Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Negative birefringence ferroelectric liquid crystals

William N. Thurmes; Michael D. Wand; Rohini T. Vohra; Charles M. Crandall; Jiuzhi Xue; David M. Walba

To cite this Article Thurmes, William N. , Wand, Michael D. , Vohra, Rohini T. , Crandall, Charles M. , Xue, Jiuzhi and Walba, David M.(1998) 'Negative birefringence ferroelectric liquid crystals', Liquid Crystals, 25: 2, 149 — 151

To link to this Article: DOI: 10.1080/026782998206281

URL: http://dx.doi.org/10.1080/026782998206281

LIQUID CRYSTALS, 1998, VOL. 25, NO. 2, 149–151

Negative birefringence ferroelectric liquid crystals

by WILLIAM N. THURMES*, MICHAEL D. WAND, ROHINI T. VOHRA,
CHARLES M. CRANDALL, JIUZHI XUE
Displaytech, Inc., 2602 Clover Basin Drive, Longmont, CO 80503, U.S.A.

and DAVID M. WALBA
Department of Chemistry and Biochemistry, University of Colorado, Boulder,
CO 80309

(*Received 10 December 1997; accepted 20 January 1998*)

The synthesis and evaluation of a negative birefringence material which possesses a wide smectic C phase is reported.

1. Introduction

Although liquid crystals derive their usefulness as optical intensity modulators from their birefringence, that birefringence is not optimized for use at all wavelengths. A ferroelectric liquid crystal light modulator behaves as a perfect halfwave plate at the halfwave thickness $d_{1/2}$ of

$$d_{1/2}=\frac{\lambda}{2\Delta n} \tag{1}$$

where Δn is the birefringence at wavelength λ. Generally, the birefringence of liquid crystals increases with decreasing wavelength (a phenomena known as positive birefringence dispersion). If $\lambda/\Delta n$ could be constant over the visible spectrum, then an achromatic liquid crystal would result, with considerable benefits in applications. A liquid crystal's optimal Δn vs its actual Δn, for a given cell thickness, over the visible spectrum, is shown in figure 1.

The further the wavelength from its optimal value (in this case 500 nm), the more the actual and optimal Δn lines diverge. The net effect of this divergence is that, at non-optimal wavelengths, the liquid crystal is no longer at a half-wave thickness and the light transmission decreases. Unless the cell is compensated in some way, the transmission of blue and red light will be much less than that of green light. This is graphically illustrated in figure 2, where the cell with positive birefringence dispersion shows only about 55% transmission of blue light and about 70% transmission of red light. By comparison, a material with no birefringence dispersion would give about 82% transmission of blue light and 83% of red light. A negative dispersion material, with dispersion inverse that of the positive dispersion material, would transmit nearly 100% of the blue light and over 90% of the red light. Hence, such a material would transmit light achromatically.

The mechanics of FLC and nematic cells differs, but for both LC types the cell thickness depends on the light wavelength. Much research has gone into making nematic cells as achromatic as possible. One solution has been to use a combination of at least two polymer retarder films as compensators [1], giving light that is reasonably achromatic. However, their use extracts a price in either viewing angle or contrast ratio, depending on the orientation used. Thus, having the liquid crystal internally compensated for birefringence dispersion would be quite beneficial.

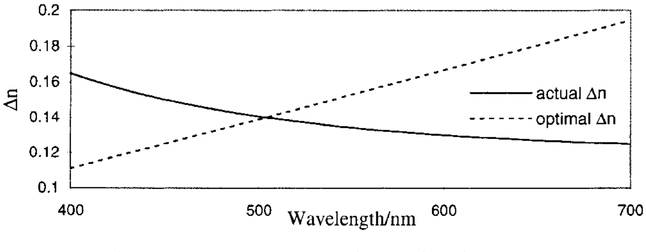


Figure 1. Actual vs optimal birefringence.

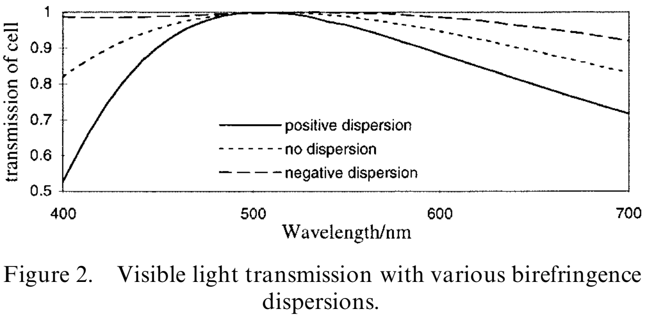


Figure 2. Visible light transmission with various birefringence dispersions.

---

*Author for correspondence.

0267–8292/98 $12·00

A recent report [2], by Walba *et al.* detailed the discovery of the first negative birefringence smectic† mesogens not containing metals‡. These materials, designed to have high NLO activity, were formed by linking two mesogenic molecules with an azo bridge; one of these mesogens had a nitro group, the other an amino group. The materials had smectic A phases over 30°C in width, and the neat materials exhibited negative birefringence. However, they were red coloured, making them unusable for chromatic compensation.

Negative birefringence materials, by themselves, are primarily of interest as birefringence moderators, allowing the birefringence of a liquid crystal to be tuned to the desired level by addition of only a small amount of dopant. We demonstrate here that, by adapting Walba's basic idea of linking two mesogenic molecules with a delocalizable bridge, we can make materials which are much more negatively birefringent. With the appropriate structural modifications, this strategy should lead to materials with negative birefringence dispersion.

2. Synthesis and evaluation

Our synthetic strategy for making negative birefringence materials is centred around linking two mesogenic compounds using a delocalizing linking group. Thus, there are three parts to the molecule: two mesogens, which need not be equivalent, and the core–link–core moiety, which we will call the linking section. The polarizability of the mesogens will ideally be as low as possible, to minimize the refractive index along the molecule's long (or extraordinary) axis. Conversely, the linking section's polarizability should be as high as possible, to maximize the refractive index along the transverse (or ordinary) axis. The net birefringence of the molecule will be some weighted average of the refractive index along the extraordinary axis (two groups in this direction) minus the refractive index along the linking section of the molecule. The ideal orientation of the linking group is perpendicular to the long axis of the mesogenic moieties. As a first approximation one can use the birefringence of each moiety to estimate the magnitude of the final compound's birefringence.

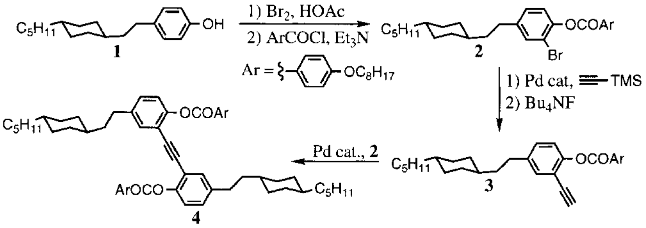
Other design constraints for negative birefringence materials include the condition that the long axis be much longer than the linking axis, for otherwise the compounds will not easily fit into the smectic C superstructure, and also that the mesogenic groups or closely related homologues have smectic phases. This will increase the chances that the final products will readily mix with the smectic C host materials.

We chose compound **4**, shown in the scheme, as the target molecule. The mesogenic compound in this is a cyclohexyl phenyl benzoate, which is known to have moderate birefringence. The parent compound has a smectic A phase, and homologues with longer tails have smectic C phases. The chosen linking group was an acetylene, which by attachment of the mesogen's phenyl rings becomes a tolane, known to have quite high birefringence and low absorption at visible wavelengths.

The starting phenol **1** was treated with 0·9 equivalents of elemental bromine in acetic acid to give 94% yield of the expected monobrominated compound, with only a trace of the dibrominated material. It was then coupled with an alkoxybenzoic acid to give 87% yield of the brominated ester **2**. This was coupled with trimethylsilylacetylene in the presence of a palladium catalyst, and the trimethylsilyl group was deprotected with tetrabutylammonium fluoride and sodium bicarbonate in a tetrahydrofuran solution, to give acetylene **3** in 29% overall yield. The acetylene was then coupled with the brominated precursor **2** using the palladium catalyst to give the product **4**, hereafter referred to as MDW 1069, in approximately 60% yield. The material had an isotropic to smectic C phase transition at 198°C, and crystallized at 116°C, with a melting point at 130°C.

The optical set-up shown in figure 3 was used to determine the sign of the birefringence of MDW 1069. The 633 nm wavelength laser light was polarized, sent through a cell containing the liquid crystal (with the LC director turned at 45° with respect to the polarizer), then sent through a compensator (also at 45°), and finally through an analyser (crossed with the polarizer) on its way to the photodiode.

The rationale for using this set-up to determine the birefringence is as follows: the proportion of light transmitted through the system, equation (2), equals the $\sin^2$ of the angle of the cell with respect to the optical axis



Scheme. The synthesis of a negative birefringence material.

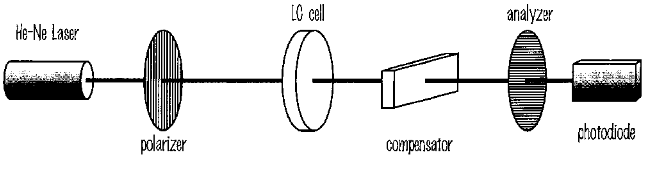


Figure 3. The optical set-up for measuring birefringence.

---

† Discotics always have negative birefringence.

‡ A thallium soap with negative birefringence and smectic phases was reported [3].

times the $\sin^2$ of the total retardance of the system, which includes both the retardance of the cell and the retardance of the compensator. The cell retardance in turn depends on the birefringence (Δn), the cell thickness (d), and the wavelength (λ).

$$\frac{I_{\text{out}}}{I_{\text{in}}} = \sin^2 2\theta \sin^2\left(\frac{\phi_{\text{total}}}{2}\right),$$

where

$$\phi_{\text{total}} = \frac{2\pi\Delta n d}{\lambda} + \phi_{\text{compensation}}. \tag{2}$$

Since the cell is rotated to 45°, this equation simplifies to

$$\frac{I_{\text{out}}}{I_{\text{in}}} = \sin^2\left(\frac{\phi_{\text{total}}}{2}\right). \tag{3}$$

If the total retardance is 0, then

$$\frac{2\pi\Delta n d}{\lambda} = -\phi_{\text{compensation}} \tag{4}$$

and minimal light will exit the system. Thus, if increasing the amount of compensation decreases the light incident on the photodiode, the birefringence of the cell (the only term on the left side of equation (4) which could possibly be negative) *must be negative*. Using this set-up, we determined the birefringence of the material at 633 nm to be −0·104, assuming that the cell was 1·8 μm thick.

The absolute value of the birefringence throughout the visible range was determined using an elipsometer. The graph of the birefringence dispersion, corrected to show its demonstrated negative value, is shown in figure 4. The measured absolute value of the birefringence at 633 nm (again assuming that the nominally 1·8 μm cell was indeed 1·8 μm thick) was 0·105, in very close agreement to the −0·104 measurement from the previous experiment. This material is not only negatively birefringent, it is *strongly* negatively birefringent.

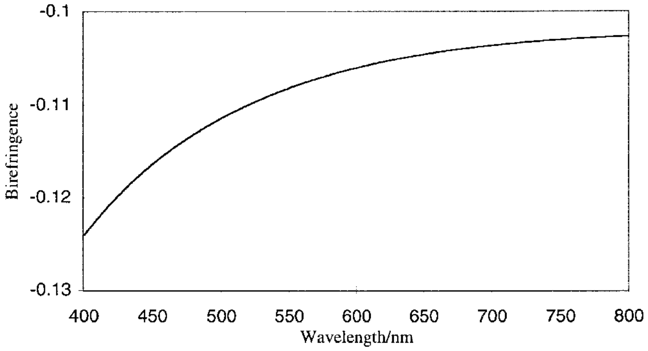


Figure 4. The measured birefringence of MDW 1069.

3. Conclusion

A mesogenic material intended to have negative birefringence was designed and synthesized. This compound indeed showed negative birefringence, with the dispersion ranging from −0·128 at 400 nm to −0·108 at 800 nm. The compound had a wide smectic C phase, from 198°C down to 116°C. This is the first negative birefringence smectic material ever made that is transparent at visible wavelengths. Research using compounds of this type to formulate liquid crystals with negative birefringence dispersion is proceeding.

This work was supported by the National Science Foundation under grant DMI-9560914. We wish to thank Piotr Kaszynski for his help in interpreting molecular modelling results.

References

[1] Scheffer, T., and Nehring, J., 1995, SID Seminar Lecture Notes, Vol. 1, M2.

[2] Walba, D. M., Dyer, D. J., Sierra, T., Cobben, P. L., Shao, R., and Clark, N. A., 1996, *J. Am. Chem. Soc.*, **118,** 1211.

[3] Pelzl, G., and Sackmann, H., 1971, *Mol. Cryst. liq. Cryst.*, **15,** 75.