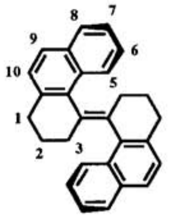
Photochemistry and Absolute Stereochemistry of Unique Chiral Olefins, *trans*- and *cis*-1,1',2,2',3,3',4,4'-Octahydro-3,3'-dimethyl-4,4'-biphenanthrylidenes

Nagatoshi Koumura and Nobuyuki Harada*
Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577

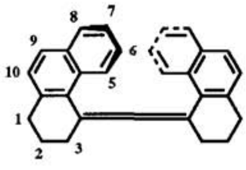
(Received August 11, 1998; CL-980615)

Photochemistry of unique chiral olefins, (3*R*,3'*R*)-(*P*,*P*)-(*E*)-(−)-1,1',2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene **3** and its isomers (3*R*,3'*R*)-(*P*,*P*)-(*Z*)-(+)-**4** and (3*R*,3'*R*)-(*M*,*M*)-(*E*)-(+)-**5**, was studied and the absolute stereostructure of (+)-**5** was determined by X-ray crystallographic and chemical correlation studies.

In the previous papers of this series,[1,2] we reported the synthesis, enantioresolution, CD spectra, and theoretical determination of absolute stereochemistry of unique chiral olefins, (*E*)-1,1',2,2',3,3',4,4'-octahydro-4,4'-biphenanthrylidene (**1**) and (*Z*)-isomer (**2**).[1a] In addition, we found a strange phenomenon that sterically hindered *cis*-olefin **2** easily racemizes at room temperature without formation of *trans*-olefin **1**, while *trans*-olefin **1** does not racemize at room temperature.[1b] Furthermore, we reported the synthesis, CD spectra, and X-ray crystallography of chiral dimethyl olefins, (3*R*,3'*R*)-(*P*,*P*)-(*E*)-(−)-1,1',-2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene (**3**) and (3*R*,3'*R*)-(*P*,*P*)-(*Z*)-(+)-isomer (**4**) (Scheme 1).[1c,2] By comparing the CD spectra of (3*R*,3'*R*)-(*P*,*P*)-(*E*)-(−)-**3** and (3*R*,3'*R*)-(*P*,*P*)-(*Z*)-(+)-**4** with those of chiral olefins (*E*)-**1** and (*Z*)-**2** respectively, the absolute stereostructures of **1** and **2** were determined, which supported our previous theoretical determination of their absolute configurations based on the MO calculation of CD spectra.[1a] We report here the unique photochemistry of chiral olefins **3** and **4** and the absolute stereostructure of a new diastereomer **5** as determined by X-ray crystallography.



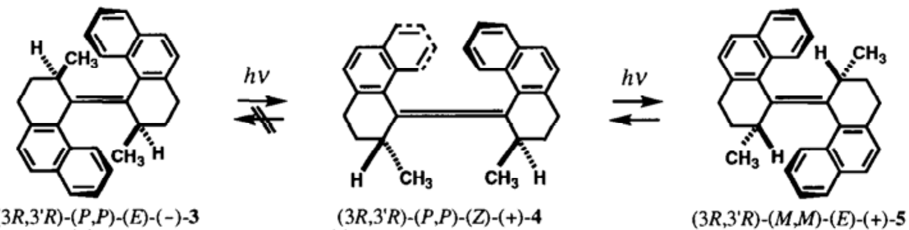
[CD(+)239.0]-(*M*,*M*)-(*E*)-**1**



[CD(+)238.1]-(*M*,*M*)-(Z)-**2**

The *cis*-isomer (3*R*,3'*R*)-(*P*,*P*)-(*Z*)-(+)-**4** was previously prepared by photochemical isomerization of the *trans*-isomer (3*R*,3'*R*)-(*P*,*P*)-(*E*)-(−)-**3** (a high pressure Hg-lamp, Pyrex filter, in acetone-d_6).[1c] Prolonged irradiation for 7 h yielded another product **5** (yield 18%) of yellow color in addition to the colorless product **4** (72%) and recovered **3** (10%). Although the yellow color of **5** implied the extension of π-electron areas, or formation of additional double bonds, the high resolution MS spectrum and elemental analysis indicated that compound **5** has the same molecular formula as those of **3** and **4**.[3,4] The ^{1}H NMR spectrum of **5** showing a C_2-symmetrical pattern, exhibited aromatic protons around δ 7.34-8.61 indicating a *trans* geometry.[1a] The methyl groups appeared at δ 0.31 as a doublet implying the high field shift due to the anisotropic effect by a neighboring naphthalene ring. These data suggested the structure of (3*R*,3'*R*)-(*M*,*M*)-(*E*)-1,1',2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene **5**, the ^{13}C NMR of which also supported the structure. In the molecule **5**, two equatorial methyl groups are in contact with naphthalene rings, causing a severe steric hindrance between methyl and naphthalene groups. We had expected the formation of **5** in the McMurry reaction of the corresponding ketone, but compound **5** had not been isolated yet. The calculation by the MOPAC 93, AM1 programs predicted that compound **5** with two equatorial methyl groups is less stable by 10.2 kcal/mol than compound **3** with two axial methyl groups. Therefore, we could unexpectedly obtained such an extremely unstable diastereomer **5**.

Starting from the racemic *trans*-olefin (*E*)-(±)-**3**, compound (±)-**5** was similarly prepared and recrystallized from hexane giving yellow prisms.[4] A single crystal was subjected to X-ray crystallography to determine the stereostructure as shown in Figure 1.[5] The ORTEP drawing clearly shows two methyl groups in the equatorial positions indicating the relative stereochemistry of (3*R**,3'*R**)-(*M**,*M**)-(*E*)-**5**. Since the *R* absolute configuration of two methyl groups of (+)-**5** is evident, the (*M*,*M*) helicity was assigned to (+)-**5**. The crystal structure revealed that the central double bond of (±)-**5** is strongly twisted due to steric hindrance: the dihedral angle, 20.6°. This is the main reason why compound **5** is colored; twist of a C=C double bond leads to a red shift of UV/Vis absorption bands. The CD and UV/Vis spectra of (3*R*,3'*R*)-(*M*,*M*)-(*E*)-**5** show red-shifted Cotton effects and absorption bands, respectively, compared with



Scheme 1. Photochemical interconversion between chiral olefins (−)-**3**, (+)-**4**, and (+)-**5**.

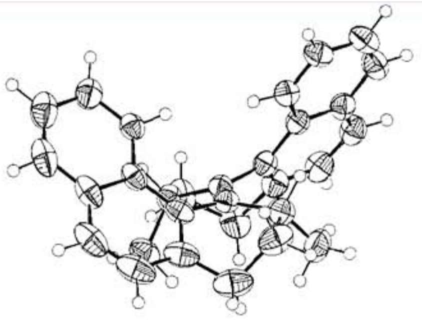


Figure 1. ORTEP drawing of racemic (3*R**,3'*R**)-(*M**,*M**)-(*E*)-(±)-dimethylolefin **5**. The atoms are drawn as 50% probability.

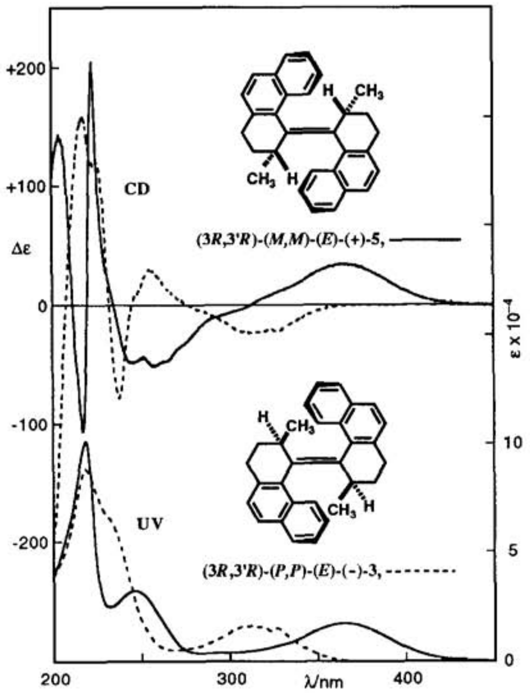


Figure 2. CD and UV spectra of (3*R*,3'*R*)-(*P*,*P*)-(*E*)-(–)-dimethylolefin **3** and (3*R*,3'*R*)-(*M*,*M*)-(*E*)-(+)-isomer **5** in ethanol.

those of (3*R*,3'*R*)-(*P*,*P*)-(*E*)-(–)-**3** (Figure 2). The Cotton effect of (3*R*,3'*R*)-(*M*,*M*)-(*E*)-(+)-**5** at 367.2 nm is positive, while that of (3*R*,3'*R*)-(*P*,*P*)-(*E*)-(–)-**3** at 313.6 nm is negative reflecting the helicity of conjugated π-electron systems.[1c]

To disclose the photochemical reaction pathway, amounts of starting material and products were checked at regular time intervals by ^{1}H NMR spectroscopy. When a solution of (3*R*,3'*R*)-(*P*,*P*)-(*E*)-(–)-**3** in acetone-d_6 (ca. 5 mM) was irradiated using a high pressure Hg-lamp and a Pyrex filter (>280 nm), the amount of **3** rapidly decreased and *cis*-olefin (3*R*,3'*R*)-(*P*,*P*)-(*Z*)-(+)-**4** was rapidly formed as if to compensate the loss of **3**. With a time lag of 1-2 h, the amount of (3*R*,3'*R*)-(*M*,*M*)-(*E*)-**5** gradually increased, implying that *trans*-olefin **5** was formed from *cis*-olefin **4**. When a solution of **4** was irradiated under similar conditions, rapid formation of **5** was observed reaching the photo-equilibrium with the ratio of *cis*-olefin **4**/*trans*-olefin **5** = 55:45 after 19 h. A similar photo-equilibrium mixture was obtained when a solution of **5** was irradiated for 18 h: the ratio of *cis*-olefin **4**/*trans*-olefin **5** = 54:46. We were very surprised to find the fact that *trans*-olefin **3** had never been formed from **4** and/or **5**, when irradiated with the light of >280 nm. Namely, the photochemical conversion of **3** to **4** is allowed, while the reverse reaction is forbidden. Usual photochemical interconversions between *cis* and *trans* isomers are two-way reactions as exemplified by the reaction between **4** and **5**. However, the *cis-trans* photochemical isomerization between **3** and **4** is a one-way reaction. To our knowledge, this is the first example of the photochemical one-way *cis-trans* isomerization of chiral olefins, although a similar behavior of achiral aromatic olefins has been intensively studied by Tokumaru, et al.[6] These chiral olefins **3**-**5** thus exhibit unique photochemical reactions.

The wavelength-dependence of the photochemical interconversion between **4** and **5** was next studied. When a solution of (±)-**5** in benzene-d_6 was illuminated by a Xe lamp (> 380 nm) for 10 h, *trans*-olefin **5** was completely converted to *cis*-olefin (±)-**4**. On the other hand, when a solution of (±)-**4** was similarly illuminated under a light of 300 nm (a Xe lamp), the reaction reached at equilibrium in favor of *trans*-olefin **5**: the ratio of **4**/**5** = 8:92. It is thus possible to control the photochemical interconversion between these unique chiral olefins by choosing the wavelength of light.[7]

This work was supported in part by grants from the Ministry of Education, Science, Sports, and Culture, Japan (to N. H.), the Ciba-Geigy Foundation (Japan) for the Promotion of Science (to N. H.), and the Japan Science Society (the Sasakawa Scientific Research Grant to N. K.).

References and Notes

1 (a) N. Harada, A. Saito, N. Koumura, H. Uda, B. de Lange, W. F. Jager, H. Wynberg, and B. L. Feringa, *J. Am. Chem. Soc.*, **119**, 7241 (1997). (b) N. Harada, A. Saito, N. Koumura, D. C. Roe, W. F. Jager, R. W. Zijlstra, B. de Lange, and B. L. Feringa, *J. Am. Chem. Soc.*, **119**, 7249 (1997). (c) N. Harada, N. Koumura, and B. L. Feringa, *J. Am. Chem. Soc.*, **119**, 7256 (1997).

2 N. Koumura and N. Harada, *Enantiomer*, in press. See also, N. Harada, N. Koumura, and M. Robillard, *Enantiomer*, **2**, 303 (1997).

3 Chiral *trans*-olefin (3*R*,3'*R*)-(*M*,*M*)-(*E*)-(+)-**5**: yellow powder; IR (KBr) ν_{max} 3051, 2960, 2930, 2869, 1507, 1457, 1375, 1208, 1033, 865, 819, 811, 748, 663, 546, 519 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.31 (6 H, d, *J* = 6.4 Hz, Me3eq), 1.49 (2 H, dddd, *J* = 12.8, 12.8, 6.4, 2.8 Hz, H2ax), 1.52 (2 H, dddd, *J* = 12.8, 3.4, 3.1, 1.5 Hz, H2eq), 2.58 (2 H, ddd, *J* = 14.3, 3.1, 2.8 Hz, H1eq), 2.74 (2 H, ddd, *J* = 14.3, 12.8, 3.4 Hz, H1ax), 3.03 (2 H, ddq, *J* = 6.4, 1.5, 6.4 Hz, H3ax), 7.34 (2 H, d, *J* = 8.0 Hz, H10), 7.42 (2 H, ddd, *J* = 7.9, 6.6, 1.2 Hz, H7), 7.45 (2 H, ddd, *J* = 8.3, 6.6, 1.6 Hz, H6), 7.75 (2 H, d, *J* = 8.0 Hz, H9), 7.87 (2 H, dd, *J* = 7.9, 1.6 Hz, H8), 8.61 (2 H, br d, *J* = 8.0 Hz, H5); ^{13}C NMR (150 MHz, CDCl$_3$) δ 19.9 (Me3eq), 28.5 (C1), 33.3 (C2), 34.7 (C3), 124.3 (C7), 126.05 (C6), 126.13 (C10), 126.6 (C5), 127.2 (C9), 128.6 (C8), 131.1 (C4b), 133.2 (C8a), 136.4 (C4a), 140.1 (C4), 142.4 (C10a); $[\alpha]_D^{26}$ +1016.8 (*c* 0.07291, CHCl$_3$); UV (EtOH) λ_{max} 365.6 nm (ε 17300), 246.0 (32200), 218.6 (101000); CD (EtOH) λ_{ext} 367.2 nm (Δε +34.5), 256.8 (–51.6), 246.0 (–48.7), 222.6 (+204.8), 216.8 (–106.9), 204.0 (+143.2); HRMS, Found 388.2192. Calcd for $C_{30}H_{28}$: 388.2190.

4 Olefin (*E*)-(±)-**5**: yellow prisms (hexane); m.p. 156-158 °C (sublimed). Anal. Found. C 92.65; H 7.49%. Calcd for $C_{30}H_{28}$: C 92.74; H 7.26%.

5 A yellow single crystal (0.45 × 0.16 × 0.14 mm) of *trans*-olefin (*E*)-(±)-**5** obtained by recrystallization from hexane was selected: Cu Kα (1.54178 Å); $C_{30}H_{28}$, *M*r = 388.55; orthorhombic; space group *Pnaa* (#56); $a = 14.119$ (2), $b = 23.273$ (4), $c = 13.232$ (2) Å; $V = 4348$ (1) Å^3; $Z = 8$; $D_x = 1.187$ g cm^{-3}; $D_m = 1.180$ g cm^{-3} by flotation using a CCl$_4$-hexane solution; unique data $Fo > 3\sigma(Fo)$, 3714; $R = 0.0579$ and $R_w = 0.0575$. The (3*R**,3'*R**)-(*M**,*M**)-(*E*) relative stereochemistry of (±)-**5** could be definitely determined.

6 T. Arai and K. Tokumaru, *J. Syn. Org. Chem. Jpn.*, **44**, 999 (1986) and references cited therein.

7 The possibility of triplet sensitization is present in the photochemical isomerization of these olefins in acetone. However, it is considered that these photochemical reactions proceed *via* a singlet excited state, because the reaction proceeds similarly in benzene.