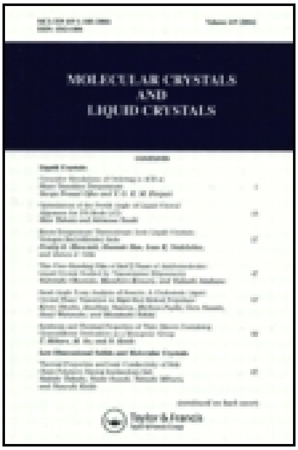

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Effects of Photo-Irradiation on the Optical Properties and Electronic Structures of an Azo-Containing Bent-Core Liquid Crystal

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With the ultraviolet-visible spectrophotometry and electronic structure calculations, we have investigated the effects of photo-irradiation on the optical properties and electronic structures of an azo-containing banana-shaped liquid crystal. The synthesized compound exhibits two optical absorptions at about 275 and 360 nm, respectively. Our electronic structure calculations reveal that the two absorptions can be attributed to the $\pi \to \sigma^*$ *and* $\pi \to \pi^*$ *transitions in the azo-chromophores of the banana-shaped liquid crystal. Our results have demonstrated that photo-dissociation takes place predominantly when dilute tetrahydrofuran solution of the azo-containing liquid crystal is exposed to the 365 nm irradiation despite* tran-to-cis *photochemical isomerization is observed.*

Keywords: azo-compound; banana-shaped liquid crystal; *cis-trans* isomerization; photo-dissociation; *trans-cis* isomerization

1. INTRODUCTION

Being one novel class of banana-shaped liquid crystals (LCs), azo-containing banana-shaped LCs bear significance in developing photo-switchable molecular electronic devices because of the

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photoactive double bond –N=N– in those substances [1–4]. The *trans-to-cis* and *cis-to-trans* photochemical isomerizations of the double bond –N=N– in azo-compounds play a critical role in the photo-switchable molecular electronic devices [5]. As documented in literature, it is a general belief that the irradiation of 365-nm ultraviolet may convert *trans* azo-containing LC to its *cis* form while the irradiation of 436-nm blue light takes *cis*- azo-containing LC back to its *trans* form [1–4,6]. For an example, the spontaneous polarization of a ferroelectric banana-shaped LC was decreased when the 365-nm ultraviolet was turned on after the LC had been doped with a photoactive azo-containing compound 4-(4-ethoxyphenylazo)phenyl hexanoate [7].

Although both the *trans-to-cis* and *cis-to-trans* photochemical isomerizations are well documented for azo-compounds, photo-dissociation may also take place when those azo-compounds are exposed to the irradiation of energetic ultraviolet photons. Whether the process of photo-dissociation takes place in azo-containing LCs is not only critical to the performance of the photo-switchable molecular electronic devices but also important to the understanding of the physics in the azo-containing banana-shaped LCs. The purpose of our work is to investigate the effects of photo-irradiation on the optical and electronic properties of an azo-containing banana-shaped LC. Our results demonstrate that the photo-dissociation is the predominant process in the azo-containing LC when it is exposed to the 365-nm irradiation.

2. EXPERIMENTAL DETAILS

Following the procedures described in Ref. [1], we synthesized an azo-containing banana-shaped compound. The synthesis route was schematically shown in Figure 1. All analytical reagents were purchased either from Alfa Aesar or from Guanghua Chemical Reagents Co. Ltd (Guangdong, China). All reagents were used as received. Intermediate compounds 4-(4-hydroxy-phenylazo)-benzoic acid ethyl ester (intermediate **A**), 4-(4-hexyloxy-phenylazo)-benzoic acid ethyl ester (intermediate **B**), 4-(4-hexyloxy-phenylazo)-benzoic acid (intermediate **C**) and 4-(3-hydroxy-benzylidene-amino)-phenol (intermediate **D**) were purified by the techniques of recrystallization and the silica gel chromatography, and then were characterized with the techniques of nuclear magnetic resonance (AVANCE 400 MHz, Brucker), Fourier transformed infrared spectroscopy, and mass spectroscopy, respectively. Following the general route [8–10], we synthesized the target compound, an azo-containing banana-shaped LC (**E**), by condensing the intermediates **C** and **D** in the solvent of dichloromethane

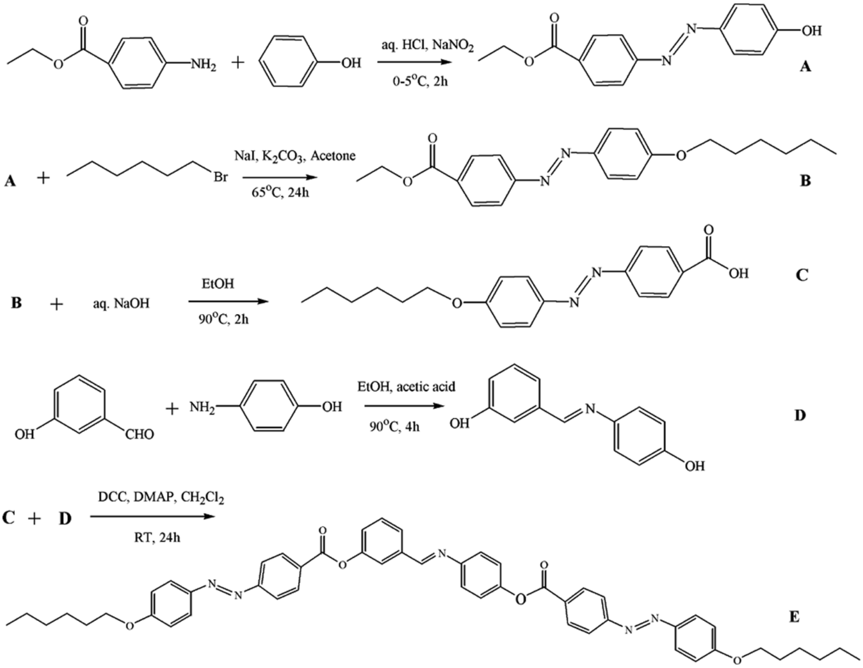

FIGURE 1 Synthesis route of the azo-containing banana-shaped LC. Intermediates **A, B, C** and **D** stand for 4-(4-hydroxy-phenylazo)-benzoic acid ethyl ester, 4-(4-hexyloxy-phenylazo)-benzoic acid ethyl ester, 4-(4-hexyloxy-phenylazo)-benzoic acid, and 4-(3-hydroxy-benzylidene-amino)-phenol, respectively.

with the addition of catalysts 4-dimethylaminopyridine (DMAP) and N,N′-dicyclohexyl carbodiimide (DCC).

Analytical reagent tetrahydrofuran was used as the solvent to prepare dilute solutions of the azo-containing banana-shaped LC. A 10-mm-thick quartz cell was used as a cuvette of the solutions for optical absorption measurements. The optical absorption spectra of our synthesized target compound **E** were measured with an ultraviolet-visible spectrometer UV-3501S (Tianjin Gangdong Ltd., China). A commercially available ultraviolet lamp was used to provide a beam of 325 nm ultraviolet light for the ultraviolet irradiation.

The electronic structures of the target compound **E** and the two intermediates **C** and **D** were calculated with the extended-Hückel tight-binding method. BICON-CEDiT, an extended Hückel band structure and oscillator strength calculation package, was developed by the group of Prof. Gion Calzaferri at University of Berne, Switzerland [11].

It is a set of FORTRAN programs that allow extended-Hückel tight-binding calculations for 1D-3D compounds to get their band structures and density of states. In order to obtain the optimal molecular structure for the electronic structure calculation, we performed a geometry optimisation of an individual molecule at AM1 level and then extracted the geometry of the molecule. The AM1 program was implemented in the MOPAC package (Quantum Chemistry Program Exchange, Indiana University, USA). The standard Slater parameters for C, H, O and N atoms were adopted from Ref. [12].

3. RESULTS AND DISCUSSION

Figure 2 shows the photo-irradiation time dependent optical absorption spectra of dilute solutions of the synthesized azo-containing banana-shaped LC. The solvent was tetrahydrofuran while the concentration of the solution and the wavelength of the photo-irradiation were 90 mg/L and 365 nm, respectively. Before the sample is exposed to the 365-nm irradiation, the azo-containing banana-shaped LC can

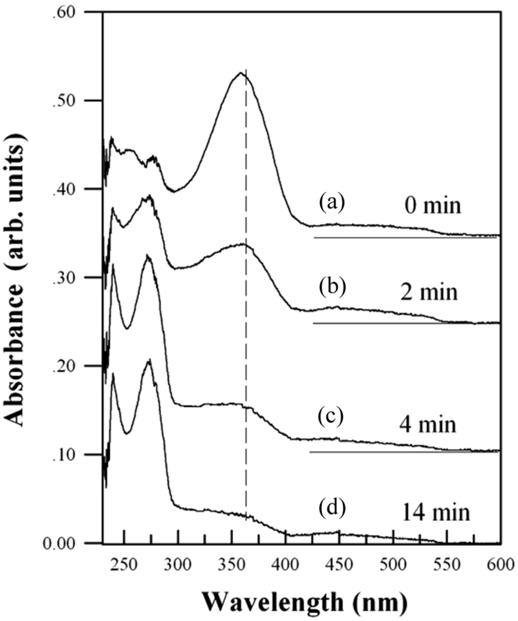

FIGURE 2 Photo-irradiation time dependent optical absorption spectra of dilute solutions of the synthesized azo-containing banana-shaped LC. The solvent was tetrahydrofuran while the concentration of the solution and the wavelength of the photo-irradiation were 90 mg/L and 365 nm, respectively.

absorb light intensively at 360 nm but weakly at 275 and 440 nm, as shown by the curve **a** in Figure 2. The broad but weak absorption at about 440 nm suggest that our synthesized azo-containing banana-shaped LC is a mixture of *trans* and *cis* azo-compounds even before the 365 nm photo-irradiation. This might be caused by the room light illumination in our lab. As the photo-irradiation time increases, the absorption at 360 nm decreases quickly while the absorption at 275 nm increases correspondingly; in the meanwhile the broad absorption at 440 nm experiences a slight increases at first with a an obvious decrease followed. As documented in literature for azo-compounds, upon ultraviolet irradiation of around 360 nm (corresponding to the π–π^* band of the azo-group) the elongated rod-like and energetically more stable *trans* configuration changes into a bent *cis*-configuration. The reverse transformation can be brought back by illuminating the molecules with visible light of about 420 nm (corresponding to the n–π^* band). If the above statement holds for banana-shaped azo-compounds, the 360 nm absorption in Figure 2 can be assigned to the electronic transition in *trans* banana-shaped LC while the 440 nm absorption in Figure 2 can be assigned to the electronic transition in *cis* banana-shaped LC. If so, the slight increase in the absorption at 440 nm suggests that the 365-nm photo-irradiation can generate *trans-to-cis* photochemical isomerization for our azo-containing banana-shaped LC.

The electronic structures are now critically important to understand the effects of the 365-nm photo-irradiation on the optical absorption of the banana-shaped LC because the optical properties and the electronic structures of the banana-shaped LC are closely related. Our previous work has demonstrated that the electronic structures calculated with extended Hückel tight-binding program are helpful to understand the optical properties of a series of LC polymers [13–17]. Before we can understand the electronic structures of our target compound, i.e., the azo-containing banana-shaped LC, the knowledge on the electronic structures of intermediate compounds **C** and **D** will be helpful. Figure 3 depicts the energy levels (left panel) and density of states (right panel) of intermediate **C**. The π, n, π^* and σ^* orbitals are labelled in Figure 3. Figure 3 shows clearly that the $\pi \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions will generate optical absorptions at 3.58 eV (346 nm) and at 4.45 eV (279 nm), respectively. Although the non-bonding orbit is also labelled, the $n \rightarrow \pi^*$ transition is prohibited due to the selection rules. The results in Figures 2 and 3 reveals a close correlation between the electronic transitions of the azo-containing intermediate C and the optical absorptions of the azo-containing banana-shaped LC.

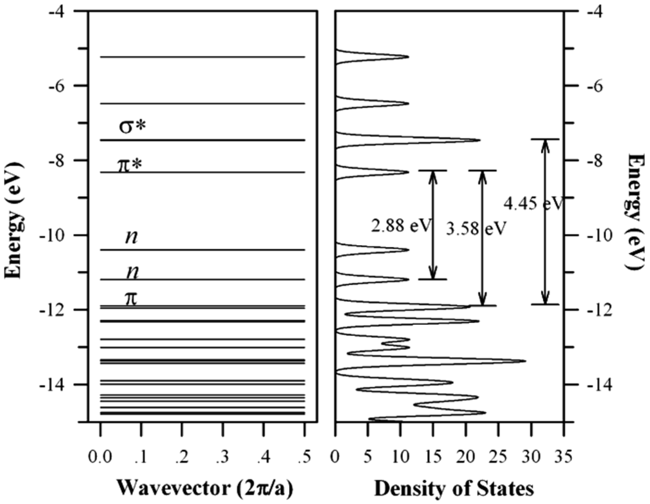

FIGURE 3 Energy levels (left panel) and density of states (right panel) of intermediate **C**: 4-(4-hexyloxy-phenylazo)-benzoic acid.

Figure 4 represents the energy levels (left panel) and density of states (right panel) of intermediate **D**. Similarly, the π, n and π^* orbitals are labelled in Figure 4 for the intermediate **D**. From Figure 4,

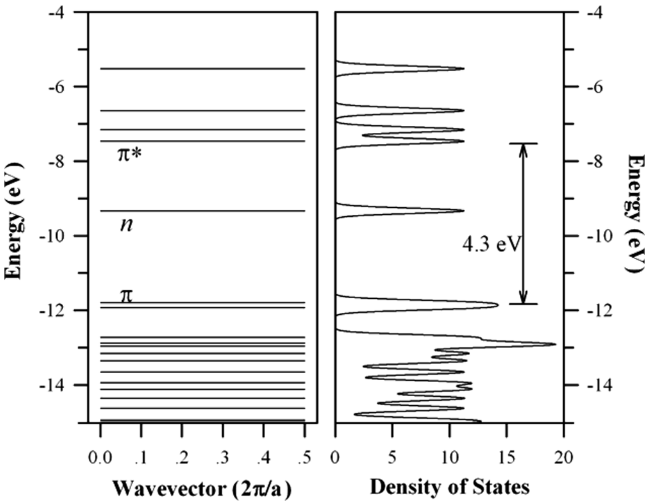

FIGURE 4 Energy levels (left panel) and density of states (right panel) of intermediate **D:** 4-(3-hydroxy-benzylidene-amino)-phenol.

optical absorption at 4.3 eV (288 nm) will be resulted from the $\pi \rightarrow \pi^*$ transition. In our experiment, we measured the optical absorption of the dilute solutions of intermediate **D**, and our optical measurement confirmed that the absorption of intermediate **D** took place at 290 nm (4.3 eV).

Figure 5 shows the energy levels (left panel) and density of states (right panel) of the azo-containing banana-shaped compound. It is obvious that the electronic structures of the azo-containing banana-shaped compound **E** are the simple summation of two independent sets of electronic structures. The first set of electronic structures is contributed by intermediate **C** while the second set of electronic structures is contributed by intermediate **D**. It is understandable because there is no overlapping in the conjugations of the two kinds of chromophores in **E**. As a result, the absorptions of our banana-shaped molecule **E** will be a simple summation of the absorption of intermediate **C** and the absorption of intermediate **D**.

On the basis of the calculated electronic structures, we can interpret the optical absorptions of the azo-containing banana-shaped compound **E**. The features of the electronic structures of **E** suggest that the optical absorptions of **E** are contributed by intermediates **C** and **D** independently. Therefore, the 360-nm absorption of **E** in Figure 2 originates from the $\pi \rightarrow \pi^*$ transitions in the azo-containing chromophores. As shown in Figure 1, the two azo-containing chromophores

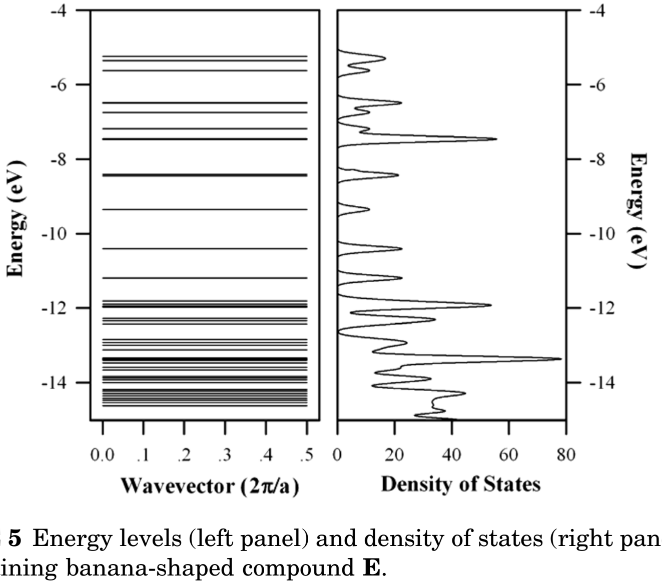

FIGURE 5 Energy levels (left panel) and density of states (right panel) of the azo-containing banana-shaped compound **E**.

are incorporated into the two branched legs of **E**. The photo-irradiation induced decrease in the absorption at 360 nm suggests that the photo-irradiation has broken some π conjugations in the azo-linkages of the banana-shaped molecule **E**. Similarly, the 275-nm absorption of **E** originates from the $\pi \rightarrow \sigma^*$ transitions in the azo-containing chromophores, and the photo-irradiation induced increase in the absorption at 275 nm suggests that the photo-irradiation has increased σ^* bonding in the azo-linkages of the banana-shaped molecule **E**. The photo-induced decrease in the π conjugations and a simultaneous increase in the σ^* bonding indicate that photo-dissociation process has taken place in the azo-containing banana-shaped LC.

4. CONCLUSION

With the ultraviolet-visible spectrophotometry and electronic structure calculations, we have investigated the effects of photo-irradiation on the optical properties and electronic structures of an azo-containing banana-shaped LC. The synthesized compound exhibits two optical absorptions at about 275 and 360 nm, respectively. Our electronic structure calculations indicate that the two absorptions can be attributed to the $\pi \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions in the azo-chromophores of the banana-shaped LC. Our results have demonstrated that photo-dissociation takes place predominantly when the dilute tetrahydrofuran solution of the azo-containing LC is exposed to the 365 nm irradiation despite *tran-to-cis* photochemical isomerization is observed. The photo-irradiation induced photo-dissociation and the *tran-to-cis* photochemical isomerization will be helpful to understand the photophysics and photochemistry in azo-containing banana-shaped LCs.

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