Synthesis of new wide nematic diaryl-diacetylenes containing thiophene-based heteromonocyclic and heterobicyclic structures, and their birefringence properties

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(Received 5 August 2013; accepted 5 December 2013)

New monocyclic and bicyclic thiophene-based diaryl-diacetylene liquid crystal (LC) materials were synthesised and demonstrated to exhibit wide enantiotropic nematic phases. One thiophenyl-benzene derivative, in particular, displayed a stable nematic phase across a temperature range of over 100°C. The birefringence properties of the compounds were measured using a multiple-beam interference (MBI) method, with the highest value found to be for the same thiophenyl-benzene molecule (Δn = 0.57, 550 nm) at 10°C above the crystal-to-nematic transition temperature. Furthermore, the effects of the cyclic structure on the mesomorphic behaviours, transition temperatures, and birefringence properties were investigated in detail from both experimental and theoretical viewpoints.

Keywords: diacetylene; thiophene; birefringence; nematic phase

Introduction

Thiophene-based liquid crystal (LC) materials are extremely useful in the molecular design of organic electronic devices such as organic light-emitting diodes (OLEDs),[1–6] photovoltaic cells,[7–10] organic thin-film transistors (OTFTs) [11–19] and other organic semiconductors.[20–23] Thiophene is a rigid aromatic ring, which makes it highly effective as the mesogen core of LC materials.[24] One of the characteristics of the thiophene ring is that it has relatively large molecular polarisability due to the presence of the electron-rich sulphur atom. Therefore, the introduction of sulphur-based heterocycles into the molecular structure is generally effective for producing optical devices with highly refractive materials.[25–29] In addition, a number of studies have reported that the thiophene ring has a relatively large atomic refractivity. However, derivatives containing thiophene rings are generally not included in the eutectic nematic mixtures used as LC display materials because of their poor mesomorphic properties.[30,31]

A 2,5-substituted thiophene ring has a non-linear or low-symmetry structure owing to the bond angle between the 2- and 5-positions, which results in a lower melting point or a lower phase transition temperature.[30,31] Although this property is essential for the use of such derivatives in various LC material devices, the structure itself makes it difficult for calamitic compounds to form the nematic phase.[30,31] To date, a variety of calamitic molecules containing thiophene-based heterocycles have been studied [32–34]; however, these molecules had only a narrow or monotropic nematic phase just above room temperature.

Many studies regarding the liquid crystallinity, ferroelectricity, photoconductivity, and/or emission and redox properties of thiophene-based LC materials in the smectic, columnar, and banana phases have been published, because the main focus has been on the use of these materials in organic electronic devices.[1–23,35–40] However, the optical properties of these materials, such as their birefringence, have received little attention. A small number of thiophene-based calamitic molecules have been reported for use as high refractive index materials.[41–45] While these compounds were demonstrated to exhibit extremely high birefringence, they showed almost no liquid crystallinity, or had only a narrow nematic phase.

Against such a background, our ultimate aim is to design thiophene-based calamitic molecules with wide nematic phases and enhanced birefringence properties for use as highly birefringent materials. Herein, we report the synthesis of new nematic LC diaryl-diacetylene derivatives containing 2,2′-bithiophene, thieno[3,2-b]thiophene, thiophenyl-benzene, or benzothiophene rings (Chart 1). The ring structures of these compounds can be grouped as monocyclic, for benzothiophene 2 and thieno[3,2-b]thiophene 4; and bicyclic, for thiophenyl-benzene 1 and 2,2′-bithiophene 3. We selected diaryl-diacetylene as the basic
skeleton for these mesogens because its structure is the most likely to form a nematic phase and exhibit high birefringence.  

All compounds, except for the derivative containing benzothiophene rings 2, exhibited a wide enantiotropic nematic phase, in addition to high birefringence. Especially, it is noteworthy that derivatives containing thieno[3,2-b]thiophene rings 4 also exhibited an enantiotropic nematic phase because they are uncommon in low molar mass liquid crystal.  

And the widest nematic range was found to be over 100°C, and the highest birefringence value ($\Delta n$) was 0.57, both of which were obtained for thiophenyl-benzene derivative 1. To further investigate the effects of the cyclic structures of these thiophene-based heterocycles on the LC behaviour and optical properties of diaryl-diacetylenes, we calculated the most stable structures and molecular polarisabilities for all compounds using the density functional theory (DFT) method. Good correlation was found between the experimental and theoretical data.

**Experimental**

**Measurements**

The $^1$H NMR and $^{13}$C NMR spectra were measured using a JEOL LNM-EX 400 at room temperature. CDC$_3$ and tetramethysilane (TMS) were used as a measurement solvent and an internal standard, respectively. The liquid crystalline textures were investigated by polarising optical microscopy (POM) (Leica DM2500P microscopy with a Mettler FP90 hot stage) and the transition temperatures and enthalpy changes were measured by differential scanning calorimetry (DSC) (Perkin Elmer DSC7) with heating and cooling scans performed at 10°C min$^{-1}$. The measurement of $n_c$, $n_o$, and $\Delta n$ were performed with a uniaxial aligned nematic cells, where the glass cells contain an indium tin oxide (ITO) layer purchased from EHC. And the cell gaps ($d$) of 2–3 µm were measured by the interferometric method. The transmittance of light under crossed nicol conditions was observed as a function of wavelength by a microscope spectroscopic method using a Nikon LV100 Pol optical microscope equipped with a USB4000 (Ocean photonics) spectrometer.

**Materials**

Synthetic procedures and spectral data of 1,4-bis[4-(5-hexylthiophenyl)phenyl-1-yl]buta-1,3-diyne (1), 1,4-bis(4-butylbenzo[b]thiophen-5-yl)buta-1,3-diyne (2), 1,4-bis(S'-hexyl-2,2'-bithiophen-5-yl)buta-1,3-diyne (3), and 1,4-bis(5-hexylthieno[3,2-b]thiophen-2-yl)buta-1,3-diyne (4) are described in Supporting Information.

**Results and discussion**

**Design and synthesis of molecular structures**

To evaluate the effects of condensed rings (fused rings) and bicyclic rings on the transition temperatures and optical properties of these materials, we designed heterocyclic diaryl-diacetylenes 1–4, containing thiophenyl-benzene, benzothiophene, bithiophene, and thieno[3,2-b]thiophene groups, respectively (Chart 1). The synthetic routes for these compounds are shown in the Supporting Information. The molecular structures were confirmed using conventional analytical methods, including $^1$H NMR, $^{13}$C NMR, and high-resolution mass spectrometry (HRMS), and the spectral data are also shown in the supporting information.

**Phase transition behaviour**

The thermal transition temperatures of all compounds are listed in Table 1 and Figure 1. Partial decomposition of compounds 1 and 3 towards their isotropic phases was observed using POM, and their textures in the nematic phases from isotropic phases did not partially reappear on cooling. Hence, the crystal-to-nematic phase transition temperatures ($T_m$) were confirmed using DSC for all compounds, and the nematic-to-isotropic phase transition temperatures ($T_i$) were confirmed through POM observation for compounds 1 and 3.

Bicyclic compound 1, which contained thiophenyl-benzene rings, exhibited high transition...
temperatures, and a wide enantiotropic nematic phase. The $T_i$ was confirmed to be 269°C. A POM image obtained at 190°C is shown in Figure 2(a), where a schlieren texture typical of a nematic phase is clearly evident.

On the other hand, for condensed ring compound 2, which contained benzothiophene rings, no LC phases were observed as previously reported in the literature,[43,58,59] which was possibly due to the condensed rings as well as the low degree of linearity. Large fused ring structures tend to enhance the $\pi$–$\pi$ interactions between molecules, as well as other intermolecular attractive forces.

Intriguingly, bicyclic compound 3, which contained thieno[3,2-b]thiophene rings, also exhibited an enantiotropic nematic phase, at approximately 30°C. The POM image of 3 (Figure 2(b)) clearly shows a schlieren texture with two and four brushes. Diaryl-acetylene homologues with thiophene rings tend to have no liquid crystallinity, which may be a result of the expansion of the mesogen when its heterocyclic structure transforms from monocyclic to bicyclic. Furthermore, condensed ring compound 4, which contained thieno[3,2-b]thiophene rings, exhibited a wide enantiotropic nematic phase at approximately 74°C; the POM image of 4 is shown in Figure 2(c).

Thus, compounds 1, 3, and 4 exhibited stable nematic phases. According to the literature,[41,42] it is difficult for calamitic structures such as tolanes and diaryl-diacetylenes that contain heterorings such as thiophenes to have LC properties. In order to generate stable nematic LCs of these compounds, the anisotropy of the molecules must be expanded by introducing condensed rings or bicyclic rings.

### Birefringence properties

The birefringence properties of compounds 1, 3, and 4, which were all found to exhibit a nematic phase, were next measured. In many reports in the literature, the birefringence properties, namely, the difference between extraordinary refractive index ($n_e$) and ordinary refractive index ($n_o$), were measured. The birefringence ($\Delta n$) is given by $\Delta n = n_e - n_o$.

| Compound | Transition temperature (°C) | Enthalpy change (kJ/mol) |
|----------|-----------------------------|--------------------------|
| 1        | Cr 136.5 (29.1) $^a$ N 240 $^b$ Iso |
| 2        | Cr 79.7 (32.3) $^a$ – Iso |
| 3        | Cr 116.8 (36.5) $^a$ N 154.6 (0.64) $^a$ Iso |
| 4        | Cr 95.8 (22.4) $^a$ N 170 $^b$ Iso |

Note: $^a$Measured by DSC, $^b$Observed by POM.
ordinary refractive index \((n_o)\), or \(\Delta n\) values, were estimated by extrapolating the values obtained from eutectic mixtures. In this report, we measured the actual \(n_e\) and \(n_o\) values of the target compounds using both a microscopic spectroscopy method, which enables \(\Delta n\) values to be obtained directly, and the recently reported multiple-beam interference (MBI) method, in which \(\Delta n\) is determined from measured \(n_e\) and \(n_o\) values. These methods have been described in detail in our previous report.[60]

The MBI transmission spectra were obtained for light polarised perpendicular and parallel to the molecules by using a uniaxially aligned nematic LC obtained by injecting the compounds in a nematic state into a rubbed cell coated with polyimide. Subsequently, the spectra were modelled using the following equation:

\[
\frac{I}{I_0} = 1 - A \sin^2 \left[ \frac{2\pi}{\lambda} \left( a + b \frac{\lambda}{\Delta n} \right) d \right]
\]

where \(A\) and \(d\) represent the refractive index constant for the LC material and glass cell, and the cell thickness, respectively, and \(a\) and \(b\) are coefficients for fitting. The \(n_e\) and \(n_o\) values were then obtained using the following equation:

\[
n_e, o = a + \frac{b}{\lambda^2}
\]

Here, we fitted the transmission spectra to the equation for wavelengths above 500 nm, since each compound exhibited an absorption edge over 400 nm, with that for compound 3 in particular being at approximately 450 nm. The measured values were successfully fitted by performing theoretical curve fitting, and the values obtained for all the compounds are listed in Table 2. The measurements were performed at the crystallisation temperature \((T_c) + 10^\circ C\), which is the lowest temperature at which the spectra could be measured for all compounds. The use of these parameters should ensure maximum birefringence, because calamitic molecules with positive birefringence properties exhibit greater values at lower temperatures.

As a representative example, the birefringence parameters concerning the wavelength dependence of compound 1 are shown in the Figure 3 and those of compound 3 and 4 are also shown in Supporting Information. The \(n_e\), \(n_o\), and \(\Delta n\) values all decreased in the longer wavelength region, as expected. The same phenomenon was observed for compounds 3 and 4.

All compounds exhibited high \(n_e\), \(n_o\), and \(\Delta n\) values, with compound 1 in particular giving values of \(n_e = 2.14\) and \(\Delta n = 0.57\) at 550 nm. Comparing 1 with 3, the \(n_e\) of 1 is larger than that of 3, and the \(n_o\) of 1 is smaller than that of 3 (Table 2). This result demonstrates that the benzene ring contributed more to the \(n_e\), i.e., the refractive index of the molecules in the parallel direction, and that its contribution in the \(n_o\), i.e., the refractive index of perpendicular direction was lower than that of the thiophene ring. With respect to the diaryl-diacetylene molecular structures, these results suggest that a benzene ring is more suitable than a thiophene ring for achieving high birefringence.

Next, it was found that the \(n_e\) value of bicyclic compound 3, which contains bithiophene rings, was larger than that of condensed ring compound 4, which contains thiene[3,2-b]thiophene rings \((n_e = 2.10\) and 1.99 at 550 nm for 3 and 4, respectively). Moreover, compounds 3 and 4 showed different \(n_o\) values of 1.60 and 1.51, respectively, at 550 nm. Thus, the contribution of the bicyclic structure to the refractive index in both the perpendicular and parallel directions of the molecules was observed to be larger than the contribution of the fused ring structure for analogues containing only a thiophene ring moiety.

### UV-visible spectra

The UV-visible spectra of compounds 1–4 in hexane solution are shown in Figure 4. Each compound

![Figure 3. (colour online) Wavelength dependence of compound 1.](Image 379x634 to 499x721)
shows relatively long-wavelength absorption, with the absorption edge reaching the visible region for all compounds except 2 (351 nm). Hence, compound 1 appeared pale yellow, and compounds 3 and 4 were deep yellow. Compounds 2 and 4, which have condensed rings, clearly display oscillating absorption behaviour, which can be attributed to their relatively large rings.

For compounds 3 and 4, where the benzene rings were replaced with thiophene rings, a redshift was observed in comparison to compounds 1 and 2, with absorption edge wavelengths being 408 nm and 351 nm, respectively. Thus, the introduction of a benzene ring in compounds 1 and 2 resulted in a higher energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

**DFT calculation**

In order to examine how the different structures produced different birefringence properties, we calculate the electronic optimised structures and polarisabilities using DFT at the ωB97X-D/6-31G(d,p) [61–63] level using Gaussian 09.[64] To facilitate these calculations, derivatives with a methyl group were employed, as shown in Figure 5. The polarisability tensors ($\alpha_{xx}$, $\alpha_{xy}$, $\alpha_{yy}$, $\alpha_{xz}$, $\alpha_{yz}$, and $\alpha_{zz}$) of each compound are listed in Table 3, with the Gaussian output values being in atomic units (a.u.). In these molecular systems, we assume that the principal molecular axis is the x-axis, and the other shorter axes are the y-axis, perpendicular to the x-axis and in the same plane as each diacetylene unit; and the z-axis, perpendicular to the x-axis or y-axis in the vertical plane. The anisotropies in polarisability, $\Delta \alpha$, represents $\alpha_{//} - \alpha_{\perp}$, in which $\alpha_{//}$ and $\alpha_{\perp}$ are polarisabilities parallel and perpendicular to the molecular long axis, respectively. Then, $\alpha_{//}$ and $\alpha_{\perp}$ were estimated from $\alpha_{xx}$ and ($\alpha_{yy} + \alpha_{zz}$)/2, respectively. The polarisability ($\alpha$) was also estimated using the following equation:

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3.$$
These parameters are also shown in Table 3.

Birefringence (Δn) is calculated from the extraordinary refractive index (nₐ) and the ordinary refractive index (n₀) using the following equation:

\[ \Delta n = n_a - n_0 \]

From comparison with the birefringence (Table 2) and polarisability data (Table 3), it is noted that αₓₓ (αᵧᵧ) makes a large contribution to the value of nₓ and that (αₓₓ + αᵧᵧ)/2 (αᵧᵧ), too, contributes to the value of nₒ. In addition, the polarisability of compound 2, whose birefringence could not be measured, is also calculated for reference purposes.

The calculated Δα values in the case of 1 and 3 were 614 and 589 a.u., respectively, which were larger than those of 2 (479 a.u.) and 4 (521 a.u.). This trend was in good agreement with the result that the values of Δα observed in 1 and 3 are larger than those in 2 and 4. Comparing with the αₓₓ and αᵧᵧ values of each compound, the polarisability tensor of the principal molecular axis (αₓₓ) was found to make a significant contribution to the value of Δn. Consequently, the bicyclic compounds appeared to have greater anisotropy of polarisability than did the condensed ring compounds. In terms of polarisability, bicyclic compounds 1 and 3 exhibited larger αₓₓ values in comparison to monomeric compounds 2 and 4. These results can be attributed to the larger anisotropic structures of the bicyclic compounds, since their calculated mesogen lengths were greater than those of monomeric compounds 2 and 4, as shown in Table 3.

The difference between the birefringence properties of compounds 3 and 4 was next examined from the viewpoint of their refractive index in the perpendicular direction (nₒ). According to the optimised structures shown in Figure 5(c), the bicyclic thiophene analogue was not only twisted, but also slightly bent, with the inner thiophene rings having a bond angle between the 2- and 5-positions. Therefore, its molecular structure was slightly more expanded in the y- and z-directions than in the x-direction (the principal molecular axis). However, the monocyclic thieno[3,2-b]thiophene ring analogue was not bent, but was twisted, with the twisted rings located orthogonal to each other (Figure 5(d)). Therefore, because the contributions of the rings to the refractive index in the y- and z-directions in compound 4 were smaller than those for compound 3, the nₒ value of the former was smaller than that of the latter. In addition, it was speculated that compound 4 exhibited a mesophase due to lowering of the molecular packing or crystallinity by the twist, as the two rings of the corresponding monocyclic compound 2, with no mesophases, were in the same plane as one another (Figure 5(b)).

**Square-wave voltammetry (SWV)**

SWV measurements were performed in order to estimate the HOMO and LUMO energy levels from the redox potentials for each compound, and the obtained voltammograms are shown in the Supporting Information. However, the reduction potential, i.e., the LUMO energy level, could not be acquired because it exceeded the measurement limit. Consequently, each HOMO–LUMO energy gap was estimated on the basis of the edge of the optical absorption band, and the LUMO energy levels were then deduced from this. Previous studies have reported good agreement between the energy gaps estimated using electrochemical methods and photochemical methods.[65,66] The oxidation potentials (Eₒₓ), HOMO energy levels obtained from the SWV measurements, and estimated LUMO energy levels obtained in the present study are listed in Table 4.

As expected from the UV-visible spectra, the optical HOMO–LUMO energy gaps (Eₒₓ) for compounds 3 and 4, which contain only thiophene rings, were smaller than those for compound 2, which contain only thiophene rings. Moreover, the Eₒₓ for compounds 3 and 4 were also smaller, corresponding to higher HOMO energy levels. In particular, the HOMO levels were −5.44 eV for 3 and −5.62 eV for 4, which are higher than the −5.67 eV and −5.90 eV found for 1 and 2, respectively. Thus, the UV-visible absorption spectra shift to longer wavelengths upon substitution of a thiophene ring for a phenyl ring.

| Table 4. The optoelectronic data for compounds 1–4 |
|--------------------------------------------------|
| Compound | λₒₓₒ (nm)a | Eₒₓ (eV)b | Eₒₓ (eV)c | Eₒₓ (eV)d | Eₒₓ (eV)e |
|----------|-------------|------------|------------|------------|------------|
| 1        | 408         | 3.04       | 1.11       | −5.67      | −2.63      |
| 2        | 351         | 3.53       | 1.33       | −5.90      | −2.37      |
| 3        | 460         | 2.70       | 0.88       | −5.44      | −2.75      |
| 4        | 427         | 2.90       | 1.05       | −5.62      | −2.71      |

Notes: a Taken as the edge of absorption band.  
bEₒₓ = 1240/λₒₓₒ.  
cEₒₓ is the value of the peak top in square-wave voltammetry (SWV).  
dEₒₓ (eV) = −e(Eₒₓ − 0.234) − 4.8, where +0.234 V is the redox potential for the ferrocene/ferrocenium (Fc/Fc⁺) couple, measured as an external standard for the system, versus a nonaqueous Ag/Ag+ reference electrode; −e is a notation indicating the acceleration of one electron through the adjusted potential; and −4.8 eV represents the work function of the Fe/Fc+ couple relative to the vacuum level.  
eEₒₓ (eV) = Eₒₓ + Eₒₓ.  


Conclusion

We have synthesised a range of diaryl-diacetylenes containing benzothiophene and thieno[3,2-b]thiophene as monomers, and 2,2′-bithiophene and thiophenyl-benzene as dicyles. Apart from the benzothiophene derivative, all of the compounds exhibited wide enantiotropic nematic phases. Notably, the derivative bearing thiophenyl-benzene rings exhibited a nematic range of over 100°C for both heating and cooling scans for POM observation and DSC analysis. Furthermore, their nematic birefringence properties were investigated using an MBI method, with each compound found to exhibit high birefringence. The Δn values for the derivatives decreased in the order: thiophenyl-benzene, 2′-bithiophene, then thieno[3,2-b]thiophene, at 550 nm at Tc + 10°C. The cyclic structure was also found to affect the refractive index values (n1 and n2). In particular, the n2 value was seen to increase when the thienophile was replaced with benzene, and when a monocycle was replaced with a dicycle. This was attributed to these structures contributing more to the molecular polarisation along the long-axis direction than in the other directions. These results provide useful information for improved design of wide nematic range LCs and high birefringence materials.[45,67–73]

Supplemental data

Synthetic procedures, spectral data, NMR, birefringence properties on wavelength dependence, CV charts.

Supplemental data for this article can be accessed here. [link to data].

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