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Chirality and Circular Polarized Properties of Photochromic Polyaromatic Molecules

Tsuyoshi Sawada, Shingo Kubo and Kazuaki Nanamura

Abstract

Dihydropyrenes (DHPs) are a particularly interesting class of photochromic polyaromatic molecules due to their negative photochromism in UV-Vis spectra. Asymmetric heterocyclic-[e]-annelated DHPs were prepared by new synthetic routes and their photochromism was studied. The optical resolution of heterocyclic-[e]-annelated DHPs was performed by chiral HPLC systems and their enantiomers indicate the photochromism for UV-Vis, and CD spectra. The absolute structures of the enantiomers were determined by using spectra predicted with time-dependent density functional theory. Photoswitchable circular dichroism properties of asymmetric heterocyclic-[e]-annelated DHPs have potential as the molecular device to control the circular polarized light.

Keywords: photochromism, planar chirality, circular dichroism, dihydropyrene

1. Introduction

Circular polarized light (CPL) has attracted considerable research attention due to its application in fields such as 3D displays, bioimaging, and optical communication systems [1, 2]. Circular polarized filters are used for the control of CPL, but this presents the problem of a large dissipation of CPL strength by the filter. Therefore, it is desirable to produce CPL light directly by using organic electronic luminescence devices that contain chiral organic materials [3, 4]. For the direct control of light, photochromic organic molecules are interested in these decades (**Figure 1**) [5–7]. Photochromic molecules are the reversible transformation of molecular structures between two forms by the photoirradiation, where the two forms have different absorption spectra.

In these compounds, dihydropyrenes (DHPs) are negative photochromic polyaromatics [8] that undergo wavelength-dependent reversible photoisomerization between dark green closed and colorless open forms (**Figure 2**) [9–13].

We have expected that asymmetrically functionalized DHPs will have a planar chirality due to the orientation of internal groups. If they have a planar chirality, their circular polarized properties will be interesting depending on the photochromic behavior.

In this chapter, we will describe about our recent topics about the syntheses, photochromism, and circular polarized properties of asymmetrical-functionalized DHPs [14–17].

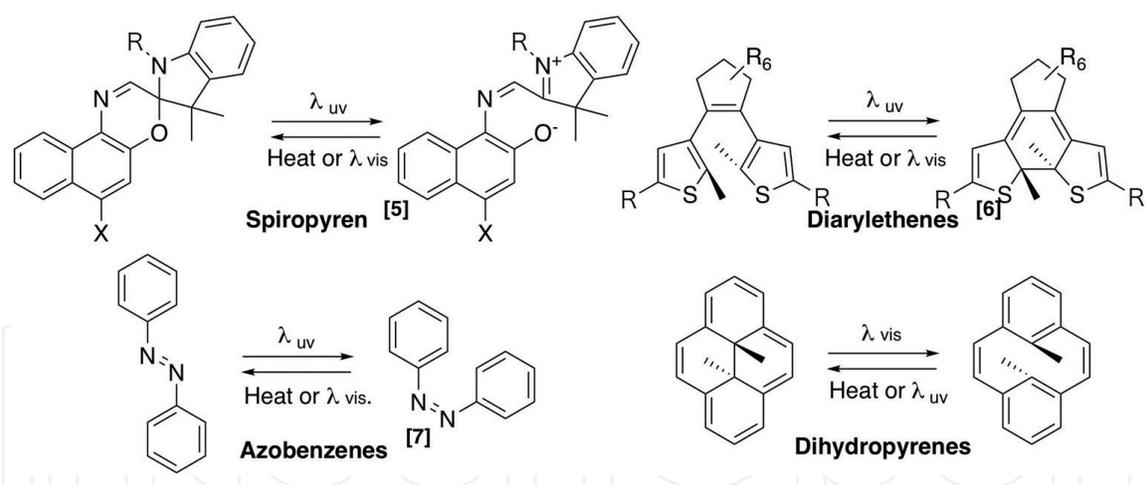


Figure 1.
Photochromic organic molecules.

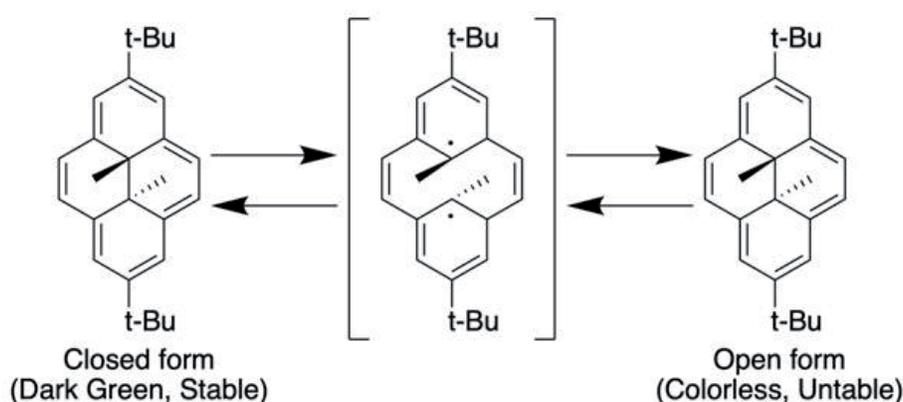


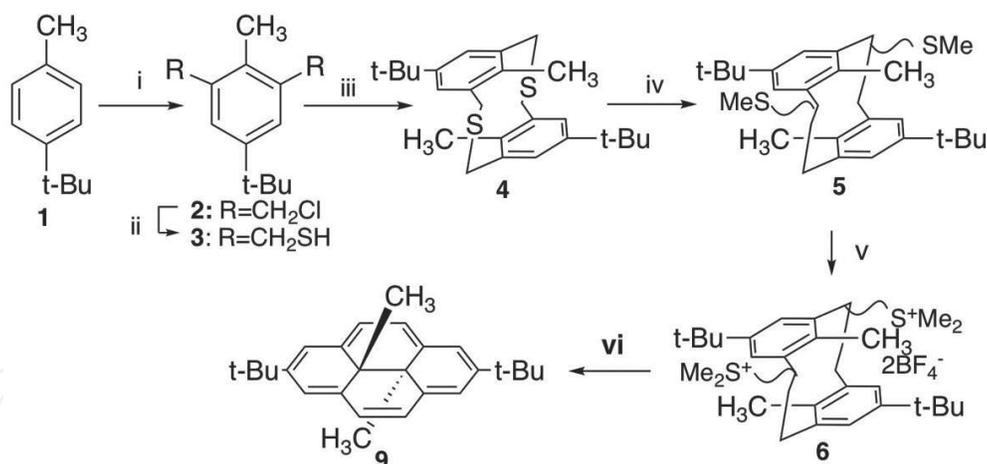
Figure 2.
Photochromism of DHP.

2. Synthesis

2.1 Preparation of parent DHP

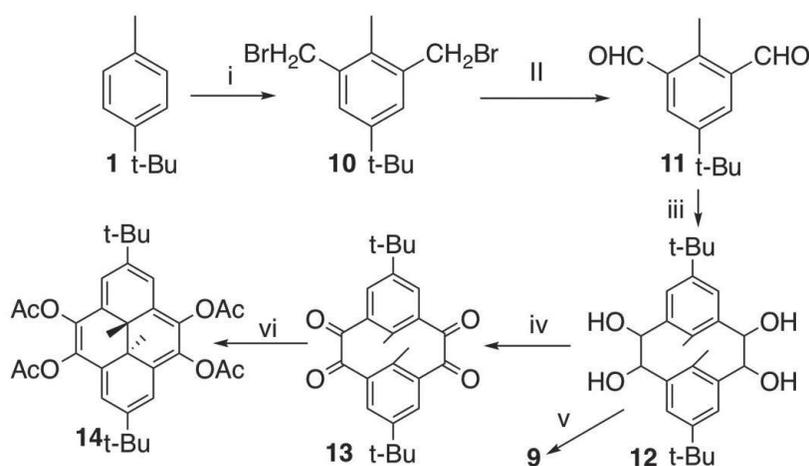
DHP is one of the polyaromatic molecules, which has 14π electron systems. In 1967, Boekelheide et al. reported the preparation and structure of DHP [18]. It was made by the oxidation of metacyclophane (MCP), which is a cyclic aromatic compound connected with ethylene chains at meta position. But it required long synthetic route and total yield is under 1%. The convenient synthetic route to di-*tert*-butyldimethyl DHP was developed by Tashiro [19] and improved by Mitchell [20]. Prof. Tashiro has studied about the application of *tert*-butyl groups for selective functionalization of toluene. This preparative route via dithia[3.3]MCP required six reaction steps, and a total yield of 45% was achieved from 4-*tert*-butyltoluene **1** (Scheme 1). This route afforded DHP **9** with a good yield, but the long reaction sequence and requirement of highly skilled techniques restricted the practical applications of DHPs as advanced materials.

In 2008, we have reported new synthetic method of DHP (Scheme 2) [17]. Tetrahydroxy-[2.2]MCP **12** was prepared from benzene-dialdehyde derivative **11** in one step [21, 22]. The MCP **12** has the potential to be the intermediate of DHPs, because the MCP **6** has two *trans*-diols at its both bridge positions and their reduction could give a MCPD, which is an equivalent of DHP **9**. The reduction of MCP **12** to DHP **9** was performed by using imidazole, chlorodiphenylphosphine, iodine,



Scheme 1.

Reagents and conditions: *i*, $\text{ClCH}_2\text{OCH}_3$, ZnCl_2 ; *ii*, (1) $(\text{NH}_2)_2\text{CS}/\text{KOH}$, (2) HCl ; *iii*, 2, KOH/NaBH_4 ; *iv*, (1) $n\text{-BuLi}$, (2) MeI ; *v*, $(\text{MeO})_3\text{CH}$, $\text{BF}_3\text{-Et}_2\text{O}$; *vi*, KOBU^t .



Scheme 2.

Reagents and Conditions: *i*, ZnBr_2 , $(\text{CH}_2\text{O})_3$, HBr in AcOH THF; *ii*, (1) Pyridine, reflux, (2) $\text{Me}_2\text{NC}_6\text{H}_4\text{NOHCl}/\text{EtOH}$, rt.; *iii*, Al powder, aq. NaOH , MeOH ; *iv*, DMSO , Ac_2O ; *v*, (1) imidazole, Ph_2PCL , (2) I_2 , (3) Zn powder; *vi*, Zn powder, Ac_2O , Et_3N in CH_2Cl_2 , rt., N_2 .

and Zn powder, to give DHP **9** at 75% yield [17]. This method had been reported by Zhengchun [23] to produce a *cis*-olefin from *trans*-diol of carbohydrate. The treatment of MCP **13** with zinc powder, Ac_2O , and Et_3N [24, 25] gave DHP **14** functionalized by acetoxy moieties at the 4,5,9,10-positions at 50% [17].

2.2 Functionalization to asymmetric heterocyclic[e]-annelated DHPs

To produce asymmetrical DHPs, we have proposed to introduce a heterocycle at [e]-position of DHPs. Mitchell et al. has reported that benzene-annelated DHP at the [e] position (benzene-[e]-annelated DHP) shows greatly improved switching rates [20]. These reports suggested that heterocyclic-[e]-annelated DHPs have improved photochromism and chirality.

We have prepared mono-heterocyclic-annelated DHPs as shown in **Figure 3**. Asymmetrical DHPs **15** and **16** were synthesized from MCP **13**, and pyrazine-[e]-annelated DHP (PZ-DHP **17**) was obtained from DHP **9**. Synthetic routes of DHP **15** and **16** were shown in **Scheme 3**.

Firstly, quinoxalino-[e]-annelated DHP (QX-DHP, **15**) was synthesized using a condensation reaction of MCP **13** with one equivalent of *o*-phenylenediamine in ethanol, followed by subsequent reduction using zinc powder in acetic anhydride. QX-DHP **15**

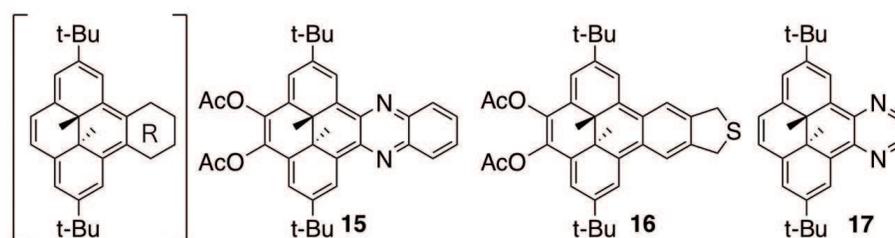
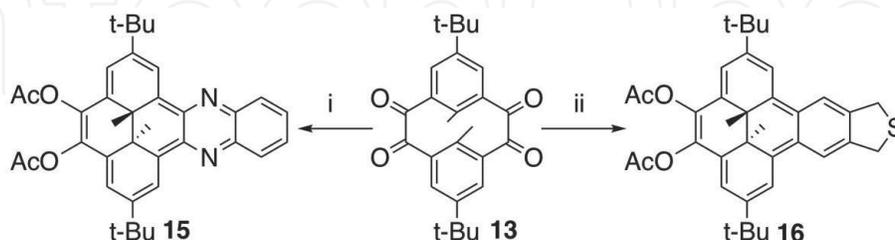
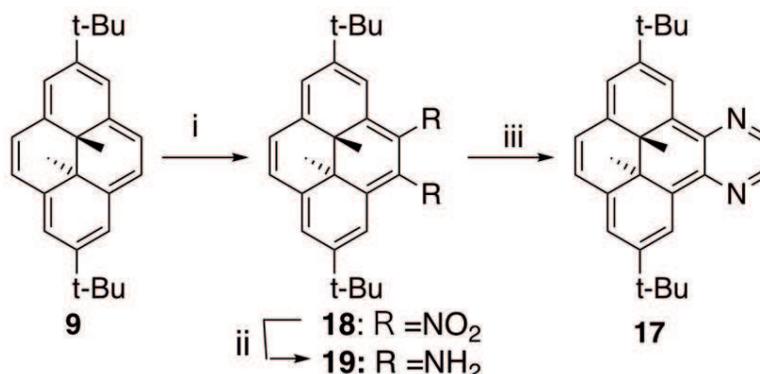


Figure 3.
Asymmetric heterocyclic-[e]-annelated DHPs.



Scheme 3.
Reagents and Conditions: *i.* (1) 1, 2-phenylenediamine (1 eq.), (2) Zn powder, Ac₂O, Et₃N, Y = 13%; *ii.* (1) 2,3-diaminothiophene (1 eq.), (2) Zn powder, Ac₂O, Et₃N, Y = 21%.



Scheme 4.
Reagents and Conditions: *i.* Cu(NO₃)₂·3H₂O, in MeOH, Y = 69%; *ii.* 5% Pd/C, HCOONH₄ in MeOH, Y = 97%; *iii.* 40% aq. Glyoxal in EtOH Y = 10%.

was obtained in 13% yield. The condensation reaction of DHP 13 with one equivalent of 2,3-diaminothiophene and subsequent reduction using zinc powders in acetic anhydride gave a tetrahydrothiophene-[e]-annelated DHP (HT-DHP, 16) at 21% yield.

The synthetic route to pyrazino-[e]-annelated DHP (PZ-DHP, 17) is shown in **Scheme 4**. The nitration of DHP 9 was performed by treatment with copper(II) nitrate in methanol, as Yamato et al. have reported that the nitration of DHP selectively afforded the 5,6-dinitro-substituted DHP [26]. The subsequent reduction and following condensation with glyoxal gave DHP 17 as a purple red powder at 10% yield. The low yield of this reaction was expected due to its unfavored conformation of glyoxal.

3. Aromaticity and photochromism

3.1 Aromaticity of heterocyclic-[e]-annelated DHPs

As DHP derivatives are one of the 14 π aromatic systems, they show a remarkable magnetic anisotropy due to a ring current of π -electrons [20]. This ring current

makes a strong upshielding effect on the internal group's protons and downshielding effect on the periphery protons of aromatic rings. Therefore, the chemical shift of internal methyl protons of DHPs can play a role of magnetic shielding probe for aromaticity of DHPs.

$^1\text{H-NMR}$ spectra of HT-DHP **16** were shown in **Figure 4** [16]. Although the methyl protons of toluene were detected at 2.31 ppm, internal methyl group of DHP **16** were observed at -1.03 ppm in toluene- d_8 . The chemical shifts of internal methyl protons of other DHPs **9**, **15**, and **17** were observed at -3.61 , [20], -0.14 [15], and -1.53 pp [14], respectively. The degree of upshielding effects was different due to the heterocycle unit and functional groups of DHPs. Parent DHP **9** shows largest upfield shift (from 2.31 to -3.61 ppm) of internal methyl protons and the order of chemical shifts were DHP **9** > **17** > **16** > **15**. These results suggested that the aromaticity of DHPs is influenced by the electron donating or withdrawing groups at 4, 5, 9, 10 positions.

3.2 Photochromic properties of DHPs

DHP derivatives undergo small changes in dimensionality when subjected to a photoswitching process [27–29], and they are potentially a new type of photochromic dyes for photoswitching devices, data storage, photochromic sensitizers, and organic electronics [13]. However, their low photochromic efficiency remains as a barrier to further applications. It has been reported that benzene-[e]-annelated DHP shows greatly improved switching rates [20, 30].

The photoisomerization of DHPs **15**, **16**, and **17** was examined by UV-Vis spectroscopies (**Figure 5**). **Figures 6–8** show UV-Vis spectral change of **15**, **16**, and **17** through visible light irradiation of >455 nm by using 110 V/500 W halogen light equipped with a long-path glass filter (Schott GG455).

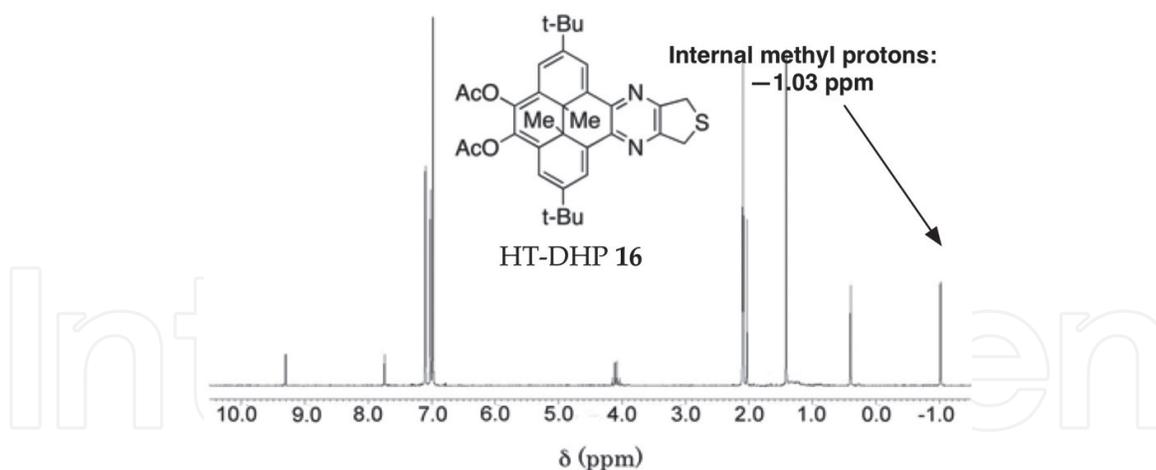


Figure 4.
 $^1\text{H-NMR}$ spectrum of HT-DHP **16**.

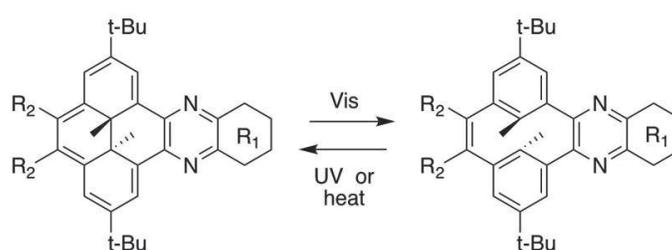


Figure 5.
Photochromism of DHP **15** ($R_1 = \text{Benzene}$, $R_2 = \text{OAc}$), **16** ($R_1 = \text{hydrothiophene}$, $R_2 = \text{OAc}$), and **17** ($R_1 = \text{H}$, $R_2 = \text{H}$).

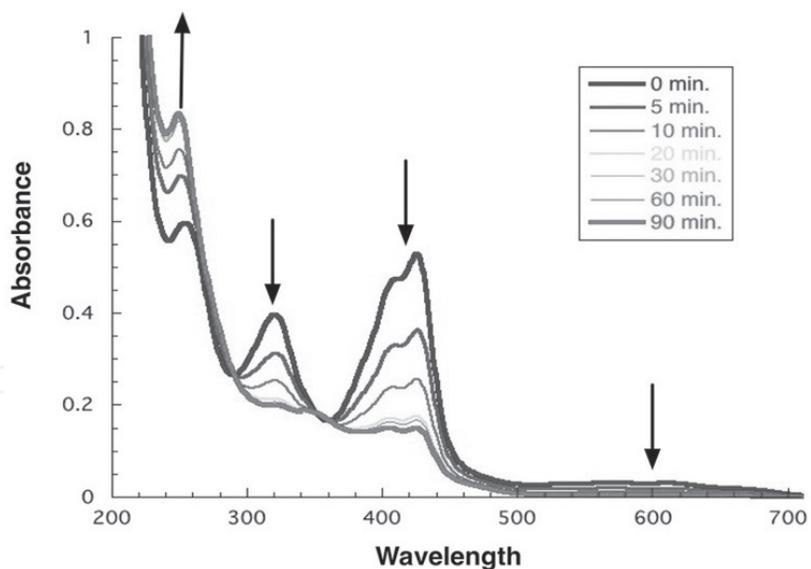


Figure 6. UV-visible spectra of QX-DHP **15** under irradiation with >455 nm light in cyclohexane.

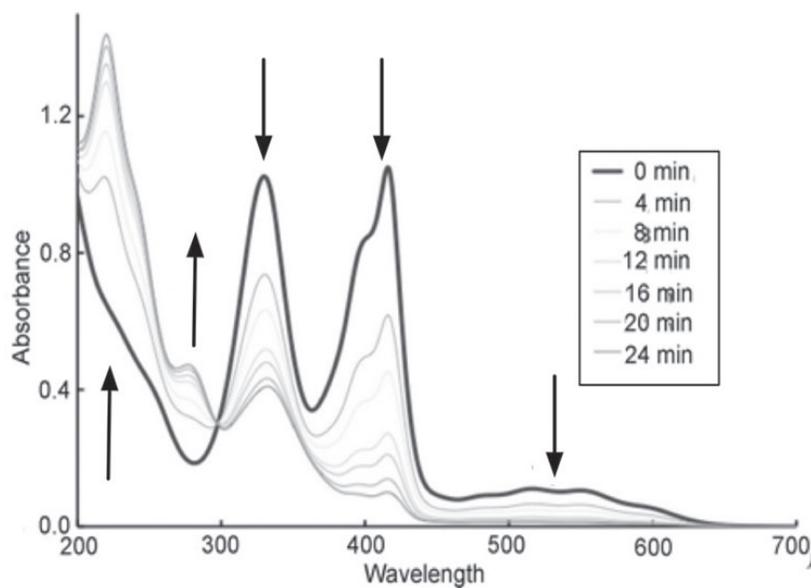


Figure 7. UV-visible spectra of HT-DHP **16** under irradiation with >455 nm light in cyclohexane.

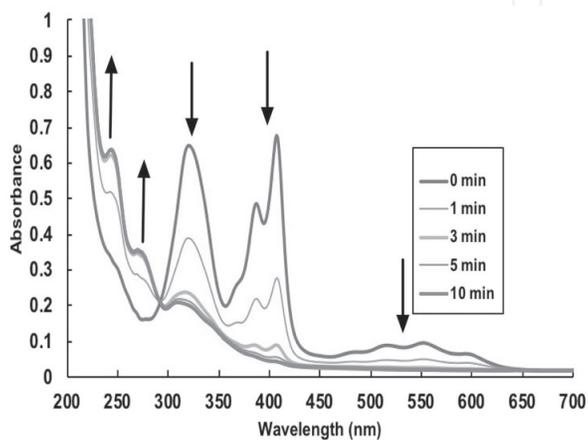


Figure 8. UV-visible spectra of PZ-DHP **17** under irradiation with 254 nm light in cyclohexane.

The closed form of DHPs has a visible light absorption over 450 nm. Especially, closed form of QX-DHP **15** indicates a longer wavelength shift (450–700 nm) than that of DHPs **16**, **17** (450–650 nm). It will be depending on the conjugated systems of annelated heterocycles. The open form of DHPs shows UV light absorptions under 300 nm. The absorption peaks around 300–350, 360–440, and over 450 nm are decreased with visible light irradiation, with the appearance of an isosbestic point near 280–300 nm.

Figure 9 shows the $^1\text{H-NMR}$ spectrum of HT-DHP **16**, resulting compound obtained after visible light irradiation for 1 h. Chemical shift of the internal methyl protons was detected at 1.69 ppm, and the peak at -1.03 ppm, which was assigned to the internal methyl protons of closed form of **16**, was almost disappeared. This result indicates that photoisomerization from closed form to open form was induced quantitatively by irradiation. Then, a photo-induced return reaction from open form to closed form was carried out by photoirradiation using UV light [16]. UV light irradiation for 1 h caused open form to almost transform quantitatively to closed form.

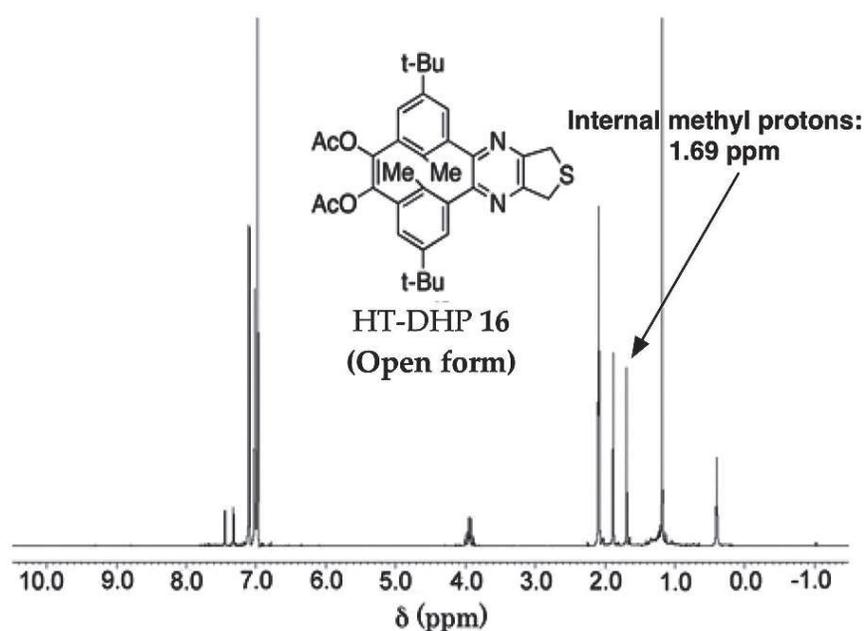


Figure 9.
 $^1\text{H-NMR}$ spectrum of open form of HT-DHP **16**.

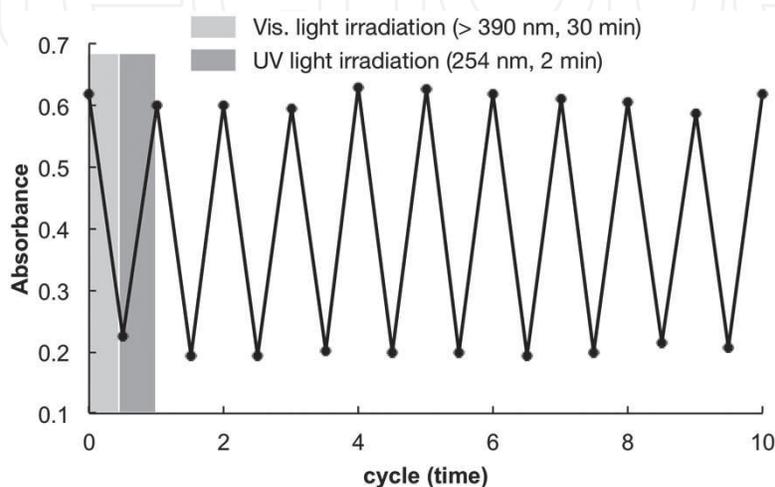


Figure 10.
Repeatability of the photoisomerization of PZ-DHP **17** in cyclohexane under photoirradiation at >390 and 254 nm.

The repeatability of photoisomerization between closed and open form was also examined. As shown in **Figure 10**, the photoisomerization of PZ-DHP **17** was repeated at least 10 times. This result indicates that **17** can be photoswitched more than 100 times in organic solutions, although its intensity is observed to decrease slightly.

Photoisomerization ratio and reaction times of DHPs **15**, **16**, and **17** are shown in **Figures 11** and **12**. The photoisomerization rate of PZ-DHP **17**, which is the fastest, was observed for the heteroaromatic annelated DHPs under the same reaction conditions. These results suggested that annelation of pyrazine ring at [e] position of DHP improved photoisomerization rate than that of quinoxaline or hydrothiophene rings. And then, ester group on DHPs **15**, **16** would have been decreasing their photochromic rate.

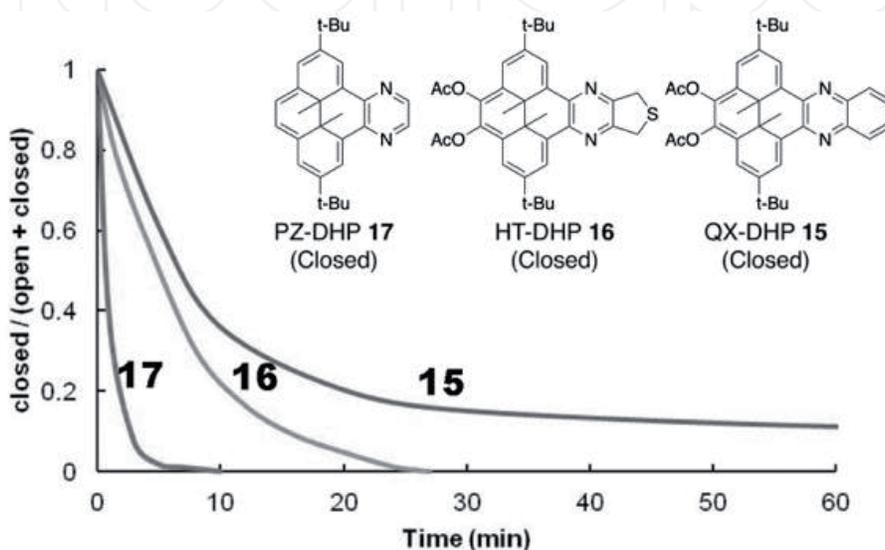


Figure 11. Relative reaction rate from closed form to open form of DHPs **15**, **16** and **17** by Vis light irradiation (>390 nm, 500w halogen light).

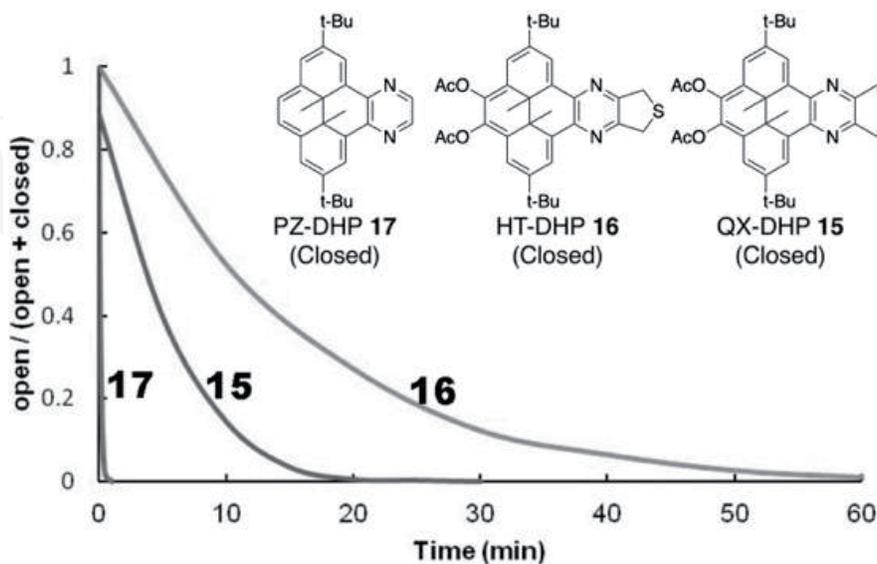


Figure 12. Relative reaction rate from open form to closed form of DHPs **15**, **16**, and **17** by UV light irradiation (254 nm, 4w black light).

4. Planar chirality and optical resolution

The heterocyclic-[e]-annulated DHPs have planar chirality because of the orientation of its internal methyl groups and heterocycle unit (**Figure 13**). About assigning of the configuration of a planar chiral DHPs, when viewed from the side of the pilot atom (**P**: internal methyl group at **Figure 13**), if the three adjacent in-plane atoms form a clockwise direction when followed in order of priority, the molecule is assigned as R, otherwise it is assigned as S. Therefore, the presence of ester groups on DHPs change the order of priority of atoms.

We have examined the isolation of the chiral isomer of DHPs, which can be used to control the circular polarization of light through photoisomerization.

For the optical resolution of photochromic DHPs, we have examined the isolation of closed and open form of DHPs, and then, S and R enantiomer of closed and open form of DHPs.

In the reverse-phase HPLC analysis of QX-DHP **15**, a signal was observed at 9.36 min before irradiation over 455 nm, but a new signal at 7.96 min was found after 60 min of irradiation (**Figure 14**). Therefore, the signals observed at 9.37 and 7.96 min are expected as the closed and open form of **15**, respectively.

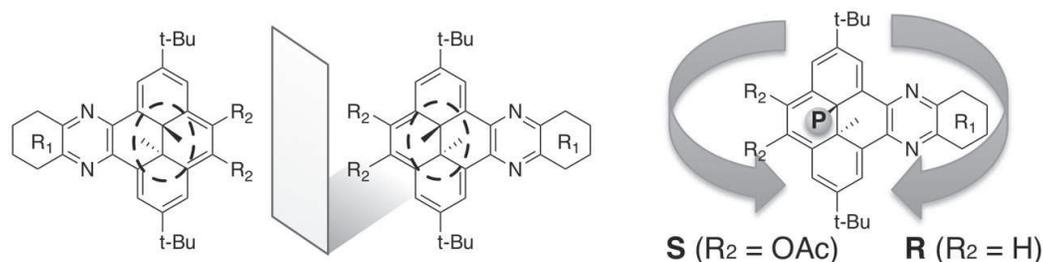


Figure 13.
Planar chirality and their absolute configuration of DHPs.

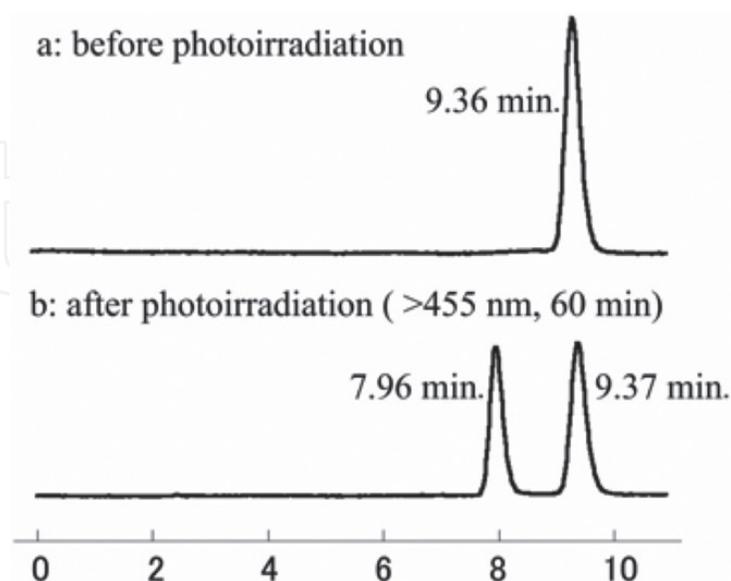


Figure 14.
Chromatograms of QX-DHP **15** (a) before and (b) after photoirradiation at >455 nm using an ODS-packed column (10 × 25 mm, GL Science). Mobile phase: methanol. Column temperature: 25°C. Flow rate: 4 ml min⁻¹. Detector: 285 nm.

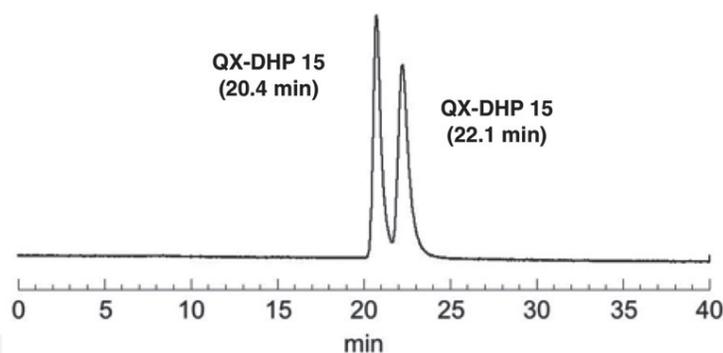


Figure 15.

Chromatograms of QX-DHP **15** (closed form) taken using a Chiral HPLC packed column (10 × 25 mm, Chiralpak IA Daicel Corp.). Mobile phase: methanol. Column temperature: 25°C. Flow rate: 1 ml min⁻¹. Detector: 395 nm.

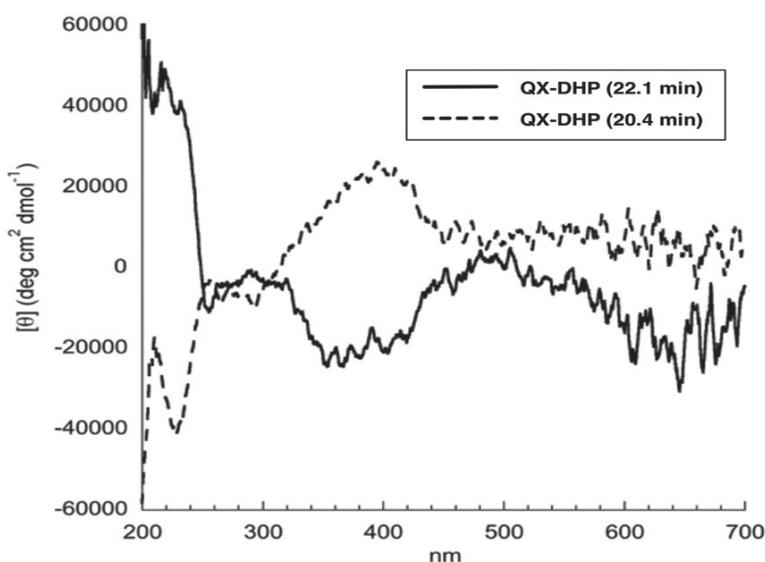


Figure 16.

CD spectra of QX-DHP **15** (closed form) isolated by chiral HPLC.

The optical resolution of QX-DHP **15** was also performed by using an HPLC system equipped with a chiral column (Chiralpak IA 10 × 25 mm, DAICEL Corp.) with MeOH as the mobile phase (**Figure 15**). Two signals were observed at 20.4 and 22.1 min, and their UV-visible spectra were almost the same as that of the QX-DHP **15** (closed form), which is before HPLC isolation. The two signals of CD bands (500–320 nm) were almost the opposite, which means that they were enantiomers of **15** (closed form) (**Figure 16**).

The photochromism of CD spectra were also examined. The enantiomer of QX-DHP **15** (22.1 min) was isolated by a HPLC system equipped with a chiral column. The photochromic CD spectra of the enantiomer **15** (22.1 min) are shown in **Figure 17**.

After photoirradiation with visible light (> 445 nm) for 120 min, remarkable positive and negative Cotton effects were observed from 281 to 323 nm and from 245 to 281 nm, respectively. Although, there is no remarkable difference in the 330–500 nm region. The absorption signals from 200 to 350 nm would be related to the conjugated stilbene structure, and it is expected that cleavage at the internal position will cause a large morphological change from the “planar” closed form QX-DHP **15** to the “step-like” open form QX-DHP **15**. This result suggests that QX-DHP **15** has photoswitching properties in terms of its circular dichroism. The almost same behavior about optical resolution and CD pattern were observed for HT-DHP **16**.

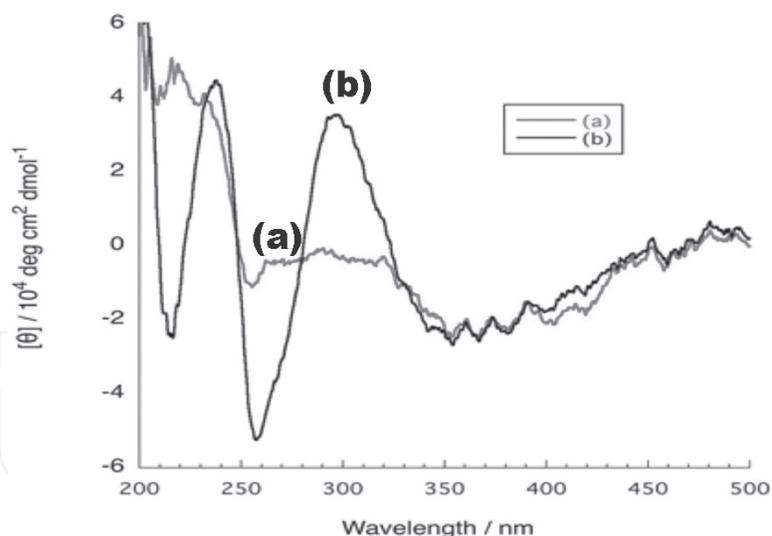


Figure 17.
CD spectra of QX-DHP 15 (22.1 min) (a) before irradiation and (b) after irradiation at >455 nm for 120 min (1.1×10^{-5} mol/L in cyclohexane).

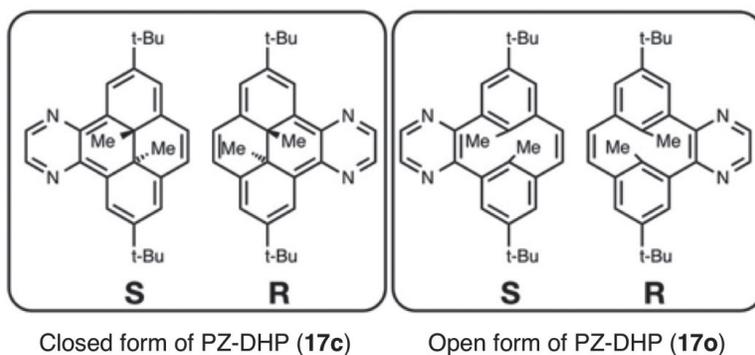


Figure 18.
Planar chirality and chiral configuration of PZ-DHP 17.

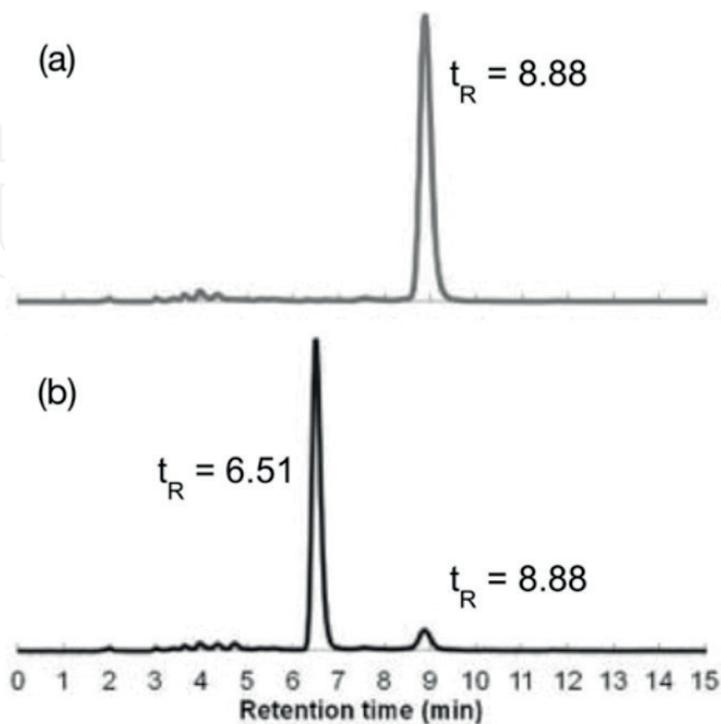


Figure 19.
Chromatogram of PZ-DHP 17 (a) before and (b) after photoirradiation (>390 nm, 10 min). (HPLC column: ODS-3 (4.6 × 250 mm), mobile phase: methanol, 1 mL/min, 25°C, detector: 293 nm).

We have also investigated about the planar chirality and optical resolution of PZ-DHP **17**. PZ-DHP **17** was also expected to show planar chirality because of the orientation of its internal methyl groups and pyrazine unit (**Figure 18**).

In the reverse-phase HPLC analysis of closed form of PZ-DHP (**17c**), only one signal was observed (at 8.88 min) before irradiation with visible light (>390 nm), but a new signal (at 6.51 min) was observed after 30 min irradiation (**Figure 19**). Therefore, the signals observed at 8.88 and 6.51 min were assigned to **17c** and open form of PZ-DHP (**17o**), respectively.

The optical resolution of **17** was examined using an HPLC system equipped with a chiral HPLC column (Chiralpak IA 10 × 250 mm, Daicel Corp.) using methanol as the mobile phase (**Figure 20**). Although before visible light irradiation, we detected only one signal (at 6.51 min) by the UV detector at 293 nm and no signal by the CD detector; after visible light irradiation for 30 min, two new signals (at 7.60 and 8.43 min) were observed by the UV detector and two signals were observed by the CD detector at the same retention times. The two signals observed by the CD detector were both positive and negative, which means that they are enantiomers of open form **17**. Therefore, using this chiral HPLC system, **17o** can be enantiomerically separated, but **17c** cannot.

Two enantiomers of **17o** were isolated with chiral HPLC and their photochromism and CD spectra were examined. The CD spectra of the isolated **17o** (**R**), (**S**) are shown in **Figure 21a**. The absolute configuration of enantiomers of **17o** were

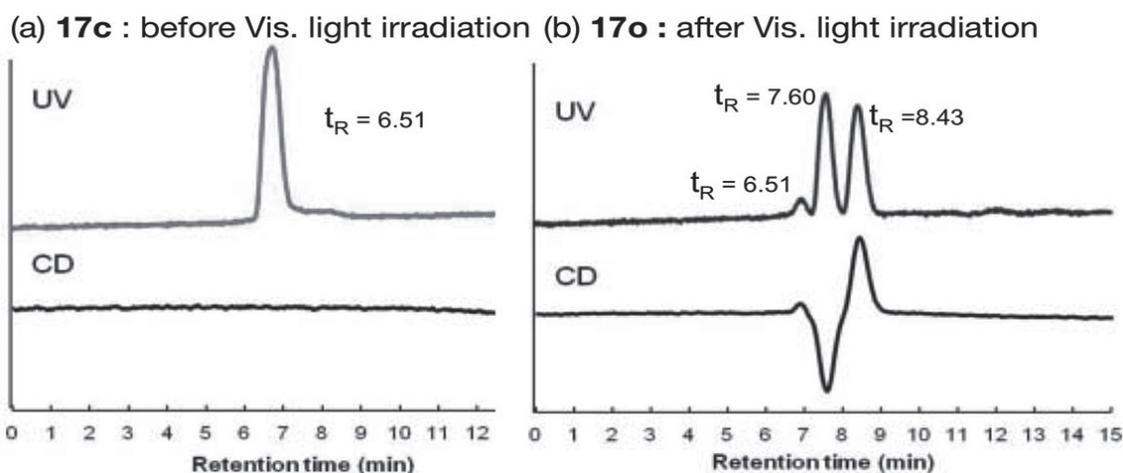


Figure 20. Chromatographs of PZ-DHP **17** equipped with CD detector (a) before (b) after visible light irradiation (>390 nm, 30 min). (HPLC column: CHIRALPAK IA (4.6 × 250 mm), mobile phase: hexane:chloroform (9:1), 0.5 mL/min, 25°C, detector: 293 nm).

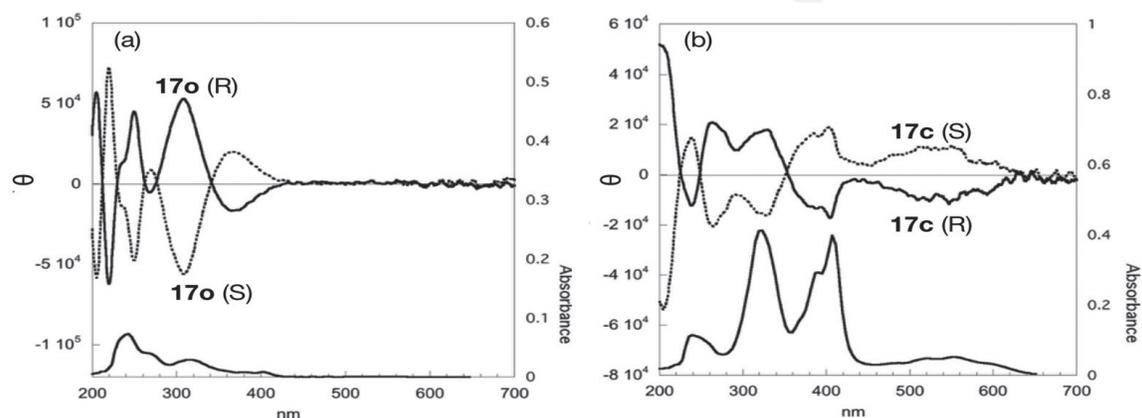


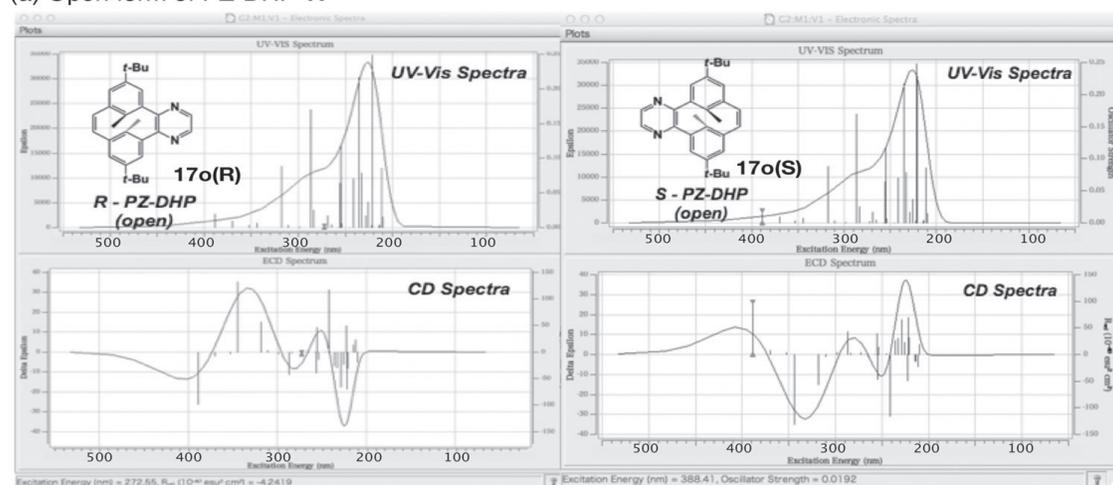
Figure 21. CD and UV-Vis spectra of isolated PZ-DHP enantiomers (a) **17o** and (b) **17c**.

determined by a comparison with CD spectra calculated using time-dependent density functional theory (TD-DFT) employing method (B3LYP/6-31G*) with Gaussian 09 (Figure 22).

After photoirradiation at 254 nm, significant positive and negative Cotton effects were observed from 450 to 600 nm for the R and S enantiomers of 17c, respectively (Figure 21b). The CD spectra of 17c(R) and 17c(S) were observed to be similar to the TD-DFT-calculated CD spectra. There is no remarkable decrease in the CD signal intensities after several photoisomerization cycles between the open (17o) and closed (17c) forms, which suggests that the absolute configuration of 17c is retained during the photoisomerization.

The photochromic CD spectra from 17c(S) to 17o(S) are indicated in Figure 23. After photoirradiation (>390 nm) for 25 min, remarkable differences in the Cotton effect were detected. There were isosbestic points at 381, 331, 281, 257, and 228 nm, and positive Cotton effects were observed at the range from 331 to 381 nm, and from 257 to 281 nm. In the photoisomerization process, the phase of the Cotton effects at 257–281 nm and 228–257 nm changed from positive to negative, and from negative to positive, respectively. The absorption from 200 to 350 nm is related to the conjugated stilbene system, and it is expected that a large morphological change from the “planar” form of 17c to the “step-like” form of 17o were influenced on Cotton effects. Although the repeatability of this CD spectral change was not investigated, this result suggests that PZ-DHP 17 has switchable circular dichroism properties.

(a) Open form of PZ-DHP 17



(b) Closed form of PZ-DHP 17

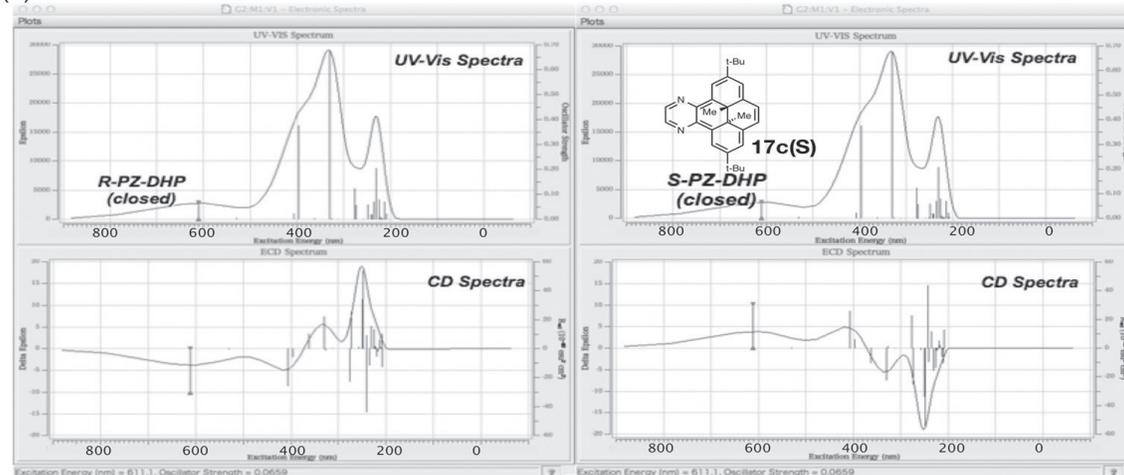


Figure 22. Simulated CD and UV-Vis spectra of isolated PZ-DHP enantiomers (a) 17o and (b) 17c by Gaussian 09 (B3LYP/6-31G*) [31].

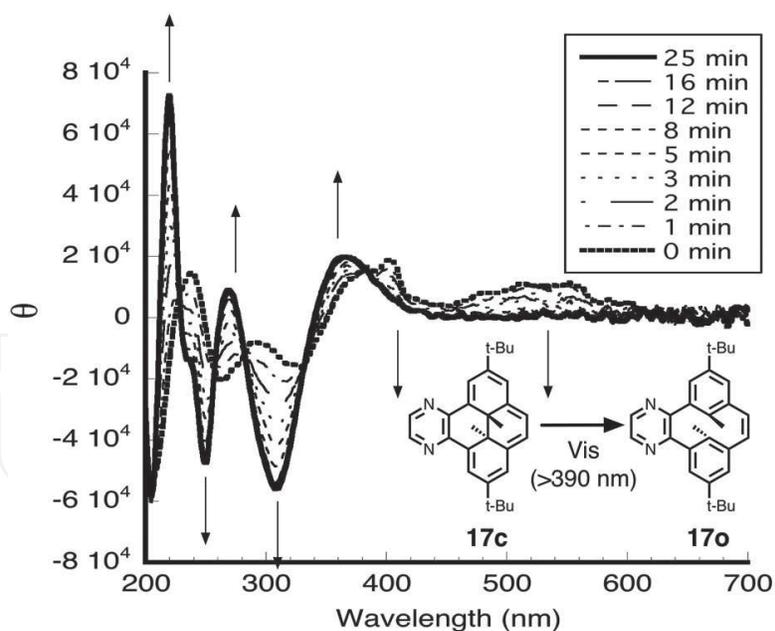


Figure 23.
Photochromic CD spectra from PZ-DHP **17c**(S) to **17o**(S) in cyclohexane.

5. Conclusion

We successfully developed a simple and convenient method for the synthesis of heterocyclic-[e]-annelated DHPs **15**, **16**, and **17**, which possess planar chirality. We experimentally confirmed their planar chirality and the repeatability of the photoisomerization between the closed and open forms. In the investigation of the CD spectra under photoirradiation, a significant photoresponse was observed. These results suggest that the DHPs have potential as a photoresponsive circularly polarized emitting material, and that other molecules based on this general structure may also show similar promise. Further research is being conducted to investigate the molecular design of heterocyclic-[e]-annelated DHPs and their application as photoswitching materials for circular-polarized light.

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