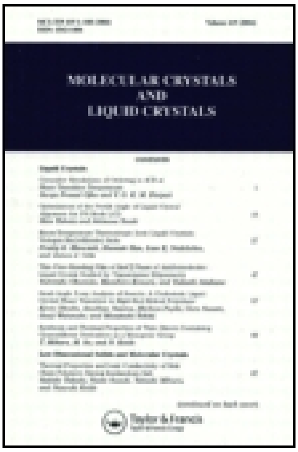

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photo-Asymmetric Synthesis of Helicenes in Liquid Crystals

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To cite this article: Yuhui Lin & L.-C. Chien (1997): Photo-Asymmetric Synthesis of Helicenes in Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 301:1, 267-282

To link to this article: http://dx.doi.org/10.1080/10587259708041777

Mol. Cryst. Liq. Cryst., 1997, Vol. 301, pp. 267–282
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PHOTO-ASYMMETRIC SYNTHESIS OF HELICENES IN LIQUID CRYSTALS

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Abstract Photo-asymmetric synthesis of pentahelicenes have been carried out in liquid crystals. The objective of this investigation is to study the feasibility of using polyhelicenes as tunable chiral materials in the color pixelation of reflective cholesteric displays (RCDs). Since the pitch of a cholesteric liquid crystal phase can be changed by the addition of a small amount of chiral compounds, *in-situ* photo-asymmetric synthesis in display cells provides a valuable method in the modification of liquid crystal properties. We describe herein attempts to use linearly/circularly polarized light to modify the pitch and hence, the color of a RCD.

INTRODUCTION

Modification of the properties of cholesteric liquid crystals with light offers access to a useful means for the display of information. One approach is the irradiation of certain additives in the cholesteric mesophase with polarized light to produce optically active compounds, which in turn changes the properties of host mesophase. It is well known that a small amount of optically active compounds are able to transform a nematic mesophase of a liquid crystal material into a cholesteric phase. The ability of an optically active compound to transform a nematic phase into a cholesteric phase can be expressed by the pitch of the resulting cholesteric phase, as shown in Eq. 1,

$$p=[\Sigma\beta C\gamma]^{-1} \qquad (1)$$

where β is the helical twisting power, C is the concentration, and γ is the optical purity (*i.e.*, the excess of one enantiomer over the other, its mirror image) of the additive. Therefore, the change of optical purity leads not only to another value of the cholesteric pitch, but also to the change of the cholesteric reflectivity band λ, according to the Bragg's reflection law(Eq. 2).

$$\lambda = p.n_{avg} \tag{2}$$

The change in the pitch of a liquid crystal material in the cholesteric phase induced by a photochemical reaction has been reported more than twenty years ago. Haas and co-workers [1] demonstrated the feasibility of forming an irreversible image upon irradiation of a cholesteric phase consisting a mixture of cholesteryl chloride and cholesteryl iodide. Candau and co-workers [2] showed that photo-decarbonylation and photo-racemization of an optically active ketone as a dopant in the cholesteric phase of 4-cyano-4'-hexylbiphenyl led to a nematic phase. Reversible color change in a cholesteric phase was achieved by selective *trans-cis* photo-isomerization of a solute, azobenzene, because the stereoisomers affected the pitch differently [3].

Basically, there are two ways to modify the pitch of a liquid crystal material in the cholesteric phase: photo-destruction of an optically active additive in the host liquid crystals and photo-asymmetric synthesis of an optically active compound in the host liquid crystals. Both methods rely on the change of the concentration of the chiral additive, but in a different manner. The latter, though more interesting, was never explored before. One of the reasons to account for this is that the photo-asymmetric synthesis in many cases gave disappointing results [4].

The photochemistry of the helicene family has been studied for a long time. Irradiation of corresponding diarylethylenes with light causes the cyclization of these compounds to form dihydrohelicenes, which will lead to the formation of helicenes upon the oxidation. Until now four procedures have been applied to obtain optically active helicenes by induced photo-asymmentric synthesis. Chemically induced photo-asymmetric syntheses were used by Martin *et al* to obtain an optically active helicene derivative from a precursor containing a chiral paracyclophane residue [5a] and in the diastereoselective photosynthesis of methoxycarbonylhelicene [5b]. Induced asymmetric syntheses in the preparation of helicenes by irradiation of optically inactive diarylethylenes with left- or right-handed circularly polarized have been reported by two other groups [6, 7]. Laarhoven and co-workers [8] demonstrated the chiral-solvent induced asymmetric synthesis of helicenes. Using the liquid crystal as reaction media to obtain optically active helicenes has been carried out by Solladie [9], Nakazak [10], and co-workers. The optical yield varied from one method to another. Photo-asymmetric synthesis in cholesteric phase is especially interesting to us, since it has been shown that the cholesteric phase has an additional effect due to its helical structure, *i.e.* the asymmetric induction comes simultaneously from the contribution of the pitch and the solute-solvent interaction [9].

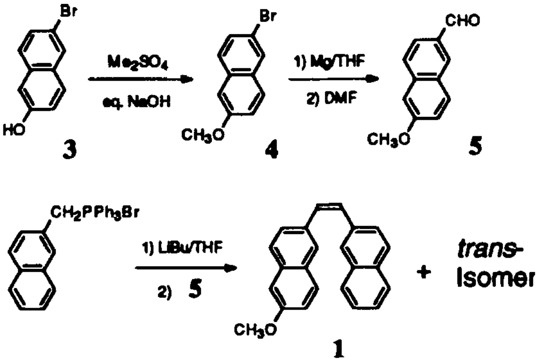
In our investigation toward the color pixelation of multicolor reflective cholesteric displays [11], we tried to modify the pitch of a cholesteric liquid crystal by employing the photo-asymmetric synthesis of helicenes *in-situ* in the display cells. The irradiation of a cell with polarized light resulted in the asymmetric photo-reaction. Different color regions were resulted from the different dose of light. Though the optical yield of helicenes is low, we realizeded that this process might be useful to change the pitch of a cholesteric liquid crystal, since the helicenes have a very high optical rotation power.

RESULTS AND DISCUSSION

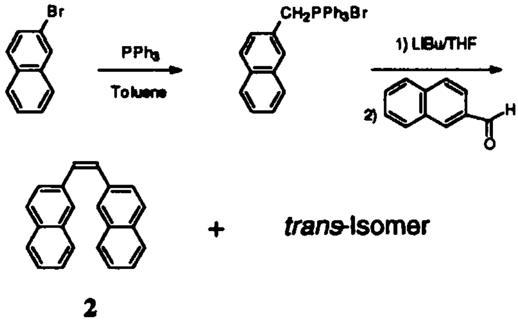
Synthesis

The synthesis of 1-(6-methoxy-2-naphthyl)-2-(2-naphthyl)ethylene **1** and 1, 2-di-(2-naphthyl)ethylene **2** are outlined in Scheme 1 and 2, respectively. Wittig olefination reaction was employed in the syntheses of both compounds. Compound **1** was synthesized beginning with 6-bromo-2-naphthanol **3**. Methylation of **3** with methyl sulfate gave compound **4**, which was converted to 6-methoxy-2-naphthaldehyde **5** by Grignard reaction. Reaction of triphenyl(naphthylmethyl)phosphonium bromide with compound **5** provided compound **1**. Details for the preparation of **1** and **2** are reported in the Experimental Section.

The *cis*-isomer of 1, 2-di-(2-naphthyl)ethylene was isolated and used for the photo-asymmetric synthesis. Its *cis*-structure was checked by comparing the obtained melting point with that of reported in the literature [12]. In the 1-(6-methoxy-2-naphthyl)-2-(2-naphthyl)ethylene case, it is unknown if the isolated compound is the *cis*- or *trans*-isomer. However, the effect of stereoisomers on photo-asymmetric reaction is negligible, since the well-known *trans-cis* photo-equilibration from the triplet state of stilbenes continuously generates the *cis*-isomer.



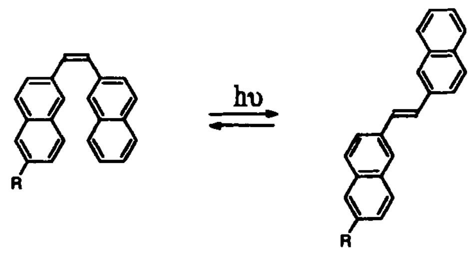
Scheme 1



Scheme 2

Photochemical properties of diarylethylenes

Irradiation of diarylethylene with UV light will lead to four possible reactions: the *cis*-*trans* isomerization(Eq. 3), the cyclization which gives the dihydrohelicene(Eq. 4), dimerization(Eq. 5), and the polymerization. Diemrization and polymerization reactions are less likely to occur due to the steric factor of the diarylethylenes. Therefore, only *cis-trans* isomerization and cyclization to dihydrohelicenes are the possible reactions during the photo-irradiation process. In order to distinguish between these two reactions, irradiation of an oxygen-free deuterated benzene solution of 1, 2-di-(2-naphthyl)ethylene **2** was carried out. Analysis of this reaction by ^{1}H NMR reveals the formation of a new peak at 4.82 ppm. Also, APT(Attached Proton Test) of ^{13}C NMR spectroscopic analysis of the reaction mixture reveals one new carbon peak at 48.9 ppm, of which one proton is attached. Both results suggested the formation of dihydrohelicene, instead of the *cis-trans* isomerization, during the photo process, since both the ^{1}H and ^{13}C chemical shifts are characteristic of the tertiary carbon in the dihydrohelicene. Irradiation of 1-(6-methoxy-2-naphthyl)-2-(2-naphthyl)ethylene **1** in an oxygen-free deuterated benzene solution was also performed. Again, analysis of this reaction mixture by ^{1}H NMR reveals the formation of new peaks at 3.06, 3.41, and 4.86 ppm. The two peaks at 3.06 and 3.41 ppm are apparently the methoxy protons, which might belong to the different stereoisomers of dihydrohelicenes. The peak at 4.86 ppm is most probably the proton attached to the tertiary carbon in the dihydrohelicene. Although the products from the photo-asymmetric reactions of both compounds **1** and **2** are not fully characterized, it supports that the dominant photochemical reaction follows the cyclization reaction (Eq. 4).



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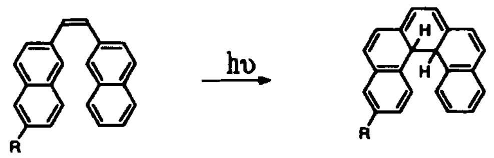

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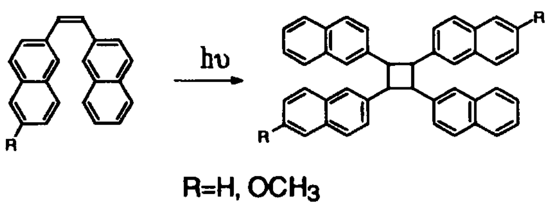


(5)

Irradiation of diarylethylenes in the cholesteric liquid crystals

A. Irradiation of the red cholesteric mixture containing 2% of compound 1 with linearly and circularly polarized UV light

Fig. 1 and 2 show the transmission spectra of the red cholesteric mixture containing 2% of compound **1** before the UV irradiation and after 7200s irradiation (UV doses 64.1 Jcm^{-2}) with linearly polarized UV light, respectively. Fig. 3 and 4 give the plots of transmission wavelength of the cholesteric mixture versus the irradiation time. As can be seen from figures 3 and 4, irradiation of the cholesteric red mixture containing 2% of compound **1** with linearly polarized light and circularly polarized light(both 45° and -45°) shifts the transmission wavelength of the cholesteric mixture toward the long wavelength direction. The $\Delta\lambda$ (the difference of wavelength before and after the irraiation) is in the range of 30 to 45 nm. It is surpring that irradiation of the mixture with linearly polarized light and circularly polarized light (45° and -45°) shifts the spectra to the same direction.

B. Irradiation of the red cholesteric mixture containing 5% of compound 1 with linearly polarized UV light

Irradiation of the red cholesteric mixture containing 5% of compound **1** with linearly polarized light has been examined. As shown in Fig. 5, irradiation of this mixture with linearly polarized light shifts the wavelength of the cholesteric mixture to the long wavelength direction with a $\Delta\lambda$ value of about 40 nm. A solubility problem occured between the red mixture and compound **1** because of the observation of crystallization in the cell when it was exposed to UV light. Crystallization was also observed in the cell which was not irradiated after several days.

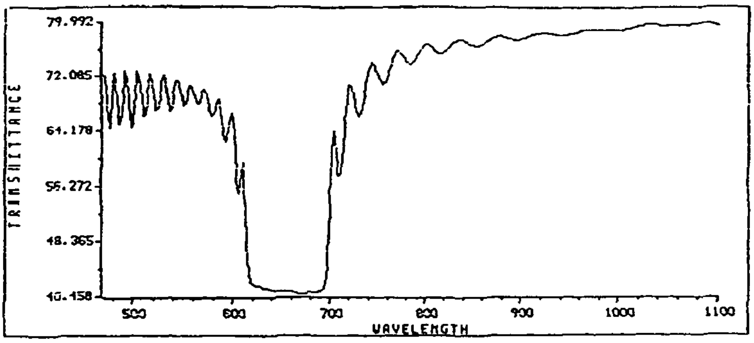


Fig. 1 Transmittance spectrum of cholesteric mixture containing 2% of compound **1** before UV irradiation.

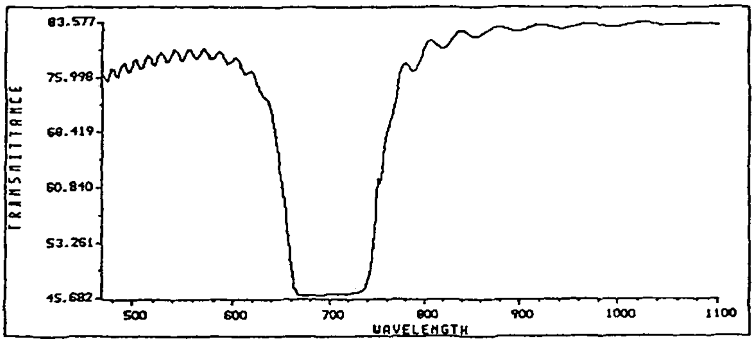


Fig. 2 Transmittance spectrum of cholesteric mixture containing 2% of compound **1** after irradiation (doses 64.1 Jcm^{-2}) with linearly UV light.

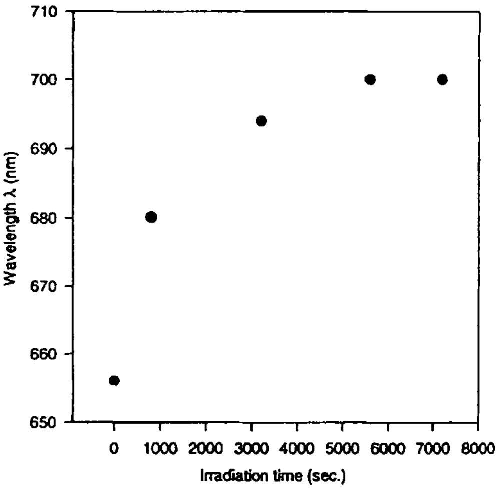


Fig. 3 Wavelength (nm) vs. irradiation time (sec.) of cholesteric mixture containing 2% of compound 1, irradiated with linearly polarized light.

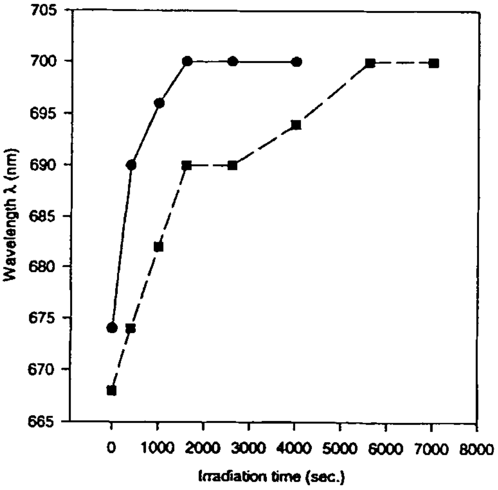


Fig. 4 Wavelength (nm) vs. irradiation time (sec.) of cholesteric mixture containing 2% of compound 1, irradiated with circualrly polarized light (45°and -45°).

C. Irradiation of the red cholesteric mixture containing 4% of compound 2 with circularly polarized UV light.

Irradiation of the red cholesteric mixture containing 4% of compound **2** with circularly polarized light has also been studied. The result, similar to the case of compound **1**, is shown in Fig. 6, *i.e*, irradiation of this mixture with circularly polarized lights shifts the transmission wavelength of cholesteric phase to the long wavelength direction with a $\Delta\lambda$ value of about 25nm. It is interesting to note that crystallization phenomenon was observed when the cell containing this mixture was not irradiated; however, no crystallization was observed when the cell was irradiated.

Discussion

The primary objective of this work was to investigate the feasibility of photo-asymmetric synthesis of chiral compounds *in-situ* in the liquid crystal display cells, in an attempt to modify the helix pitch, and hence the color, of cholesteric liquid crystals. Achievement of the objective of this research requires compounds that undergo photo-asymmetric reaction and are able to change the cholesteric pitch with high efficiency. According to Eq. 1, the helix pitch can be changed in the whole visible spectrum region, *i.e.*, from the red to blue or *vice versa*, when the chiral concentration is higher enough. We are unable to achieve this goal by employing the asymmetric synthesis of helicenes *in-situ* in cholesteric materials. The reason for this failing is because of the inefficient photo-asymmetric synthesis of helicenes from their precursor diarylethylenes. We, indeed, achieved some degree of photo-asymmetric synthesis. The irradiation of both compounds **1** and **2** in cholesteric liquid crystals changed the reflectivity band λ at a range of 20-45 nm. Though the *cis-trans* isomerization will also affect the helix pitch of a cholesteric mixture, since the *cis-* and *trans*-isomers of a diarylethylene have different molecular shapes, it is unlikely in our cases that the change in reflectivity band λ is caused by the change in the molecular shape, as we have learned from the NMR studies on the photoreaction of diarylethylenes in the isotropic solvent.

The difference in the abilities to change the transmission wavelength has been observed between compounds **1** and **2**. Using compound **1**, the $\Delta\lambda$ value is about 45 nm, whreras, the $\Delta\lambda$ is only about 25 nm for compound **2**. The difference might result

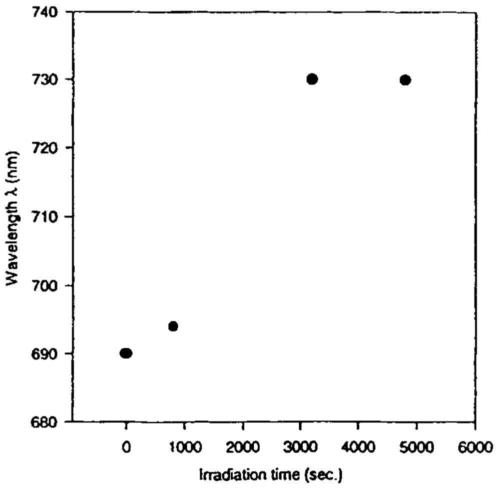


Fig. 5 Wavelength (nm) vs. irradiation time (sec.) of cholesteric mixture containing 5% of compound 1, irradiated with linearly polarized light.

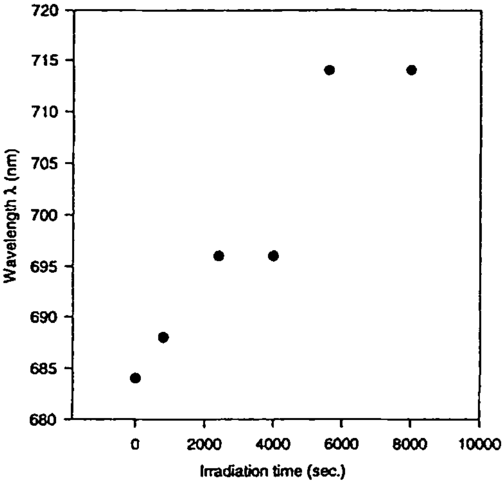
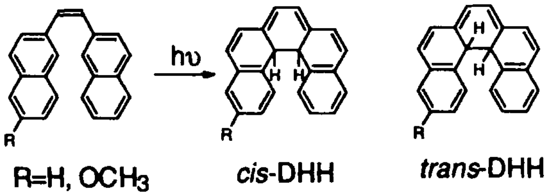


Fig. 6 Wavelength (nm) vs. irradiation time (sec.) of cholesteric mixture containing 4% of compound 2, irradiated with circularly polarized light (-45°).

from the different degree of asymmetric induction and the difference in the stereochemistry of dihydrohelicenes. The higher degree of asymmetric induction in compound **1** might be attributed to the methoxy group at one of the naphthyl rings in compound **1**. It has been reported that the substituent at the aryl ring affected the stereochemical outcome of the product and optical yield.[5b] The structural difference between compound **1** and **2** can also explain the difference in $\Delta\lambda$. Cyclization of diarylethylene can give either *cis*-dihydrohelicene(*cis*-DHH) or *trans*-dihydrohelicene (*trans*-DHH), as shown in Eq. 6. In the *trans*-DHH, the molecule will lack any element of symmetry regardless of whether the substituent R is equal to H or not, and must be chiral. In the *cis*-DHH, however, chiral products are obtained only if the double bond of the parent *cis*-isomer is substituted by two different aryl groups, as in the case of compound **1** (R=OCH_3). Therefore, cyclization of compound **1** will always give the chiral products, no matter if the products are *cis*-DHH or *trans*-DHH. On the other hand, only *trans*-DHH is chiral when compound **2** (R=H) is photocyclized.



(6)

It is surprising to us that the irradiation of both compounds **1** and **2** in studied liquid crystals with linearly polarized and circularly polarized light shifted the transmission wavelength to the same direction. The explanation of these results are not clear; however, we prefer to leave it open.

None of the compounds we have described is suitable for the color pixelation of reflective cholesteric displays by utilizing the photo-asymmetric synthesis *in-situ* in display cells. The major reason for this is that the yield of asymmetric induction of chirality by the liquid crystals and with polarized light is too low. On the basis of unsuccessful findings, we are continuing the research on the multicolor reflective cholesteric displays by other methods which have shown promising results [11].

CONCLUSION

We investigated the photo-asymmetric synthesis of helicenes in display cells in order to assess their chirality in the color pixelation of cholesteric reflective displays. This application requires the photo-asymmetric synthesis is efficient enough in order to change the reflective wavelength of a cholesteric liquid crystal in the whole visible spectrum region. The findings reveal that the compounds we explored do not satisfy this requirement, though short range of change in the reflective wavelength was obtained.

EXPERIMENTAL

Melting points are uncorrected and were determined on a Thomas-Hoover melting point apparatus. Infrared spectra were measured with a Nicolet Magna IR spectrometer 550. The NMR spectra were recorded on a Varian 200 MHz spectrometer. The purities of compounds were examined by using a Waters 600E HPLC with a 994 photo diode array detector. Transmission spectra were run on HP8452 UV-visible spectrometer.

Triphenyl(naphthylmethyl)phosphonium bromide: Triphenylphosphine(6.8 g, 26 mmol) in 40 mL of dry toluene was placed in a 250 mL round-bottomed flask, 2-bromomethylnaphthalene(6.9 g, 31 mmol) was added into the flask. The flask was sealed and the mixture was stirred at R.T. overnight. The white precipitate was filtered off under suction and washed with cold toluene, and dried in the oven at 90°C. The yield was 11.6 g, m. p. 245-248°C. It was used without purification.

1, 2-Di-(2-naphthyl)ethylene: Into a 250 mL round-bottomed flask were placed 50 mL of dry THF and 4.84 g(10 mmol) of triphenyl(naphthylmethyl)-phosphonium bromide. Then 4.2 mL of n-butyl lithium(2.5 M in hexane) was added. Under nitrogen condition, this mixture was stirred at R.T. overnight and 1.56 g(10 mmol) of 2-naphth-aldehyde was added. The mixture was stirred at R.T. for 3 hr and refluxed for an additional 2 hr. The solids were filtered from the hot solution and washed with THF. Evaporation of the filtrates gave a yellow residue. Trituration of the residue with cold methanol left some yellow solids. The solids were filtered and the methanol filtrate was slowly evaporated to give 1, 2-di-(2-naphthyl)ethylene(*cis*) as yellow solid. A second recrystallization from methanol gave pure compound, m. p. 100-102°C, yield, 1.15g (45%). R_f=0.62(2:1 hexanes/EtOAc). IR(KBr, cm^{-1}): 3054, 3018, 1625, 1591. ^1H NMR(200 MHz, $CDCl_3$) δ: 6.83(2H, s), 7.23-7.46(6H, m), 7.65-7.77(4H, m). HPLC: 100%.

6-Bromo-2-methoxynaphthalene: 6-Bromo-2-naphthanol(10.0g) dissolved in a solution of 3.6g of sodium hydroxide in 200 mL of water was methylated by heating with two portion of methyl sulfate(5.65g and 2.83g) to 70°C. The mixture was thoroughly cooled after the addition of each portion. The product was filtered with suction and purified by silica gel column using 2:1 hexanes/EtOAc as the eluent. The yield is 7.1g(66.8%), m. p. 103-106°C. IR(KBr, cm^{-1}): 3061, 3010, 2941, 2868, 1625, 1586. ^1H NMR(200 MHz, $CDCl_3$) δ: 3.89(3H, s), 7.08(1H, d, J=2.5Hz), 7.15(1H, dd, J=9.0 and 2.5Hz), 7.46-7.66(3H, m), 7.90(1H, d, J=1.8Hz).

6-Methoxy-2-naphthaldehyde: (a) Grignard reagent: Under nitrogen condition, 0.7g of magnesium and 30 mL of dry THF was placed in a 250 mL of three-necked flask equipped with a dropping funnel and a reflux condenser. Then, 5.6g of 6-bromo-2-methoxynaphthalene was added dropwise. The mixture was heated under reflux during and after the addition of 6-bromo-2-methoxynaphthalene until most of the Mg was consumed. The mixture was cooled and transferred to a dropping funnel for the next step.

(b) The solution of the Grignard reagent was added to a stirred solution of 3.45g DMF in 25 mL of dry THF dropwise at 0-5°C under the nitrogen condition. The solution was stirred at R.T. for 1 hr and then refluxed for 10 hr. The reaction mixture was concentrated and 100 mL of 5% H_2SO_4 was added to the residue and stirred at R.T. for 4 hr to give 6-methoxy-2-naphthaldehyde as a precipitate. The precipitate was extracted with ethyl acetate. After evaporating the solvent, the residue was purified by silica gel column(1:1 hexanes/EtOAc) and recrystallized from hexane/EtOAc. The yield is 2.5g(57%), m. p. 78-80°C. IR(KBr, cm^{-1}): 3069, 3009, 2948, 2928, 1684. ^1H NMR(200 MHz, $CDCl_3$) δ: 3.97(3H, s), 7.18-7.28(2H, m), 7.79-7.95(3H, m), 8.26(1H, s).

1-(6-Methoxy-2-naphthyl)-2-(2-naphthyl)ethylene: Into a 250 mL round-bottomed flask were placed 50 mL of dry THF and 4.84g(10mmol) triphenyl-(naphthylmethyl)phosphonium bromide. Then 4.2 mL of n-butyl lithium(2.5 M in hexanes) was added. Under nitrogen condition, this mixture was stirred at R.T. overnight and 1.86g(10mmol) of 6-methoxy-2-naphthaldehyde was added. The mixture was stirred at R.T. for 3 hr and refluxed for an additional 2 hr. The solid were filtered from the hot solution and washed with THF. Evaporation of the filtrates gave a yellow residue. Trituration of the residue with cold methanol left some yellow residue, which was recrystallized from acetone/methanol. A second recrystallization from the same solvents gave pure 1-(6-methoxy-2-naphthyl)-2-(2-naphthyl)-ethylene(*cis*?) as yellow solid, m. p., 138-140°C, yield, 1.6g(52%). R_f=0.55(2:1 hexanes/EtOAc). IR(KBr, cm^{-1}): 3058, 3009, 2996, 2972, 2938, 1624, 1600. ^1H NMR(200 MHz, $CDCl_3$) δ: 3.89(3H, s), 6.79(2H, s), 7.06-7.12(2H, m), 7.32-7.78(9H, m). HPLC, 100%.

Preparation of liquid crystal composites and cells: To investigate the photo-asymmetric synthesis of helicenes in liquid crystals, samples of cholesteric mixtures with different amounts of compounds **1** and **2** were prepared. The cholesteric red mixture was used, which was prepared from commercially available materials E48, CB15, CE1, and R1011. The standard concentration (24 wt %) of chiral materials CB15, CE1, and R1011 (at a weight ratio of 3:3:1) for the red mixture was followed.

To prepare the cell, a mixture of red cholesteric composite and diarylethylene were dissolved in about 1 mL of CH_2Cl_2. The solvent was then removed by passing the N_2 through the mixture and the small amount of solvent was further removed under vacuum. An ITO coated, rubbed polyimide surface glass cell that was separated by 10 microns spacers was used. The cell was filled with the above mixture by vacuum.

Photo-asymmetric reaction in the display cells: The photo-asymmetric synthesis of helicenes was carried out by irradiating the filled cell with polarized UV light(intensity 8.9 $mWcm^{-2}$, λ_{max}=313 nm). We varied the UV irradiation time. The visible transmission spectra were recorded before and after each irradiation.

REFERENCES

1. W. Haas, J. Adams, and J. Wysocki, Molecualr Crystal and Liquid Crystals, 7, 371(1969).

2. C. Mioskowski, J. Boufuignon, S.Candau, Chemical Physical Letters, 38(3), 456(1976).

3. E. Sackmann, J. Am. Chem. Soc., 93, 7088(1971).

4. Y. Inoue, Chem. Rev. 92. 741(1992).

5. (a) J. Tribout, R. H. Martin, M. Doyle. and H. Wijnberg,Tetrahedron Letters, 2839(1972). (b) Y. Cochez,R.H.Martin, J. Jespers, Israel Journal of Chemistry, 15, 29(1976)

6. (a) H. Kagan, A. Moradpour, G.Balavoine, J. F. Nicouid, R. H. Martin, and J. P. Cosyn, Trtrahedron Letters, 2479(1971). (b) A. Moradpour, H. Kagan, M. Base, and R. H. Martin, Tetrahedron, 31, 2139(1975).

7. (a) W. J.LBernstein, M. Calvin, and O.Buchardt, J. Am.Chem.Soc. 95(2), 527(1972). (b) O.Buchardt, Angew. Chem. Int. Ed. Engl. 13(3),179(1974).

8. W. H. Laarhoven and T. J. Cuppen, J. Chem. Soc. Perkin II, 315(1978).

9. M. Hibert, and G. Solladie, J. Org. Chem, 45, 5393(1980).

10. (a) M. Nakazaki, K. Yamamoto, and K. Fujiwara, Chemistry Letters, 863(1978). (b) M. Nakazaki, K. Yamamoto, K. Fujiwara, and M. Maeda, J. Chem. Soc. Chem. Comm.1086(1979).

11. L.-C. Chien, F. Vicentini, Y. Lin, and U. Muller, Third Color Imaging Conference: Color Science, Systems, and Applications, Scottsdale, Arizona, 58(1995).

12. Dictionary of Organic Compounds, Fifth Edition (Champman and Hall, 1982), Vol. 2, pp. 2245.

ACKNOELEDGEMENT

This work was supported in part by ARPA Low Power Displays Contracts #N61331-94-K-0042.