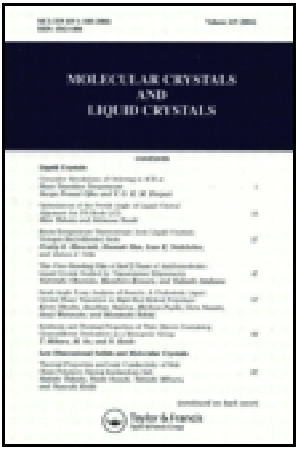

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Development of the Nematic Liquid Crystal Compounds Derived from Phenyl Acetylene Group with Large Birefringence

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Novel liquid crystal compounds with extraordinary large birefringence have been studided from the viewpoint of optical anisotropy. A large birefrinence was obtained in the compounds compared with that in 5CB, while the orientational order parameters determined by FT-IR measurement are almost the same. From the calculated results of molecular polarizability, it is concluded that the large optical anisotropy is mainly caused by the electric anisotropy.

Keywords: birefringence; conjugated group; polarized FT-IR; molecular polarizability

INTRODUCTION

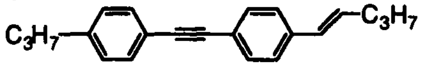
Reflective-type liquid crystal display device is one of the most remarkable devices for usage in portable multimedia displays. In order to perform a high contrast reflective liquid crystal displays (LCDs), materials with refractive index anisotropy as large as possible are requested. From this viewpoint, in the development of the reflective LCDs, it is one of the most important subjects to synthesize liquid crystal compounds with large optical anisotropy.

In this paper, we introduce novel nematic liquid crystal compounds having a phenyl acetylene unit and discuss the relationship between birefringence, orientational order parameter and the anisotropy of molecular polarizability. We measured the temperature dependence of the optical birefringence and the order parameter of these compounds by polarized FT-IR. In the optical birefringence measurement, these compounds show a large optical birefringence more than 0.35 in the nematic phase, which is much larger than that in 5CB. In contrast, the order parameter in these compounds estimated from the dichroic ratio of IR absorption peaks of phenyl C-C stretching and acetylene group stretching is almost the same as that estimated from the dichroic ratio of the phenyl ring C-C stretching of 5CB. It was found that the anisotropy of the molecular polarizability more effectively influences the optical anisotropy in the nematic phase than the macroscopic order parameter does.

EXPERIMENTAL

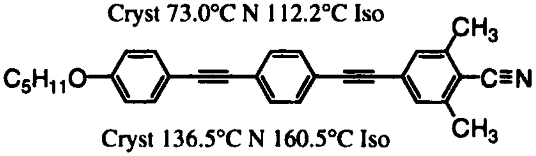
Sample used were nematic liquid crystal compounds derived from a phenyl acetylene group synthesized by Sumitomo Chemical Co., Ltd. Chemical structures and phase sequences of them are as follows.

Compound1



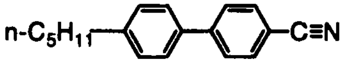
Cryst 73.0°C N 112.2°C Iso

Compound2



Cryst 136.5°C N 160.5°C Iso

Compound3 (5CB)



Cryst 22.8°C N 34.8°C Iso

5CB was used as a reference. For the FT-IR measurement, we prepared 4 μm-thick homogeneously aligned cells. Substrate used were 1 mm-thick SrF_2 single crystal plates and were coated with polyimide (SP550, Toray) and rubbed. FT-IR spectrometer used was WINSPEC 50 (JEOL). In the refractive index measurement, wedge-type cells with a wedge angle of 2.2° were used. As shown in Fig. 1, Ar^+ laser (λ = 514 nm) light impinges normally upon one side of the substrates of the sample cell. The beam is deflected to make two spots on a screen, from which we can calculate ordinary and extraordinary refractive indices, n_o and n_e, respectively. Molecular polarizabilities were estimated by MOPAC calculation.

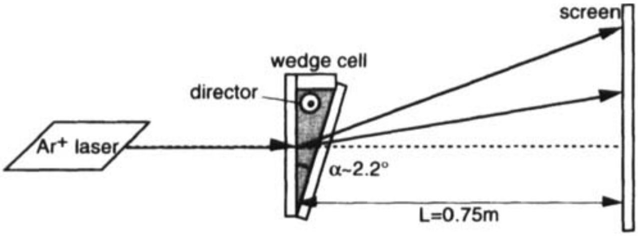


FIGURE 1 Optical geometry for refractive index (birefringence) measurement.

RESULTS and DISCUSSION

Figure 2 shows the temperature dependence of refractive indices of the three compounds. T_{NI} is the phase transition temperature from the isotropic liquid to the nematic phase. The compounds 1~3 show larger refractive indices than that in the nematic phase of 5CB. It is also found that the birefringences Δn of these compounds attain to more than 0.3 at lower temperatures and are larger than that in 5CB (Δn~0.2). The maximum value was 0.38.

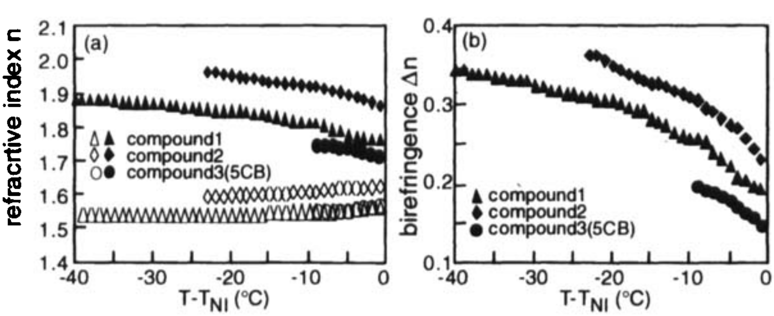


FIGURE 2 Temperature dependence of (a) the refractive indices, n_o (open symbol) and n_e (closed symbol), and (b) the birefringence.

Figure 3 shows the typical polar plot of the polarized angular dependence of the IR absorption peak intensity corresponding to the cyano C-N stretching, acetylene C-C stretching and phenyl ring C-C stretching. The peak corresponding to the acetylene C-C stretching was very weak in the compound 1.

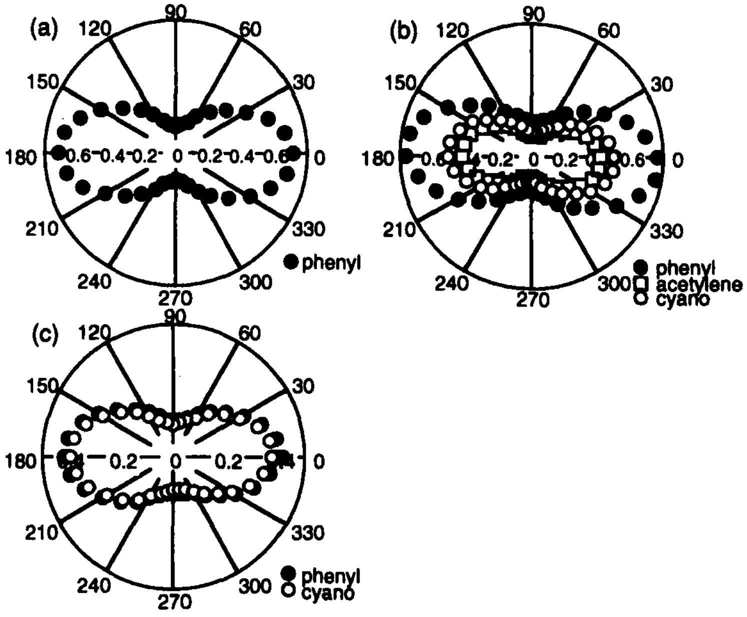


FIGURE 3 Polar plot of the of the polarized angular dependence of the IR absorption peak intensities at T-Tc=-10°C, in (a) compound1, (b) compound2 and (c) compound3 (5CB).

From these results, we calculated the dichroic ratio of the absorbance *D* by

$$D = \frac{A_{0^\circ}}{A_{90^\circ}} \quad ,$$

where $A_{0°}$ and $A_{90°}$ are the absorbance when the polarizer is parallel and normal to the molecular long axis, respectively, and determined by fitting to the following equation[1].

$$A_{\Omega} = -\log\left(I_{0°}\cos^2\Omega + I_{90°}\sin^2\Omega + \left(I_{45°} - I_{135°}\right)\sin\Omega\cos\Omega\right)$$

Eventually, the orientational order parameter was obtained using the following equation,

$$S = \frac{D-1}{D+2} \quad .$$

Figure 4 shows the temperature dependence of the orientational order parameter S of the three compounds. In contrast with the result of optical birefringence measurement, their order parameters are not so different for three compounds.

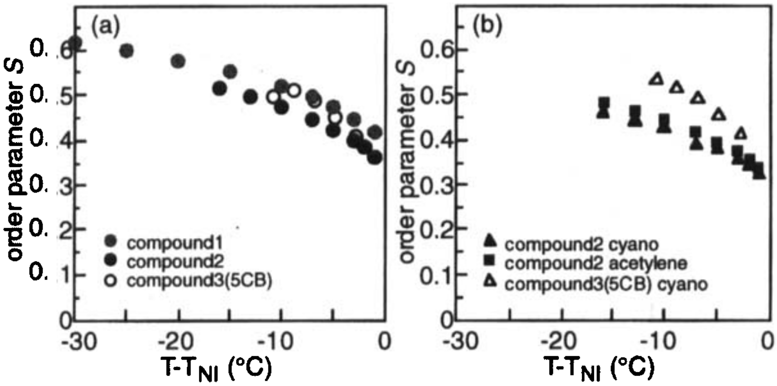


FIGURE 4 Temperature dependence of the order parameter determined from (a) phenyl ring C-C stretching and (b) the other group stretching.

What is the major cause of the high optical anisotropy? Generally, optical anisotropy is proportional to the orientational order parameter and the molecular polarizability. According to Vuck's law, we can calculate the order parameter using the following equation[2],

$$S = \frac{\alpha}{\Delta\alpha} \times \frac{n_e^2 - n_o^2}{\left(n^2 - 1\right)}, \quad n^2 = \frac{n_e^2 + 2n_o^2}{3},$$

where α and $\Delta\alpha$ are an average polarizability and the anisotropy of the polarizability, respectively. Table I shows the molecular polarizability of each compound obtained by MOPAC calculation. α and $\Delta\alpha$ are calculated by $(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})/3$ and $\alpha_{xx}-(\alpha_{yy}+\alpha_{zz})/2$, respectively. As expected, the two compounds with acetylene units have larger anisotropy of molecular polarizability than that of 5CB.

TABLE I Molecular polarizability by MOPAC calculation

	α_{xx}	α_{yy}	α_{zz}	α	$\Delta\alpha$
compound1	452.7	192.4	71.8	239	320.6
compound2	729.2	263.5	91.7	361.5	551.6
compound3(5CB)	290.5	150.3	55.1	165.3	187.8

Figure 5 shows the calculated order parameters of the three compounds. It is found that the order parameters of each compound are almost the same, which is consistent with the result in Fig. 4 apart from the absolute value. Therefore, we can conclude that the large birefringences of novel compounds are attributed to the large anisotropy of the molecular polarizability.

CONCLUSION

We measured an optical birefringence and an orientational order parameter in novel liquid crystal compounds with acetylene units. These compounds have an extraordinary large birefringence, while the order parameter determined by polarized FT-IR are almost the same as that in a typical nematic

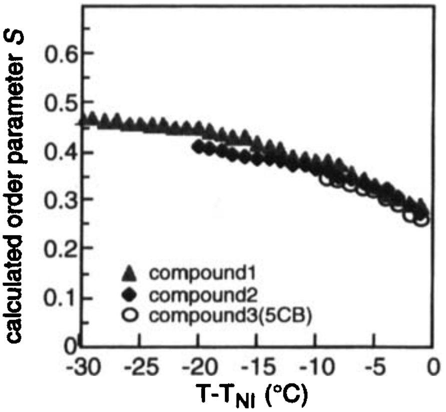


FIGURE 5 Temperature dependence of the calculated order parameter.

liquid crystal, 5CB. From the results of the calculation of molecular polarizability, we concluded that the large optical anisotropy is mainly caused by the large anisotropy of the molecular polarizability.

Acknowledgment

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