeric interconversion, *i.e.*, racemization. From this magnetization transfer effect, the reaction rate of the enantiomeric interconversion is obtainable.

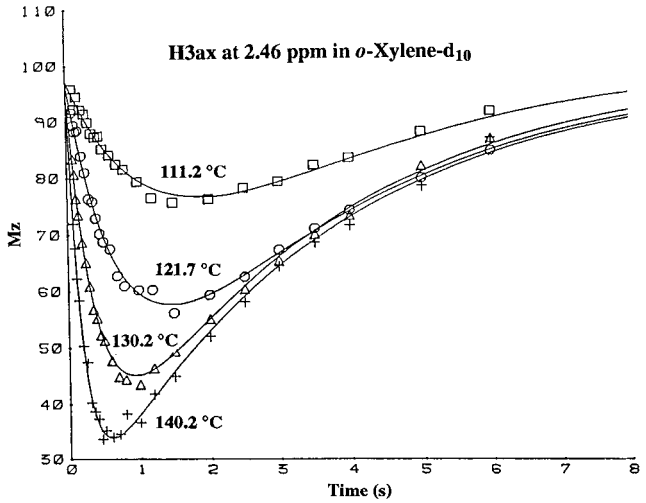


Figure 6. Temperature dependence of the magnetization transfer of *cis*-olefin (±)-**2** in *o*-xylene-d_{10}: decrease and recovery of the H3ax signal at 2.46 ppm when the spin of H3eq proton at 3.10 ppm was inverted.

Magnetization transfer experiments[11] were performed at various temperatures from 101.1 °C to 150.2 °C; after selective inversion of the H3eq proton, the intensity of the H3ax proton

(10) Sandstrom, J. *Dynamic NMR Spectroscopy;* Academic Press: London and New York, 1982.
(11) Chenard, B. L.; Dixon, D. A.; Harlow, R. L.; Roe, C. D.; Fukunaga, T. *J. Org. Chem.* **1987**, *52*, 2411.
(12) Forsen, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2892.

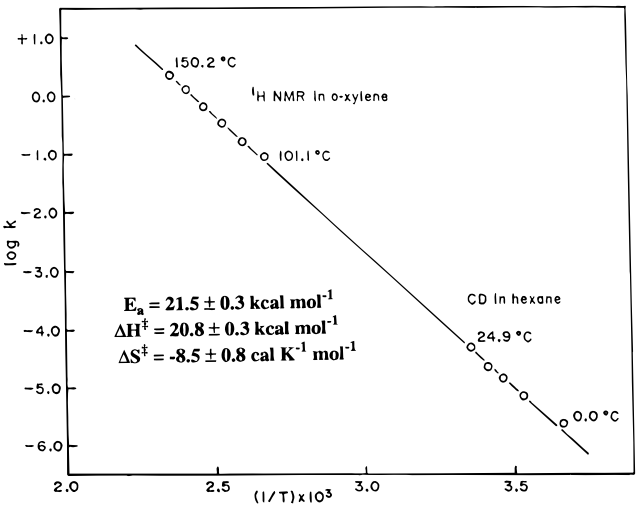


Figure 7. Arrhenius plot for the enantiomeric interconversion of *cis*-olefin **2** based on the CD and NMR data.

signal was monitored from 30 ms through 15 s (Figure 5). The respective magnetization intensities (Mz) are shown in Figure 6 as a function of time at the indicated temperatures. In each case, a second data set was obtained by selectively inverting the H3ax proton, and the two data sets were combined and analyzed together (see later) to provide the single best-fitting rate constant to describe the exchange process. The resulting rate constants were used to provide the smooth curve in Figure 6.

Since both H3eq and H3ax protons are attached to the same carbon, it is to be anticipated that irradiation of one of these protons will generate a nuclear Overhauser effect (NOE) at the other. Manifestation of the NOE is phenomenologically identical to exchange except for a change of sign (for small molecules, $\omega_o\tau_c \ll 1$). If the protons are spatially close to each other, a positive change in intensity occurs at the noninverted site, and the term that corresponds to the exchange rate is referred to as the cross-relaxation rate. Such an effect is observed at 80 °C (see the Supporting Information) and corresponds to a cross-relaxation rate $\sigma = 0.136$ s^{-1}. The exchange rates quoted at higher temperatures are corrected for this cross-relaxation rate which is taken to be relatively insensitive to temperature (see figures in the Supporting Information for the magnitude of the NOE relative to the exchange phenomenon and also for the importance of the cross-relaxation correction to the exchange rate constants).

Kinetic Data of the Racemization of *cis*-Olefin 2 Obtained by Combination of CD and NMR Data. Even though the rate constants determined by CD and ^{1}H NMR differ from each other by a factor of 10^5, they describe the same process, namely the racemization of *cis*-4,4′-biphenanthrylidene **2** (see Figure 7). Since the temperature of CD and NMR measurements spans the range from 0.0 to 150.2 °C, the activation parameters determined from the combined rate constants are more reliable than those obtained from the individual rate determinations. The rate constants presented in Table 1 lead to the activation parameters $E_a = 21.5 \pm 0.3$ kcal mol^{-1}, $\Delta H^{\ddagger} = 20.8 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.5 \pm 0.8$ cal K^{-1} mol^{-1}. The latter activation parameters can be used to estimate the exchange rate $k = 0.027$ s^{-1} at 80 °C which is sufficiently small compared to the apparent cross-relaxation rate σ to give a self-consistent determination of these competing rate processes.

Confirmation of the Stereostructure of *cis*-Olefin 2 by X-Ray Crystallographic Analysis of Its Racemate. As discussed above, it is unexpected that *cis*-olefin **2** undergoes easy thermal racemization at room temperature, while *trans*-olefin **1** does not racemize at room temperature. It is a challenging problem to clarify the mechanism of this unusual phenomenon. However, if the structure assignment of *cis*- and *trans*-configuration is erroneous, the problem becomes trivial. The stereostructure of *trans*-olefin **1**, however, was established by X-ray analysis as described in the first paper of this series.[2a] The *cis*-geometry olefin **2** was also determined by X-ray crystallographic analysis of its racemate, as described below.

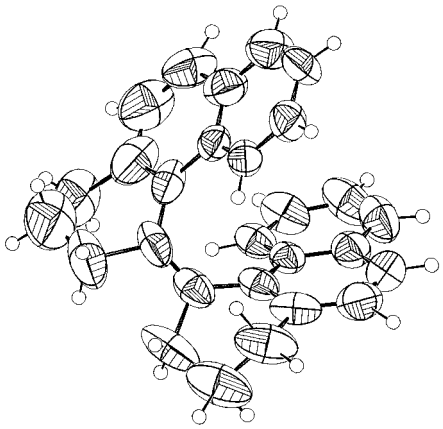


Figure 8. X-ray ORTEP drawing of racemic *cis*-olefin (±)-(*Z*)-**2**. The figure does not express its absolute stereochemistry. The atoms are drawn at 50% probability.

After several trials of recrystallization of olefin (±)-**2**, single crystals of plate form suitable for X-ray analysis were obtained when recrystallized from hexane: mp 192−195 °C. The crystal was found to be monoclinic: space group $P2_1/n$ (No. 14). The skeletal structure was solved by direct methods and successive Fourier syntheses, and all hydrogen atoms were found by the difference Fourier syntheses. Full-matrix least-squares refinement of positional and thermal parameters led to the final convergence with $R = 0.1131$ and $R_w = 0.1210$. Since the thermal parameters of carbon atoms take large values, the crystal packing may be loose and/or atoms of *cis*-olefin molecule may vibrate more than *trans*-olefin even in the crystal. Although the final *R*-value remained at a higher level, it is now clear that compound **2** has the *cis*-geometry with two overlapped naphthalene rings as shown in Figure 8.

The stereochemistry of *cis*-olefin **2** in the solid state is characterized as follows: central double bond, C4−C4′ = 1.316 Å; average value of the dihedral angle between naphthalene plane and central double bond, C4−C4′−C4′a−C4′b = −47.5°; dihedral angles, C3−C4−C4′−C4′a = +175.1° (average), C3−C4−C4′−C3′ = −9.2°, C4a−C4−C4′−C4′a = −0.7°; dihedral angle between planes C3−C4−C4′ and C4a−C4−C4′ = −175.7°. The bond length of the central double bond is thus similar to that of *trans*-olefin (1.318 Å), and therefore, the central double bond is not loosened in *cis*-olefin **2**. As seen from the dihedral angle data, the central double bond is a little twisted and the component sp^2 carbon atoms are a little deviated from a planar structure. The distance between the two overlapped naphthalene planes is represented by the interatomic distance (3.265 Å) between C4b and C4′b. Two naphthalene groups in *cis*-olefin **2** are thus in contact with each other within twice the van der Waals' radius (1.70 Å) of aromatic planes.

The proton−proton distance correlating to the observed ^{1}H NMR NOESY phenomena[2a] was calculated from the X-ray data: H1eq−H10 = 2.30 Å, H1ax−H5′ = 2.70 Å. The X-ray analysis thus confirmed the relationship between proton−proton distance and NOESY data.

Kinetics of Racemization of *trans*-Olefin 1 Studied by Polarimetry. As described above, *trans*-olefin **1** does not

Table 2. Temperature Dependence of the Rate Constant of Enantiomeric Isomerization of (*E*)-1,1′,2,2′,3,3′,4,4′-Octahydro-4,4′-biphenanthrylidene (**1**) Studied by Polarimetry at 436 nm in *p*-Xylene

T (°C)	k (s^{-1})
55.0	2.857×10^{-6}
60.0	5.589×10^{-6}
65.0	9.925×10^{-6}
70.0	1.678×10^{-5}
75.0	3.024×10^{-5}
80.0	4.440×10^{-5}
85.0	7.873×10^{-5}
90.0	1.269×10^{-4}
95.0	2.037×10^{-4}

appear to racemize at room temperature, but can be observed to racemize around 55 °C. To obtain the kinetic parameters of the racemization of *trans*-olefin **1**, the decrease of optical rotation value at 436 nm was followed at various temperatures (55.0−95.0 °C) and analyzed using the equations of a first-order reaction. The rate constant (k') of the racemization and the rate constant of enantiomeric isomerization ($k = k'/2$) were determined (Table 2). The activation parameters of enantiomeric isomerization were determined: $E_a = 25.2 \pm 0.7$ kcal mol^{-1}, $\Delta H^{\ddagger} = 24.6 \pm 0.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9.1 \pm 1.9$ cal K^{-1} mol^{-1}.

Why Does *cis*-Olefin 2 More Easily Racemize Than *trans*-Olefin 1? From the results discussed above, it is now evident that *cis*-olefin **2** easily racemizes at room temperature without formation of *trans*-olefin **1** as an intermediate (Figure 9). The racemization of *cis*-olefin **2** is a purely thermal reaction, not catalyzed by acid or light. Why does sterically more-hindered *cis*-olefin **2** racemize so easily at room temperature?

As an intermediate of the racemization, *meso*-olefin (*M*,*P*)-(*Z*)-**2** is considered (Figure 9). If the racemization takes this reaction route, it implies that aromatic rings are much more flexible than is generally perceived. This point has been accepted in some cases, *e.g.*, the racemization of helicene compounds.[6] There is still another problem. If aromatic rings are flexible, apparently less-hindered *trans*-olefin **1** should racemize much more easily than *cis*-olefin **2**. However, this is not the case. What are the reaction mechanisms of these racemizations? This challenging problem will be solved by theoretical studies.

Experimental Section

General Procedures. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a General Electric QE-300 (300 MHz), a Jeol JNM-LA400 (400 MHz), or a Jeol JNM-LA600 (600 MHz) spectrometer. ^{13}C NMR spectra were obtained on a Jeol JNM-LA400 (100 MHz) spectrometer. All NMR data are reported in ppm (δ) downfield from tetramethylsilane. UV and CD spectra were recorded on Jasco Ubest-50 and Jasco J-400X or J-720WI spectrometers, respectively. The low-temperature CD spectra were measured using a Oxford OX2 0DX cryostat. X-ray single-crystal diffraction measurement was performed on a Rigaku AFC-6B automated four-circle diffractometer.

HPLC Enantioresolution of (±)-(*Z*)-1,1′,2,2′,3,3′,4,4′-Octahydro-4,4′-biphenanthrylidene (2) at Low Temperature. To obtain the enantiopure *cis*-olefin **2**, the HPLC column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate) connected in series with a short HPLC column of silica gel was mounted in a HPLC system, cooled at −20 °C by circulating cold methanol, and equilibrated with hexane as eluent. Receiver flasks for collecting eluate were placed in a dry ice/methanol bath. The sample of (±)-*cis*-**2** was injected as a hexane solution, and separation of enantiomers was monitored by a UV detector. The first-eluted fraction was collected, and its CD spectrum was immediately measured.

Measurement of CD Spectra at Low Temperature. To measure CD spectra at low temperature (222.7 K, −50.4 °C), a cryostat containing liquid nitrogen was used. A sample solution in a CD cell was placed in the cryostat and cooled at the desired temperature. The temperature of the solution was regulated by an automatic controller.

Since the volume contraction of solution occurred at low temperature, the CD intensity observed was corrected by using the following equations[7]

$$\Delta\epsilon(\text{corrected}) = \Delta\epsilon(\text{uncorrected})V^{t}_{20}$$

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

where α and β are empirical parameters and T is temperature expressed in °C. For isopentane, $\alpha = 1.654$, $\beta = 3.26$, for isopentane/methylcyclohexane (5:1), $\alpha = 1.521$, $\beta = 2.71$, and for EtOH, $\alpha = 1.058$, $\beta = 0.69$. Since the parameter values for hexane were not found in the literature,[7] the values were approximated by those of isopentane/methylcyclohexane (5:1).

CD Spectra of Chiral Olefins at −50.4 °C: *cis*-Olefin [CD(+)-238.1]-(*M*,*M*)-(*Z*)-2. The CD spectrum of the first-eluted enantiomer (*M*,*M*)-(*Z*)-**2** was measured at −50.4 °C (222.7 K), and the observed CD values were corrected for volume contraction, $V^{t}_{20} = 0.906$: CD (corrected, hexane) λ_{ext} 338.0 nm ($\Delta\epsilon$ −14.0), 282.5 (+11.9), 256.8 (−80.1), 239.6 (+222.2), 224.0 (−281.3), where the concentration of the sample was determined from the UV absorption intensity. ***trans*-Olefin [CD(+)239.0]-(*M*,*M*)-(*E*)-1.** The CD spectrum of the first-eluted enantiomer (*M*,*M*)-(*E*)-**1** was similarly measured at −50.4 °C (222.7 K), and the observed CD values were corrected for volume contraction by using the parameters of EtOH: CD (corrected, MeOH) λ_{ext} 330.3 nm ($\Delta\epsilon$ +23.2), 253.0 (−20.8), 238.5 (+55.6), 221.6 (−281.3), 213.9 (−150.5), where the concentration of the sample was determined from the UV absorption intensity.

HPLC and CD Check of the First-Eluted Enantiomer of *cis*-Olefin 2 Kept at Room Temperature. The first-eluted enantiomer of *cis*-olefin **2** obtained by HPLC separation at −30 °C was kept in the dark at room temperature for 24 h. The sample was checked by HPLC under the same condition used for separation. As shown in Figure 3, two peaks corresponding to (*M*,*M*)-*cis*-**2** and (*P*,*P*)-*cis*-**2** were observed. However, no peak corresponding to *trans*-olefin was found. The CD spectra of the first- and second-eluted fraction were almost identical with those of [CD(+)238.1]-(*M*,*M*)-(*Z*)-**2** and [CD(−)238.1]-(*P*,*P*)-(*Z*)-**2**, respectively.

Kinetics of Racemization of *cis*-Olefin 2 Studied by CD Spectra. The CD spectra of the first-eluted enantiomer (*M*,*M*)-*cis*-**2** were measured consecutively at room temperature. The CD spectra showed rapid decrease as shown in Figure 1, and the CD curve became totally flat after 6 h, while the UV spectra retained the original pattern and intensity. The half-life time of CD intensity was ca. 1.2 h at room temperature.

To obtain the kinetic parameters of the racemization of *cis*-olefin **2**, the decrease of CD intensity at 238.1 nm was followed at various temperatures (0−24.9 °C). The sample was placed in a cryostat, the temperatures of which was controlled within the error of ±0.1−0.2 °C. The wavelength of a CD spectrometer was fixed at 238.1 nm, and the CD spectrometer was scanned against time for 150 min. The decrease of CD intensity was recorded and analyzed using the equations of the first-order reaction. The rate constant (k') of the racemization and the rate constant of enantiomeric isomerization ($k = k'/2$) were determined (Table 1).

Kinetics Studies of Racemization of *cis*-Olefin 2 by the ^{1}H NMR Magnetization Transfer Method. The NMR magnetization transfer experiments of *cis*-**2** were carried out at elevated temperature (101.1−150.2 °C) using a solution of (±)-*cis*-**2** in *o*-xylene-d_{10}. The H3eq signal at 3.10 ppm was selectively irradiated and the H3ax signal at 2.46 ppm was traced from 30 ms to 15 s (Figures 5 and 6). After correction for NOE, the rate constant k of enantiomeric interconversion was obtained as shown in Table 1.

X-ray Crystallography of (±)-(*Z*)-Olefin 2. Single crystals of (±)-**2** were obtained as colorless prisms by crystallization from hexane: mp 192−195 °C. A single crystal (dimensions of 0.41 × 0.32 × 0.19 mm) was selected for data collection and mounted on a Rigaku AFC-6B automated four-circle diffractometer. The crystal was found to be monoclinic, and the unit cell parameters and orientation

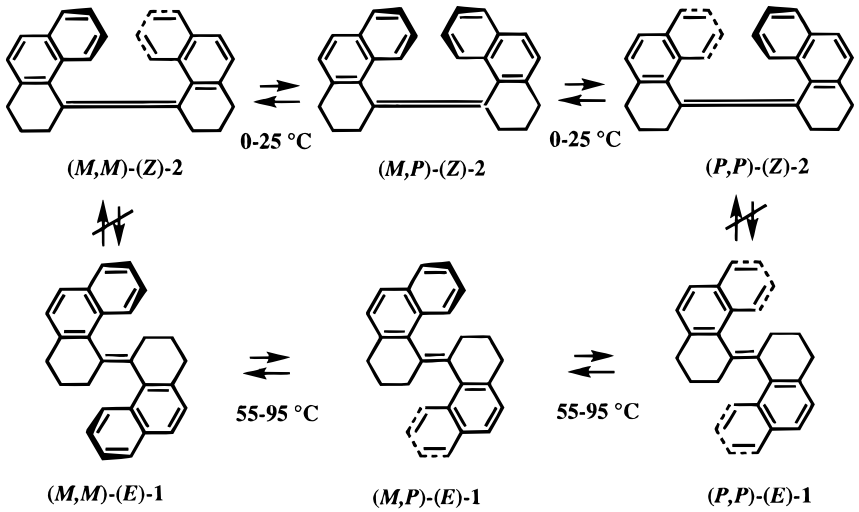


Figure 9. Reaction pathways of the thermal racemization of *trans*- and *cis*-olefins.

matrix were obtained. Data collection was carried out by using a $2\theta - \theta$ scan: formula, $C_{28}H_{24}$; $M_r = 360.50$; space group $P2_1/n$ (No. 14); $a = 15.987(2)$, $b = 11.0372(6)$, and $c = 11.450(1)$ Å, $\beta = 101.125(8)°$; $V = 1982.4(3)$ Å^3; $Z = 4$; $D_x = 1.208$ g cm^{-3}; $D_m = 1.211$ g cm^{-3} by flotation using a CCl_4/hexane solution; radiation, Cu Kα (1.541 78 Å); monochromator, graphite crystal; linear absorption coefficient, 4.39 cm^{-1}; temperature, 20 °C; scan speed, 2.0°/min; scan range, $1.3° + 0.3°$ tan θ; 2θ scan limits, 2°−130°; standard reflections, 3 per 50 reflections; indices, (2,0,2), (0,−2,−2), (1,0,−3); crystal stability, no indication of standard reflection decay during data collection; total reflections scanned, 3706; unique data $F_o > 3\sigma(F_o)$, 3127. The skeletal structure was solved by direct methods and successive Fourier syntheses. All hydrogen atoms were found by the difference Fourier syntheses. Full-matrix least-squares refinement of positional and thermal parameters led to the final convergence with $R = 0.1131$ and $R_w = 0.1210$. The *cis*-geometry of **2** with overlapped naphthalene rings was thus established (Figure 8).

Kinetics of Racemization of *trans*-Olefin 1 Studied by Polarimetry. Optical rotations with *p*-xylene as solvent were taken on a Perkin Elmer 241 polarimeter with a Colora thermostated waterbath. To obtain the kinetic parameters of the racemization of *trans*-olefin **1**, the decrease of rotation value at 436 nm was followed at various temperature (55.0−95.0 °C), and analyzed using the equations of a first-order reaction. The rate constant (k') of the racemization and the rate constant of enantiomeric isomerization ($k = k'/2$) were determined as shown in Table 2.

Acknowledgment. DuPont Contribution No. 7575. This work was supported in part by grants from the Ministry of Education, Science, Sport, and Culture, Japan (General (A) No. 07408032, General (B) No. 01470026, Priority Areas Nos. 02250103, 03236101, 04220101, and 06240204, Developmental Research No. 05554017, and International Joint Research No. 02044014 to N. H.). Part of this research (W.F.J., B.d.L., B.L.F) was supported by the Stichting Technische Wetenschappen (STW) and the Dutch Foumdation for Scientific Research (NWO).

Supporting Information Available: HPLC check of the stability of (*M*,*M*)-(*E*)-**1**, observed CD and UV spectra of (*M*,*M*)-(*E*)-**1** at −50 °C, the Arrhenius plot for the thermal racemization of *cis*-olefin **2** based on the CD data, the H3(equatorial) part of temperature dependence of the magnetization transfer of *cis*-olefin (±)-**2**, NOE of *cis*-olefin (±)-**2** in *o*-xylene-d_{10}, the Arrhenius plot for the enantiomeric interconversion of *cis*-olefin (±)-**2** based on the NMR data (6 pages). See any current masthead page for ordering and Internet access instructions.

JA970668M