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ASYMMETRIC CONVERSION OF (*Z*)-*N*-BENZOYL-α-DEHYDRO(9-PHENANTHRYL)ALANINE *N*´-METHYLAMIDE INTO ITS CYCLIZATION INTERMEDIATES VIA PHOTOINDUCED ELECTRON TRANSFER

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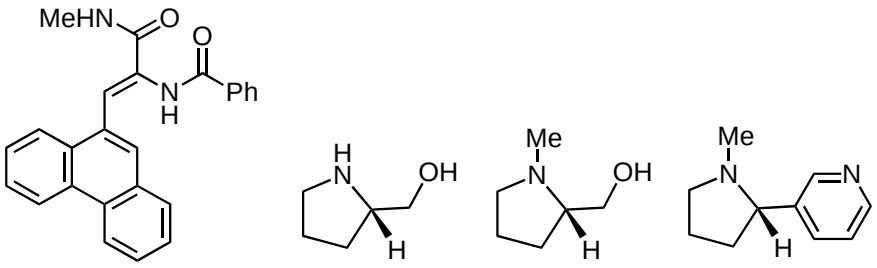
Abstract – Irradiation of (*Z*)-*N*-benzoyl-α-dehydro(9-phenanthryl)alanine *N*´-methylamide [(*Z*)-**1**] in 2-propanol-methanol (4:1 v/v) containing (*S*)-nicotine afforded the (3*S*,8a*S*)-3,8a-dihydrodibenzo[*f*,*h*]quinolinone derivative [(3*S*,8a*S*)-**2**] and (3*R*,8a*S*)-**2** in 20% and 35% enantiomeric excess (ee), respectively. Analysis of the effects of a chiral amine and solvent on the electron transfer-initiated enantioselective photocyclization of (*Z*)-**1** revealed that the magnitude of the ee is predominantly determined by the ability of this amine to form hydrogen bonds at the two sites of the enol intermediate as the precursor of **2**.

Organic photochemistry continues to contribute to the development of efficient methods for synthesizing various heterocyclic compounds.[1–3] In particular, owing to the fact that some of these compounds exhibit potent pharmacological activities, recent photochemical research has focused on the diverse photocyclization and photocycloaddition reactions of heteroatom-containing organic compounds, including their asymmetric photoreactions.[2,3] In the course of our systematic study of the photocyclization reactions of α-dehydroamino acid derivatives, we discovered that *N*-acyl-α-dehydronaphthylalaninamides in their excited states readily undergo novel one-electron reduction in the presence of tertiary aliphatic amines to eventually afford the corresponding 3,4-dihydrobenzo[*f*]quinolinones in high yields.[4] The large photostability of these products possessing one asymmetric carbon in the dihydroquinolinone ring enabled us to explore unprecedented asymmetric cyclization reactions initiated by photoinduced electron transfer (PET).[5] These PET-initiated reactions were found to proceed in a wide range of diastereomeric excess (de) and ee according to chiral auxiliary, amine, and temperature. However, it was impossible to estimate the magnitude of de for the cyclization

process of chiral auxiliary-substituted *N*-acetyl-α-dehydro(1-naphthyl)alaninamide-derived biradicals, owing to the unsuccessful isolation of the 3,8a-dihydrobenzo[*f*]quinolinone cyclization intermediates that are the precursors of 3,4-dihydrobenzo[*f*]quinolinone final products. Very recently, we found that the irradiation of (*Z*)-*N*-benzoyl-α-dehydro(9-phenanthryl)alanine *N*′-methylamide [(*Z*)-**1**] in methanol selectively afforded the corresponding 3,8a-dihydrodibenzo[*f,h*]quinolinone intermediate, which serves as the precursor of the 3,4-dihydrodibenzo[*f,h*]quinolinone cyclization product.[6] The additional finding that even in the presence of triethylamine (TEA), this cyclization intermediate is formed as the major product along with minor amounts of the final cyclization product enables the estimation of the ee for the asymmetric cyclization to the 3,8a-dihydrodibenzoquinolinone intermediate in the presence of a chiral amine. Thus, in the present paper, we report the synthesis of (*Z*)-**1** and explore the effects of the chiral amine and solvent on the magnitude of the ee for the PET-initiated asymmetric conversion of (*Z*)-**1** into the corresponding cyclization intermediates (Chart 1). (*S*)-Pyrrolidine-2-methanol (S-PM), (*S*)-1-methylpyrrolidine-2-methanol (S-MPM), and (*S*)-nicotine (S-NT) were chosen as the chiral amines (Chart 1).

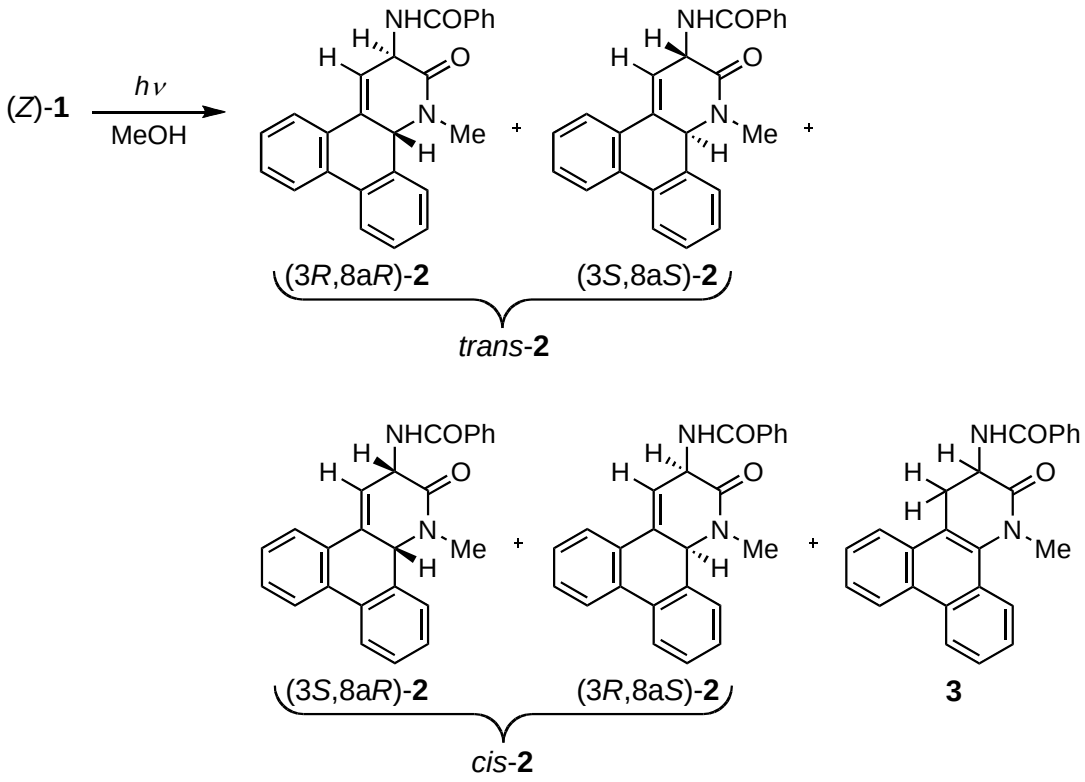


(*Z*)-**1** S-PM S-MPM S-NT

Chart 1

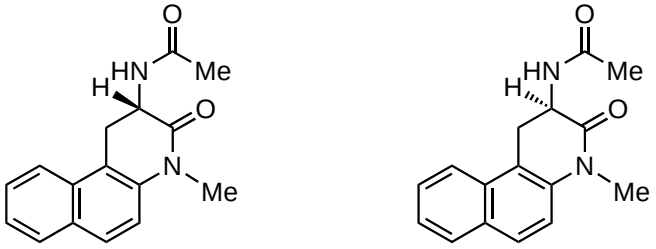
The starting *N*-benzoyl-α-dehydrophenanthrylalaninamide (*Z*)-**1** was prepared in good yield by a Knoevenagel-type condensation between 9-phenanthrenecarbaldehyde and *N*-benzoylglycine in acetic anhydride containing sodium acetate, followed by the reaction of the resulting (*Z*)-4-(9-phenanthrylmethylene)-2-phenyl-5(4*H*)-oxazolone with methylamine in tetrahydrofuran.[7] To examine the effect of chiral amines on the (*Z*)-**1**-derived product composition, S-MPM was chosen as a typical chiral amine, and nitrogen-saturated methanol solutions of (*Z*)-**1** (4.0×10^{-3} mol dm^{-3}, 10 mL × 5) containing S-MPM (0.10 mol dm^{-3}) were irradiated (at wavelengths greater than 280 nm from a 400 W high-pressure Hg lamp) in parallel using a carrousel irradiation apparatus for 30 min at room temperature (conversion, 100%). After the irradiated solutions were combined and evaporated to dryness *in vacuo*, the resulting residue was dissolved in chloroform and washed with 0.20 mol dm^{-3} hydrochloric acid to remove the chiral amine. Preparative thin layer chromatography (TLC) of the dried reaction mixture on silica gel allowed us to isolate the *trans*-3,8a-dihydrodibenzo[*f,h*]quinolinone intermediate (*trans*-**2**,

54% yield) and *cis*-**2** (18% yield), along with a minor amount of the 3,4-dihydrodibenzo[*f*,*h*]quinolinone product **3** (< 1% yield) (Scheme 1). In addition, the nuclear magnetic resonance (NMR) spectral analysis of this reaction mixture showed the sum of compositions for *trans*-**2** and *cis*-**2** to be 95%, which is nearly consistent with the previous result for the (*Z*)-**1**/TEA system (92%), and hence, demonstrates that chiral amines exert minor effects on the product composition.[6]



Scheme 1

Prior to the evaluation of the ee for these cyclization intermediates by high-performance liquid chromatography (HPLC), it is necessary to determine the retention times (t_R) of HPLC signals for the *trans*-**2**-derived (3*S*,8a*S*)- and (3*R*,8a*R*)-enantiomers and the *cis*-**2**-derived (3*R*,8a*S*)- and (3*S*,8a*R*)-enantiomers. In a previous study, we found that the chiral 3,4-dihydrobenzo[*f*]quinolinone cyclization product in methanol exhibits circular dichroism (CD) bands for (*S*)-**4** at 228 ([θ]/deg cm^2 dmol^{-1} = +1120), 257 (–1050), and 302 nm (+40) and for (*R*)-**4** at 228 (–1120), 257 (+1110), and 302 nm (–30) (Chart 2).[5d] On the basis of this finding, it is possible to determine the absolute configuration of the *trans*-**2**- and *cis*-**2**-derived enantiomers at the 3-position on the



(*S*)-**4** (*R*)-**4**

Chart 2

dihydroquinolinone ring by converting these intermediates into the corresponding cyclization product **3** and comparing the CD spectral data of **3** with those of **4**. After the *trans*-**2**-derived (t_R = 20 min) and *cis*-**2**-derived (t_R = 21 min) enantiomers with shorter retention times were isolated using a chiral HPLC column, these enantiomers were converted into the corresponding product **3** in refluxing methanol in the presence of TEA. Repeated preparative TLC on silica gel allowed us to isolate the targeted 3,4-dihydrodibenzoquinolinone derivatives, the CD bands of which in methanol were observed at 235 ($[\theta]$/deg cm^2 dmol^{-1} = +1950), 275 (–1200), and 317 nm (+660) for the *trans*-**2**-derived enantiomer and at 235 (–1320), 275 (+1240), and 317 nm (–610) for the *cis*-**2**-derived enantiomer. A comparison of the CD spectral data for **3** and **4** described above revealed that on fusing a benzene ring to the *h* side of the dihydroquinolinone ring in the latter derivative, all of the first, second, and third CD bands were shifted by 10–20 nm to higher wavelengths without changing their signs. Thus, this result led to conclude that the *trans*-**2**- and *cis*-**2**-derived enantiomers with shorter retention times are assigned to (3*S*,8a*S*)-**2** (t_R = 20 min) and (3*R*,8a*S*)-**2** (t_R = 21 min), respectively, and also the corresponding (3*R*,8a*R*)- and (3*S*,8a*R*)-enantiomers cause their HPLC signals to appear at longer retention times; namely, at t_R = 26 min for the former and t_R = 32 min for the latter.

For determining the ee values for the enantiomers formed in excess, nitrogen-saturated methanol, acetonitrile, or dichloromethane solutions of (*Z*)-**1** (1.0×10^{-3} mol dm^{-3}, 10 mL × 5) containing a given chiral amine were irradiated in parallel for 30 min under the conditions described above. An aliquot (10 mL) of the irradiated solution was treated with 0.20 mol dm^{-3} hydrochloric acid and subjected to ^{1}H NMR spectral analysis to estimate the relative compositions of *trans*-**2** and *cis*-**2**. The remaining solution was similarly treated and subjected to preparative TLC on silica gel, leading to the isolation of these two cyclization intermediates. The respective enantiomeric mixtures isolated were subjected to the normal phase HPLC analysis. The ee values for *trans*-**2** and *cis*-**2** were calculated on the basis of the area ratios of HPLC signals for the (3*S*,8a*S*)- and (3*R*,8a*R*)-enantiomers as well as for the (3*R*,8a*S*)- and (3*S*,8a*R*)-enantiomers. These ee values are presented in Table 1.

The data in Table 1 show that in the presence of S-PM or S-MPM bearing one basic nitrogen atom, there is a tendency for (3*R*,8a*R*)-**2** and (3*S*,8a*R*)-**2** to form in excess, whereas asymmetric induction in the photochemical transformation process into these cyclization intermediates is observed only to a slight extent (ee ≤ 6%). Interestingly, the use of S-NT bearing two basic nitrogen atoms (instead of S-MPM) enhanced the ee for both *trans*-**2** and *cis*-**2** by factors of approximately 4, although the configuration of enantiomers formed in excess is reversed. Because we have already demonstrated the involvement of the hydrogen-bonding interaction with chiral amine in the ee-determining step of asymmetric photocyclization of *N*-benzoyl-α-dehydronaphthylalanine *tert*-butyl esters,[7] this suggests that the two-site hydrogen-bonding interactions are involved in the ee-determining step of the S-NT-catalyzed asymmetric photocyclization of (*Z*)-**1** in methanol. In addition, the finding that almost the same ee is obtained in

acetonitrile suggests that the polar solvents methanol and acetonitrile exert almost the same effects on these interactions. Thus, the use of the less polar protic solvent, 2-propanol, instead of methanol is expected to strengthen such hydrogen-bonding interactions, resulting in an increased ee for the cyclization intermediates *trans*-**2** and *cis*-**2**. As shown in Table 1, the increased ee values in 2-propanol-methanol are consistent with our expectations and hence substantiate the involvement of the two-site hydrogen-bonding interactions.

Table 1. Chiral amine and solvent effects on the relative composition and ee value for each enantiomer of *trans*-**2** and *cis*-**2**, obtained by the irradiation of (*Z*)-**1** (1.0×10^{-3} mol dm^{-3}) in the presence of the chiral amine (0.10 mol dm^{-3}) at room temperature[a]

Chiral amine	Solvent	Relative composition[b] and ee (%)					
		trans-**2**			*cis*-**2**		
		(3*S*,8a*S*)-**2**	(3*R*,8a*R*)-**2**	ee	(3*R*,8a*S*)-**2**	(3*S*,8a*R*)-**2**	ee
S-PM	MeOH	34	35	1	15	16	3
S-MPM	MeOH	33	35	3	15	17	6
S-NT	MeOH	42	33	12	15	10	20
S-NT	MeCN	37	27	16	22	14	22
S-NT	*i*-PrOH-MeOH (4:1 v/v)[c]	36	24	20	27	13	35

[a] Conversions of (*Z*)-**1** were 100% in MeOH, MeCN, and MeOH-*i*-PrOH (1:4 v/v).
[b] Relative composition for each enantiomer of *trans*-**2** and *cis*-**2** was evaluated by dividing the composition for each enantiomer by the sum of compositions for (3*S*,8a*S*)-**2**, (3*R*,8a*R*)-**2**, (3*R*,8a*S*)-**2**, and (3*S*,8a*R*)-**2**.
[c] MeOH was used as a cosolvent owing to the low solubility of (*Z*)-**1** in *i*-PrOH.

In a previous study we proposed an excited-state zwitterion (depicted in Chart 3) as a key intermediate in the selective photocyclization of (*Z*)-**1** to *trans*-**2** and *cis*-**2** in methanol.[6] On the basis of the fact that (*Z*)-**1** undergoes only photoisomerization without forming any cyclization products in acetonitrile, it was assumed that the stabilization of the zwitterion intermediate by hydrogen-bonding and electrostatic interactions with methanol molecules is a driving force for the efficient photocyclization. In addition to this assumption, the PET mechanism for the amine-catalyzed cyclization of *N*-acyl-α-dehydronaphthylalaninamides led us to propose Scheme 2 providing a rationale for the efficient formation of **2** in methanol, acetonitrile, and 2-propanol-methanol.[4,5] The transfer of an electron from a given chiral amine to (*E*)-**1*** adopting a zwitterion structure may proceed in competition with the

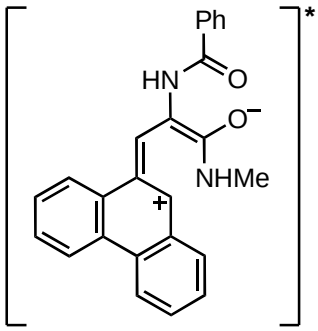
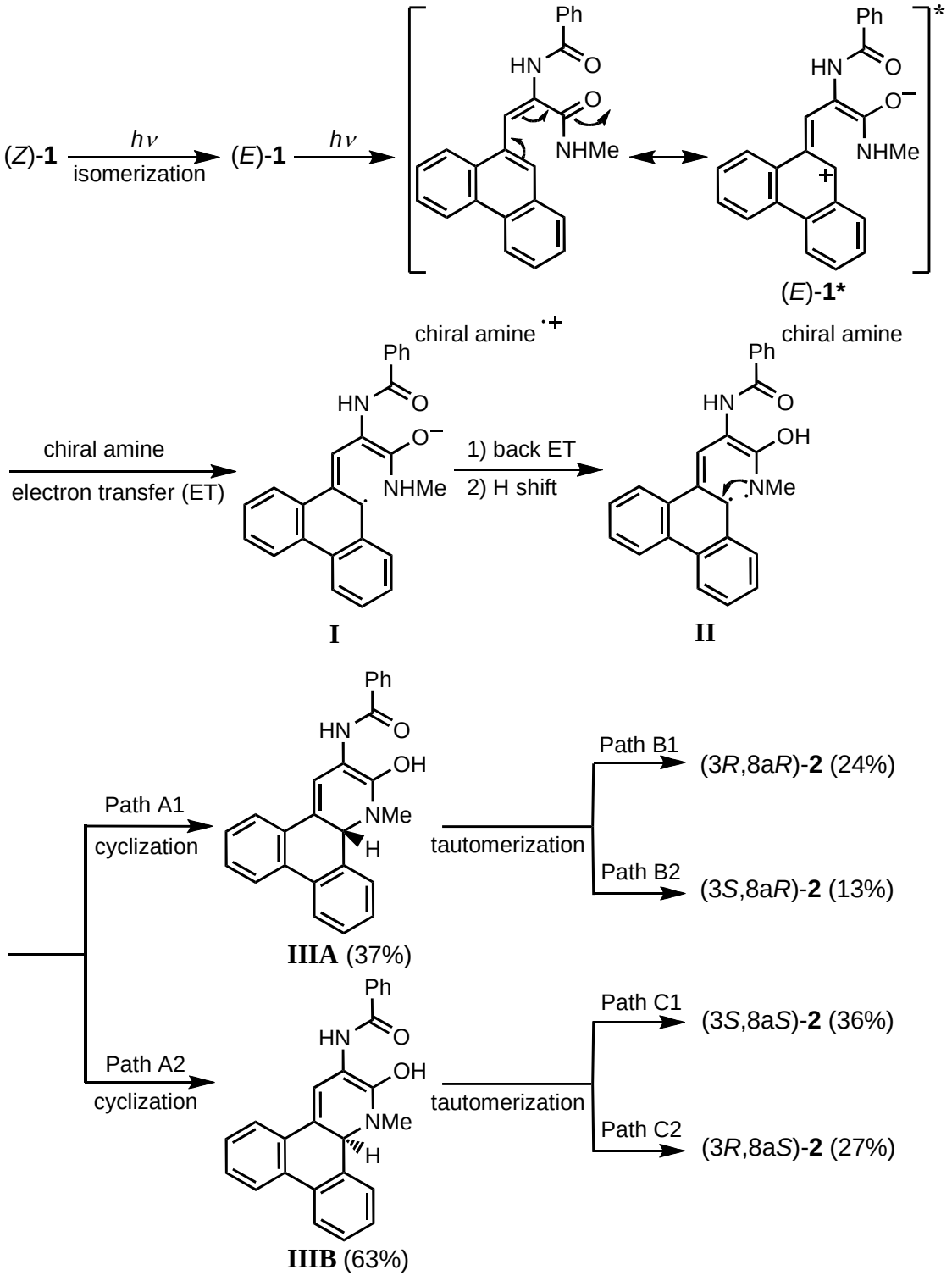


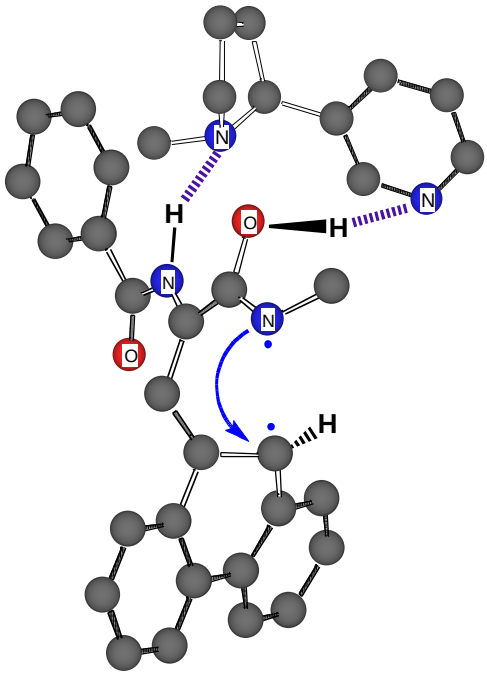
Chart 3

deactivation of this excited-state (*E*)-isomer to afford the radical ion pair **I**. Back electron transfer within **I** and the subsequent hydrogen shift should yield the key biradical **II**. This biradical ultimately undergoes cyclization (Path A) and tautomerization (Paths B and C) to yield the corresponding cyclization intermediate **2** by way of the enol **III**.



Scheme 2

Since configurational interconversion between **IIIA** and **IIIB** is unlikely to occur during the irradiation, it is possible to estimate the relative composition of these two enol intermediates using the composition of each enantiomer for *trans*-**2** and *cis*-**2**, collected in Table 1. As an example, the relative compositions of **IIIA** and **IIIB** in 2-propanol-methanol containing S-NT were estimated to be 37% and 63%, respectively. These compositions reveal that the (*E*)-**1**-derived biradical **II** cyclizes to the enol cyclization intermediate **IIIB** in 26% ee. Furthermore, the observation of ee = 35% for the *cis*-enantiomer (3*R*,8a*S*)-**2** demonstrates the remaining ee (9%) to be gained at the stage of tautomerization of **IIIA** and **IIIB**, and hence leads to the conclusion that the magnitude of the ee for *trans*-**2** and *cis*-**2** is determined by the Path A1/Path A2, Path B1/Path C1, and Path B2/Path C2 rate ratios. On the other hand, we previously suggested that the two-site hydrogen-bonding interactions with S-NT are involved in the asymmetric induction process for the PET-initiated cyclization reaction of (*Z*)-**1** in the presence of this chiral amine. Since the enol intermediate **IIIB** was formed in excess, the key biradical **II** may preferentially cyclize to **IIIB** in the *si* face of **II**, hence forming hydrogen bonds to S-NT (preferentially existing in the *si* face) at the two sites of this biradical intermediate. As depicted in Figure 1, both the benzoylamino hydrogen and the enol hydroxy hydrogen are considered to participate in these hydrogen bonds. It seems that a hydrogen atom at the 10 position on the phenanthrene ring, existing in the *re* face, exerts a greater steric hindrance to the two-site hydrogen-bonding interactions in the *re* face than in the *si* face.



II

Figure 1. Schematic illustration for the two-site hydrogen-bonding interactions of the enol biradical **II** with S-NT.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA500 spectrometer. Chemical shifts were determined using tetramethylsilane as an internal standard. Electrospray ionization time-of-flight (ESI-TOF) mass spectra were recorded using a JEOL JMS-T100LC AccuTOF mass spectrometer. Matrix-assisted laser desorption/ionization (MALDI)-TOF mass spectra were recorded on a Shimadzu/Kratos TOF mass spectrometer. Elemental analyses were performed on a Perkin-Elmer PE2400 series II CHNS/O analyzer. CD spectra were recorded on a Nihonbunko J-820

spectropolarimeter. HPLC analysis was performed on a Shimadzu LC-10AT HPLC system equipped with a Daicel CHIRALPAK IA column and a Shimadzu SPD-10A UV detector. Methanol and acetonitrile were purified according to the standard procedures and freshly distilled prior to use.[8] Spectrophotometric grade 2-propanol was used without further purification. All other chemicals were obtained from commercial sources at the highest grade available.

Procedure for the synthesis of (*Z*)-4-(9-phenanthrylmethylene)-2-phenyl-5(4*H*)-oxazolone

9-Phenanthrenecarboxaldehyde (24 mmol) was slowly added to an acetic anhydride solution (20 mL) of *N*-benzoylglycine (29 mmol) and sodium acetate (19 mmol) at rt and the resulting mixture was heated at 60–65 °C for 2 h with stirring. The reaction mixture was cooled overnight in an ice bath. The solid separated out was collected by suction filtration and washed with water, a small amount of cold EtOH, and dry hexane. After the crude product was air-dried at rt, it was recrystallized from hexane-$CHCl_3$ to afford the title oxazolone as a yellow crystal in a 71% yield: mp 197.5–198.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (2H, dd, *J* = 7.4, 8.0 Hz), 7.64 (1H, d, *J* = 8.0 Hz), 7.67 (1H, d, *J* = 8.0 Hz), 7.70–7.76 (3H, m), 8.07 (1H, d, *J* = 8.0 Hz), 8.13 (1H, s), 8.23 (2H, d, *J* = 8.0 Hz), 8.34 (1H, dd, *J* = 4.5, 8.0 Hz), 8.69 (1H, d, *J* = 8.0 Hz), 8.76 (1H, dd, *J* = 4.5, 8.0 Hz), 9.26 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 122.6, 123.3, 123.5, 125.6, 126.8, 127.0, 127.2, 127.3, 127.8, 128.4 (2C), 128.6, 128.9 (2C), 130.35 (2C), 130.39, 131.1, 131.5, 133.4, 134.26, 134.29, 164.2, 167.6.

Procedure for the synthesis of (*Z*)-*N*-benzoyl-α-dehydro(9-phenanthryl)alanine *N*'-methylamide [(*Z*)-1]

(*Z*)-4-(9-Phenanthrylmethylene)-2-phenyl-5(4*H*)-oxazolone (4.6 mmol) was dissolved in THF (40 mL) containing methylamine (40 wt% aqueous solution, 6.0 mmol) and the resulting solution was allowed to stand for 30 min with stirring at rt. The removal of the solvent gave a crystalline solid, which was recrystallized from EtOAc-hexane to afford (*Z*)-**1** as a colorless crystal in a 89% yield: mp 236.5–237.0 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 2.76 (3H, d, *J* = 4.1 Hz), 7.39 (2H, dd, *J* = 7.6, 7.6 Hz), 7.48 (1H, dd, *J* = 7.6, 7.6 Hz), 7.58 (1H, dd, *J* = 7.6, 8.2 Hz), 7.66 (1H, dd, *J* = 7.6, 8.2 Hz), 7.68 (1H, dd, *J* = 7.6, 8.2 Hz), 7.72 (1H, dd, *J* = 7.6, 8.2 Hz), 7.75 (1H, s), 7.75 (1H, d, *J* = 8.2 Hz), 7.81 (2H, d, *J* = 7.6 Hz), 7.92 (1H, s), 8.09 (1H, d, *J* = 8.2 Hz), 8.23 (1H, q, *J* = 4.1 Hz), 8.80 (1H, d, *J* = 8.2 Hz), 8.86 (1H, d, *J* = 8.2 Hz), 9.78 (1H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 26.4, 122.8, 123.3, 125.1, 126.2, 126.9 (2C), 127.0, 127.1, 127.3, 127.8 (2C), 128.1 (2C), 128.5, 129.7, 129.8, 130.0, 130.2, 130.8, 131.5, 132.9, 133.9, 165.1, 166.3. Anal. Calcd for $C_{25}H_{20}N_2O_2$: C, 78.93; H, 5.30; N, 7.36. Found: C, 78.97; H, 5.22; N, 7.27.

Procedure for the irradiation of (*Z*)-1

To determine the structure and composition of the (*Z*)-**1**-derived photoproducts, nitrogen-saturated methanol solutions of (*Z*)-**1** (4.0×10^{-3} mol dm^{-3}, 10 mL × 5) containing S-MPM (0.10 mol dm^{-3}), placed in Pyrex test tubes, were irradiated in parallel for 30 min at wavelengths longer than 280 nm from a 400 W high-pressure Hg lamp set in a Pyrex cooling jacket. Parallel irradiation of the solutions was carried out at rt using a carrousel irradiation apparatus immersed into a water bath (RIKO model RH400-10W). The irradiated solutions were combined and concentrated to dryness under reduced pressure affording the residual solid, which was dissolved in $CHCl_3$. The chloroform solution was washed with 0.2 mol dm^{-3} hydrochloric acid and water and dried over sodium sulfate. The removal of the solvent afforded the residual solid, which was subjected to preparative TLC on silica gel (70–230 mesh) using $CHCl_3$-EtOAc (6:1 v/v) as a developing solvent. Standard workup led to the isolation of *trans*-3-benzoylamino-3,8a-dihydro-1-methyl-2(1*H*)-dibenzo[*f*,*h*]quinolinone (*trans*-**2**) and *cis*-3-benzoylamino-3,8a-dihydro-1-methyl-2(1*H*)-dibenzo[*f*,*h*]quinolinone (*cis*-**2**), in addition to 3-benzoylamino-3,4-dihydro-1-methyl-2(1*H*)-dibenzo[*f*,*h*]quinolinone (**3**).

For determining the absolute configuration and enantiomeric excess (ee) of the *trans*-**2**- and *cis*-**2**-derived enantiomers, nitrogen-saturated methanol solutions of (*Z*)-**1** (1.0×10^{-3} mol dm^{-3}, 10 mL × 5) containing chiral amine (0.10 mol dm^{-3}), placed in Pyrex test tubes, were irradiated in parallel for 30 min at wavelengths longer than 280 nm from a 400 W high-pressure Hg lamp. The same procedure as above led to the isolation of *trans*-**2** and *cis*-**2**. The isolation of these two isomers-derived enantiomers and the determination of their retention times and relative compositions (ee) were accomplished by HPLC apparatus equipped with a 4.6 × 250-mm Daicel CHIRALPAK IA column using the mixture of 2-propanol (20 vol%), $CHCl_3$ (20 vol%), and hexane (60 vol%) as a mobile phase (detection wavelength, 250 nm; flow rate, 1.0 mL min^{-1}). After each enantiomer dissolved in MeOH had been heated for 2 h under reflux, the reaction mixture was evaporated to dryness under reduced pressure. The resulting residue was subjected to preparative TLC on silica gel (developing solvent, ethyl EtOAc:hexane = 3:1 v/v). This workup enabled us to isolate the corresponding cyclization product **3**. The absolute configuration of each enantiomer was determined by comparing its CD spectrum in MeOH with that of the 3,4-dihydrobenzo[*f*]quinolinone derivative **4** described in a previous paper.[5d] The physical and spectroscopic data for *trans*-**2**, *cis*-**2**, and **3** are as follows.

trans-**2:** mp 204.0–205.0 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.18 (3H, s), 5.20 (1H, ddd, J = 2.5, 5.0, 8.0 Hz), 5.40 (1H, dd, J = 2.0, 5.0 Hz), 5.87 (1H, dd, J = 2.0, 2.5 Hz), 7.30 (1H, d, J = 7.5 Hz), 7.39–7.52 (7H, m), 7.57 (1H, dd, J = 7.0, 7.5 Hz), 7.88 (1H, d, J = 7.5 Hz), 7.94 (2H, d, J = 7.0 Hz), 7.99 (1H, d, J = 7.5 Hz), 9.05 (1H, d, J = 8.0 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 35.4, 47.2, 62.5, 120.9, 122.8, 123.7, 124.4, 125.3, 127.4 (2C), 127.7,128.0, 128.3 (2C), 128.6, 129.1, 131.4, 132.5, 133.1, 133.4, 133.9, 134.0, 136.1, 166.0, 166.9. ESI-TOF-MS *m*/*z* calcd for $C_{25}H_{20}N_2NaO_2$: 403.1422 $[M + Na]^+$. Found: 403.1421.

cis-**2:** mp 120.0–121.0 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 3.20 (3H, s), 5.24 (1H, ddd, J = 4.0, 4.0, 8.0 Hz), 5.39 (1H, dd, J = 2.0, 4.0 Hz), 5.94 (1H, dd, J = 2.0, 4.0 Hz), 7.34 (1H, dd, J = 5.0, 5.0 Hz), 7.39–7.43 (5H, m), 7.45–7.51 (2H, m), 7.59 (1H, d, J = 7.5 Hz), 7.80 (2H, d, J = 7.5 Hz), 7.85–7.87 (1H, m), 7.99 (1H, d, J = 7.5 Hz), 9.07 (1H, d, J = 8.0 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 37.3, 48.4, 62.4, 119.6, 124.0, 124.6, 125.4, 125.5, 127.9, 128.0 (2C), 128.3, 128.7 (2C), 129.0, 129.8, 131.8, 133.1, 133.4, 134.5, 134.6, 134.7, 136.8, 166.6, 167.2. ESI-TOF-MS m/z calcd for $C_{25}H_{20}N_2NaO_2$: 403.1422 $[M + Na]^+$. Found: 403.1365.

3: ^{1}H NMR (500 MHz, DMSO-d_6) δ = 3.36 (1H, dd, J = 14.5, 16.0 Hz), 3.44 (3H, s), 3.69 (1H, dd, J = 6.0, 16.0 Hz), 4.95 (1H, ddd, J = 6.0, 8.0, 14.5 Hz), 7.54 (2H, dd, J = 7.0, 7.5 Hz), 7.60 (1H, dd, J = 7.5, 7.5 Hz), 7.67–7.76 (4H, m), 8.00 (2H, d, J = 7.0 Hz), 8.06 (1H, d, J = 7.5 Hz), 8.15 (1H, d, J = 7.5Hz), 8.87 (2H, d, J = 8.0 Hz), 8.91 (1H, d, J = 8.0 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 37.9, 49.1, 67.0, 121.8, 123.2, 123.7, 123.8, 124.2, 124.9, 126.1, 126.6, 126.7, 127.4 (2C), 127.6, 127.9, 128.4 (2C), 129.3, 130.5, 131.5, 134.0, 135.3, 166.2, 171.2. MALDI-TOF-MS m/z calcd for $C_{25}H_{20}N_2O_2$: 380.47 $[M]^+$. Found: 380.31.

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