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High birefringence laterally fluorinated terphenyl isothiocyanates: Structural, optical and dynamical properties

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ABSTRACT

High birefringence liquid crystals are important for fast switching display and various other applications. One such singly fluorinated isothiocyanato terphenyl compound 2TP-3′F-4NCS which exhibits very broad range nematic (68 °C) and a narrow range smectic phase have been studied by X-ray, dielectric and optical methods. Optical birefringence and order parameters of its doubly fluorinated homologue 2TP-3′,3F-4NCS have also been determined. Contrary to common perception weak antiparallel correlation of molecules is observed in both the compounds. Observed dielectric anisotropy (around 11), though less than cyano compounds, is strong enough to ensure a driving voltage suitable for thin (< 2 μm) TFT based LC display cell. Measured splay elastic constant suggests that singly fluorinated compound will exhibit faster response. Flip-flop mode relaxation is observed lowest at 510 kHz and 2.81 MHz respectively in the doubly and singly fluorinated compound. Thus the singly fluorinated compound excludes the possibility of undesirable energy absorption below MHz range applications. Above all both the compounds exhibit high birefringence, highest values being 0.373 and 0.357 respectively in the singly and doubly fluorinated compounds. Although Δn decreases with temperature it is found to be greater than 0.3 till 164 °C in 2TP-3′F-4NCS and 136 °C in 2TP-3′,3F-4NCS. In addition, both the compounds exhibit high value of order parameters in low temperature region. These two compounds are, therefore, expected to be very suitable for formulating high birefringence nematic mixtures for fast switching displays.

1. Introduction

Response time of a nematic liquid crystal (LC) based display device is proportional to rotational viscosity and square of the display cell thickness [1]. But reduced cell thickness (d) necessitates high birefringence material to attain the appropriate optical path given by Gooch–Tarry first minima condition ($d.\ \Delta n = \sqrt{3}\lambda/2$) in a twisted nematic cell [2]. Fast response time is especially important for color-sequential liquid crystal displays (LCDs) using blinking backlight [3] or primary-color (RGB) light-emitting diodes (LEDs) [4,5]. In the RGB LED-backlit color-sequential LCDs, the pigment color filters can be eliminated, which not only reduces the LCD cost but also triples the device resolution. High Δn materials ($0.3 < \Delta n < 0.5$) are also useful in non-display applications like laser beam steering [6], tunable colour filters [7], focus tunable lens [8], electrically controlled phase shifter in GHz and THz region [9]. High birefringence also enhances the display brightness and contrast ratio of polymer-dispersed liquid crystals (PDLC), holographic PDLC, cholesteric LCD and LC gels [10–13]. In order to meet the demand for faster electro-optic response in nematic liquid crystal based display devices, new high birefringence (Δn) materials are, therefore, synthesized and their properties are studied in both pure and mixture state. Cyano (CN) and isothiocyanato (NCS) are two commonly employed polar groups for elongating the molecular conjugation in biphenyls, terphenyls or tolanes. As a result of longer p-electron conjugation, the NCS-based LC compounds exhibit a larger birefringence than the corresponding CN compounds. Moreover, due to lower dipole moment of NCS group (μ=3.7 D) compared to CN group (μ=3.9 D), viscosity of the NCS compounds is observed to be lower than the nitrile based systems. This is thought to be due to formation of dimmers as a result of strong intermolecular interactions between the nitrile groups which is less probable in isothionato systems. However, a major concern of the CN- and NCS-based LC materials is their relatively low resistivity because of ion trapping near the polyimide alignment interfaces in device structure. Low resistivity leads to a low voltage holding ratio resulting in increased image flickering in thin film transistor (TFT)

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addressed liquid crystal displays. Fluorinated NCS compounds show high resistivity, at the same time they retain high birefringence. Moreover, lateral fluorine substitution in the core substantially reduces melting point and hinders formation of smectic phases because of increased lateral force due to increased volume effect and lateral dipole moment. For example, laterally singly fluorinated terphenyl isothiocyanato compound 2TP-3′F-4NCS exhibits both smectic and nematic phase (Cr 102.5 °C SmA 120.5 °C N 188.2 °C I). Introduction of another lateral fluorine atom in the core (2TP-3′,3F-4NCS) results in sharp decrease of melting point and complete suppression of smectic phase although clearing point remains same (Cr 80.2 °C N 188 °C I). Molecular formulae of both the compounds are given in Fig. 1. Results of optical polarizing microscopy, X-ray diffraction and dielectric spectroscopy studies on the nematogenic 2TP-3′, 3F-4NCS have recently been published [14]. In this paper we communicate high optical birefringence and order parameters of both the compounds along with X-ray and dielectric properties of singly fluorinated smectogenic compound 2TP-3′F-4NCS. Eutectic mixtures of high birefringence nematogenic compounds are developed in order to satisfy various other physical properties including wide phase range, smectic compounds are also used in such mixture formulation [1,15,16]. In this respect both the compounds are expected to be very useful in such mixture formulation.

2. Experimental methods

The phase behavior of 2TP-3′F-4NCS was studied under an Olympus BX41 polarizing microscope, temperature was regulated within ±0.1 °C using Mettler FP 82 central processor and FP84 hot stage. Small and wide angle X-ray scattering measurements on randomly oriented samples were made using Ni filtered Cu*K*α radiation and a custom built high temperature camera; X-ray photographs were scanned in 24 bit RGB colour format using HP2400C scanner and analyzed following procedures as detailed in earlier publications [14,17–19]. Intensity distribution, obtained from the linear scan of X-ray photographs along the equatorial and meridional diffraction peaks, was used to determine average intermolecular distance (D) and apparent molecular length (l) in nematic phase or smectic layer spacing (d) with an accuracy of 0.02 Å and 0.1 Å, respectively. Static and frequency dependent dielectric properties have been studied using computer controlled impedance analyzers HIOKI 3532-50 (50 Hz–5 MHz) and HP 4192A (100 Hz–13 MHz). Low resistivity (about 20 Ω/□) polyimide-coated homogeneous (HG) cells in the form of a parallel plate capacitors with indium tin oxide (ITO) electrodes of ~5 μm cell gap were used for static dielectric measurements. By applying sufficient DC bias field (~5 V μm^{-1}) homeotropic (HT) alignment of the molecules was achieved in the same cell. Perpendicular and parallel components of the dielectric constants were obtained from capacitive measurements in HG and HT cells, respectively. On the other hand, custom-built gold cells of thickness ~19 μm were used for frequency dependent complex dielectric permittivity measurements. In both cases, the cells were filled by capillary action with samples in isotropic state and cell temperature was maintained within ±0.1 °C using Eurotherm 2216e temperature controller. Very slow regulated cooling of the sample was made to get proper alignment.

Temperature dependent refractive indices were measured with He–Ne laser source (λ=633 nm) using Chatelain-Wedge principle. Thin prisms, with angles ~1°, were constructed using optically flat glass slides rubbed with polyvinyl alcohol solution (1%) in such a way that the molecules are aligned with nematic director lying parallel to the edge of the wedge. Prisms were filled with samples in isotropic phase and cooled down very slowly. From the measured angular deflections of the ordinary and extraordinary rays on a graduated scale placed at around 5.0 m away from the sample, respective refractive indices (n_o and n_e) were determined as function of temperature. The density was measured at different temperatures using a dilatometer of capillary type, a travelling microscope, and a temperature controller; correction for glass expansion was made. The temperature was controlled within ±0.5 °C in both cases and the accuracy of density and refractive index measurement was 0.001.

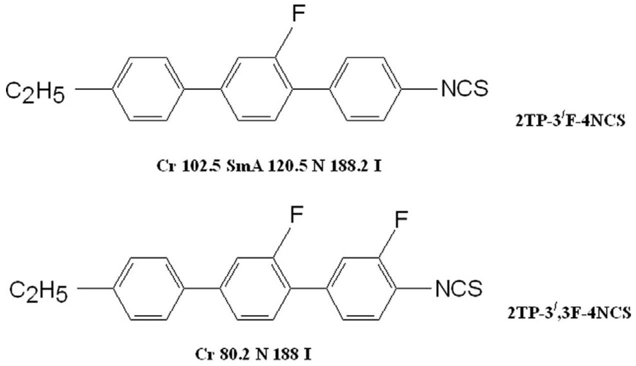

Fig. 1. Molecular structures and phase behaviour of the compounds under investigation.

Molecules in the nematic phase have no positional correlation but they do have long-range orientational ordering. The extent of ordering is usually qualified by orientational order parameters (OOPs), which are uniaxial and are expressed by a traceless symmetric tensor of rank 2. Many physical properties like optical birefringence, dielectric anisotropy, threshold voltage for switching, etc., which are important device parameters, depend upon the OOPs. Orientational order parameter $\langle P_2 \rangle$ was calculated using the principal molecular polarizabilities α_o and α_e, perpendicular and parallel to the direction of optic axis, following de Gennes relation [20].

$$\langle P_2 \rangle = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}}$$

α_o and α_e were calculated using the following Lorenz–Lorentz equations modified for anisotropic systems by Neugebauer [21].

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3}\left[\frac{n_e^2+2}{n_e^2-1} + \frac{2\,(n_o^2+2)}{n_o^2-1}\right]$$

$$\alpha_e + 2\alpha_o = \frac{9}{4\pi N}\left[\frac{n^2-1}{n^2+2}\right]$$

$\alpha_{\parallel}$ and $\alpha_{\perp}$ are the principal polarizabilities parallel and perpendicular to the long axes of the molecules in the perfectly ordered crystalline state where $\langle P_2 \rangle = 1$, which are difficult to measure experimentally. Haller's extrapolation procedure [22] was used to get those values.

3. Results and discussion

3.1. Optical polarization microscopy

Observed textures, topological defect structures observed under optical polarizing microscope, confirmed presence of SmA phase over 18 °C as well as broad range nematic phase exceeding 67 °C, transition temperatures are shown in Fig. 1. Observed focal conic texture in SmA phase and schlieren texture in nematic phase are shown in Fig. 2.