

# Study on the Preparation and Photoreresponse of Binaphthyl Chiral Azo Molecule

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**Abstract**—Multi-reflective band cholesteric liquid crystal thin films have attracted much attention because of their great commercial value. The main reason is that the broadband reflective film can not only be used as a brightening film in liquid crystal display, but also as a reflective layer in energy-saving glass and other aspects. These advantages make it receive great attention in these areas. In order to fabricate multi-reflective band cholesteric liquid crystal thin films with photoresponsive properties, the first step is to configure photoresponsive cholesteric liquid crystals. As mentioned above, photoresponsive chiral compounds become the key here. As more and more intensive study of the special photoisomerization mechanism of azobenzene, the optical materials based on azobenzene derivatives have aroused widespread concern. The photoresponsive chiral azobenzene compounds have the advantages of simple synthesis, good compatibility with liquid crystals and great changes in helical twisting force during cis-trans isomerization. In this paper, a chiral binaphthyl compound containing azo group was synthesized and doped into liquid crystal to determine its helical twist force. The spectral properties of n-hexane solution were also studied. The experimental results show that the twist force of the target molecule is up to 37  $\mu\text{m}^{-1}$ .

**Keywords**—Azobenzene, chirality, binaphthyl, photoreponse, helical twisting force

## I. INTRODUCTION

With the development of science and technology, intelligent molecular devices have attracted much attention because of their unique properties. The development of intelligent molecular devices has been greatly promoted by the self-assembled superstructures of controllable molecules with expected performance obtained by external stimuli [1-5]. The common external stimuli include temperature, PH value, electric field, magnetic field, chemical or electrochemical reaction. Compared with these stimuli, light induction has become a research hotspot because of its precise controllability in distance, space or time [6-9].

Generally speaking, a substance can be photoresponsive, its molecules can exist in at least two different states, and can realize the transition between different states under illumination conditions. Thus, some compounds with special structures such as azobenzene, diaryl ethylene, spiroxazine and caprylic anhydride are the best choice for photoresponsive chiral compounds. Photoisomerization of azobenzene occurs under ultraviolet irradiation because of the presence of - N = N - optically active groups. The molecular shape of azobenzene changes from rod structure to bending structure. Due to the special photoisomerization of azobenzene, azobenzene-based optical control materials have been extensively studied, including optical storage, optical switch, optical display and so on. It also provides a broad application prospect for azobenzene compounds in optical control materials [10-14].

The reversible cis-trans isomerization of azobenzene chiral molecules under light irradiation can cause significant changes in the structure of chiral molecules. Different isomers have different helical twisting forces, and the corresponding pitches of cholesteric liquid crystals are different. Thus changing the location of the selected reflection spectrum of cholesteric liquid crystals [15,16].

Photoresponsive chiral azobenzene compounds have been chosen for their advantages such as simple synthesis, good compatibility with liquid crystals and great changes in HTP during cis-trans isomerization. However, azobenzene does not have chiral centers, so we choose binaphthalene as chiral centers to synthesize chiral compounds with azobenzene chromophores.

## II. EXPERIMENTAL

### A. Experimental material

(R) - (+) - 1,1'-Bis-2-naphthylamine, 1-bromoethane, 1-bromo-n-octane were provided by Budesonide; sodium nitrite, phenol, sodium hydroxide, hydrochloric acid, potassium carbonate, dimethylformamide, petroleum ether, dichloromethane, ethyl acetate, n-hexane were provided by Beijing Chemical Reagent Company.

## B. Experimental facilities

Electronic Balance, BS221-S, Beijing Sedoris Instrument Co., Ltd; Magnetic Stirrer, 95-2 Shanghai Sile Instrument Co., Ltd; Vacuum Drying Box, DGF25007, Chongqing Huamao Instrument Co., Ltd; Rotary Evaporator, RE-52A, Shanghai Yarong Biochemical Instrument Factory; Constant Temperature Water Bath, HS-4, Chengdu Instrument Factory; Electrical Thermal Constant Blast Drying Box, SFG-01B, Huangshi Hengfeng Medical Devices Co., Ltd; Desk Leveler, KW-4A, Institute of Microelectronics, Chinese Academy of Sciences. Fourier Infrared Spectrometer (FT-IR), Spcetrum One, Perkin Elmer Company, USA; Nuclear Magnetic Resonance Spectrometer ( $^1\text{H}$  NMR), DMX-400, Bruker Company, Germany. Differential Scanning Calorimetry (DSC), Pyris 6 DSC, Perkin Elmer Company, USA; Polarization Microscope (POM) (with thermometer and precise thermometer), Olympus BX51, Olympus Company, Japan; Ultraviolet-Visible-Near Infrared Spectrophotometer, JASCO-V570, Jasco Company, Japan.

## C. Molecular synthesis

1.00 g (R) - (+) - 1,1'-bi-2-naphthylamine was dissolved in a solution of 17 mL water and 2.5 mL concentrated hydrochloric acid. The solution was cooled to 0 °C with ice water. After mixing with sodium nitrite (0.58 g) in aqueous solution (10 mL), the solution becomes yellow brown suspension. Water (15 mL) solution of phenol (0.73 g) and sodium hydroxide (0.90 g) was prepared and the suspension droplets were added to the solution. The suspension was then acidified to PH(5-7) by hydrochloric acid solution and filtered. The obtained cake was washed and dried with water, and then purified by column chromatography. Finally, brown solid (d) 1.4 g was obtained with a yield of 80.5%.

The 1.40 mmol intermediate (d), 4.20 mmol 1-bromoethane and 4.20 mmol potassium carbonate were dissolved in 50 mL dimethylformamide and heated for 5-48 hours. The mixture was purified by silica gel column chromatography after vacuum distillation, and the orange solid 2C 0.6 g was obtained. FT-IR (KBr):  $\nu = 2974, 1597, 1498, 1386, 1248, 1142, 1113, 1038, 920, 819, 748, 537$ ;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.14$  (d,  $J = 6.0$  Hz, 2H), 8.03 (d,  $J = 6.0$  Hz, 2H), 7.96 (d,  $J = 6.0$  Hz, 4H), 7.47 (d,  $J = 6.0$  Hz, 4H), 7.28 (t, 4H), 6.70 (d,  $J = 6.0$  Hz, 4H), 3.96 (m, 4H), 0.96 (t, 6H). The synthetic route of chiral azo compound 2C is shown in Fig. 1.

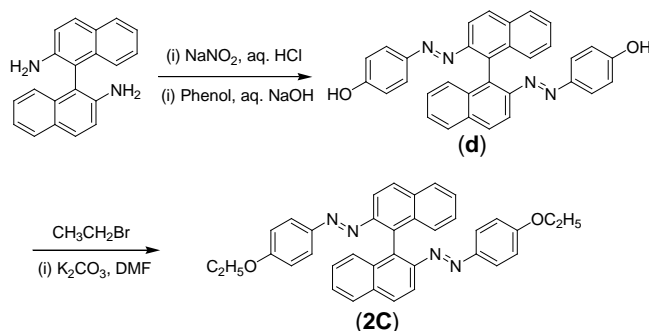


Figure 1. Synthesis route of chiral azo compound 2C.

## III. RESULTS AND DISCUSSION

### A. UV absorption curves of azo molecule 2C and their changes under illumination

Fig. 2 shows the absorption curve of 2C dissolved in dichloromethane and the effect of UV and visible light on it. It can be seen from the diagram that there are two absorption peaks of azo molecules in the range of 300 nm to 500 nm.

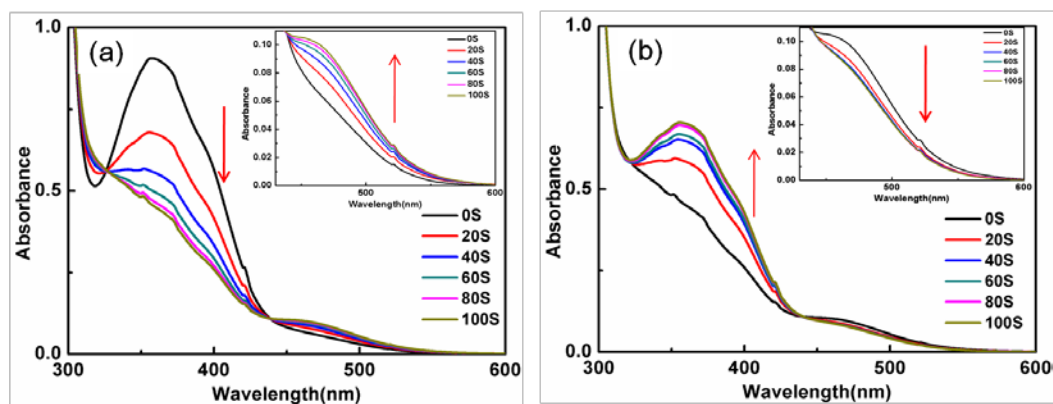


Figure 2. Changes of 2C absorption curves after UV and visible irradiation: (a) UV irradiation; (b) Visible irradiation.

The maximum absorption peak at 360 nm corresponds to the absorption of the  $\pi$ - $\pi^*$  conjugate transition of the azo group, while the absorption peak at 450 nm corresponds to the  $n$ - $\pi^*$  absorption. Since azobenzene can undergo isomerization transition from trans to cis isomer after uv irradiation, the intensity of azobenzene's teton-time conjugated absorption peaks gradually

decreases, while  $n-\pi^*$  absorption peaks gradually increase. Moreover, the intensity of absorption peaks does not change with uv irradiation when the uv irradiation time reaches to the 80s, It is evident from Fig. 2 that the absorption curve will recover when visible light is used again.

#### B. Effect of UV irradiation on helical twisting force of azo molecules

Fig. 3 shows the variation of helical twist force with ultraviolet irradiation calculated by adding azo chiral compound 2C to nematic liquid crystal SLC-1717 (SLC-1717/2C:95/5). The illustration shows the variation of transmission peak position of cholesteric phase.

The helical twisting force of chiral compounds is mainly calculated by the following formula:

$$\text{HTPs} = \frac{\bar{n}}{\lambda_m \chi_c}$$

Among them,  $\bar{n}$  is the average refractive index,  $\lambda_m$  is the cholesteric center reflection wavelength,  $\chi_c$  is the chiral compound concentration. It can be found from Fig. 3 that the central reflection peak of the cholesteric phase will be red-shifted when the azo chiral compound is added, and from the formula (1) it can be seen that the helical distortion force is inversely proportional to the central reflection peak, so the corresponding helical distortion force will decrease with the ultraviolet irradiation. After calculation, it is found that the change value can be changed from  $37 \mu\text{m}^{-1}$  to  $13 \mu\text{m}^{-1}$ .

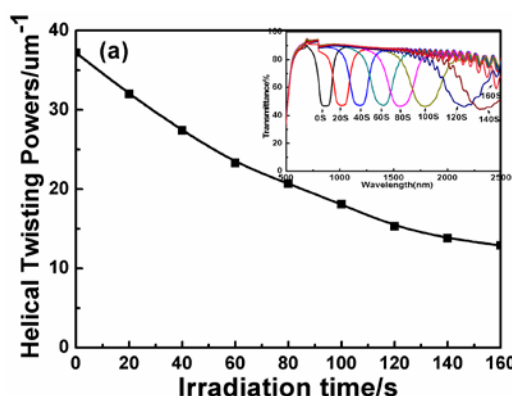


Figure 3. Variation of helical torsional force of chiral compound 2C after UV irradiation (illustration: position changes of cholesteric transmittance peaks after adding chiral azobenzene compounds into nematic liquid crystals).

#### IV. CONCLUSIONS

In this paper, the chiral molecules of dinaphthalene, which contains azobenzene chromophore, can occur cis-trans isomerism under the action of ultraviolet light, which lays a foundation for its application in the light corresponding cholesteric liquid crystals. In the cholesteric liquid crystals mixed with nematic liquid crystal SLC1717, they have better solubility and greater helical twisting force. Under the action of ultraviolet light, the helical twisting force gradually decreases and the reflecting wavelength of the cholesteric liquid crystals gradually turns red.

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