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Synthesis and mesogenic properties of a novel family of oligothiophene derivatives

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With the aim of developing new oligothiophene-based liquid crystals involving hydrogen bonding, new terthiophene derivatives containing an alkylamide group, *N,N'*-distearyl-2,2':5,2''-terthiophene-5,5'-dicarboxamide (DNC₁₈3T) and *N,N'*-dialkyl-5,5'-dibromo-2,2':5,2''-terthiophene-4,4''-dicarboxamides (DNC_{*n*}DBr3T, *n* = 5, 8, 16, 18), were designed and synthesized, and their thermal behaviour examined. While DNC₁₈3T did not exhibit liquid crystallinity, DNC_{*n*}DBr3T compounds with *n* = 8, 16, 18 were found to form smectic A phases. In addition to liquid crystal behaviour, crystal polymorphism was also observed for DNC₁₆DBr3T. It is shown that both the position of the amido group and the alkyl chain length greatly affect liquid crystal phase formation. The absence of liquid crystallinity in the corresponding ester derivatives suggests that intermolecular hydrogen bonding also plays a role in the formation of liquid crystal phases in the DNC_{*n*}DBr3T system.

1. Introduction

Oligothiophenes with well defined structures have recently received a great deal of attention not only as model compounds for electrically conducting polythiophenes but also as a new class of functional π -electron systems. A variety of oligothiophenes have been synthesized [1–9] and their molecular and crystal structures [10–13], self ordering [14–16], electrochemical [17–20], photophysical [21–23], optical [24–30] and electrical [31–40] properties have been studied. In addition their potential application for field-effect transistors [41–46], photovoltaic devices [47–49], and organic electroluminescent devices [50–59] has been investigated.

Oligothiophenes are crystalline in nature because of their planar molecular structures. Vacuum-evaporated and spin-coated films of oligothiophenes have been reported to be polycrystalline [60, 61]. Since the properties and functionality of a material are greatly affected by its morphology, it is of both fundamental and technological interest to exert control over morphology of oligothiophenes in the design of novel functional organic materials. For example, we have synthesized amorphous molecular materials containing oligothiophene moieties of varying conjugation length [53–58]. These novel amorphous molecular materials, which readily form stable amorphous

glasses with relatively high glass transition temperatures, have found application as colour-tunable emitting materials for organic light-emitting diodes [53–58].

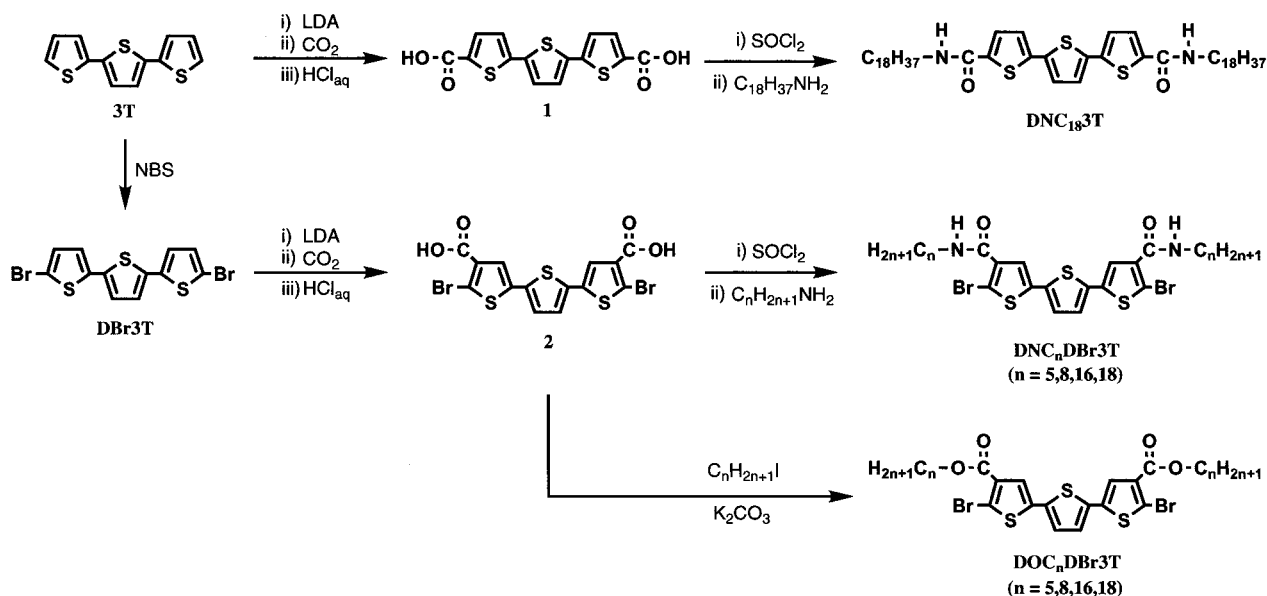
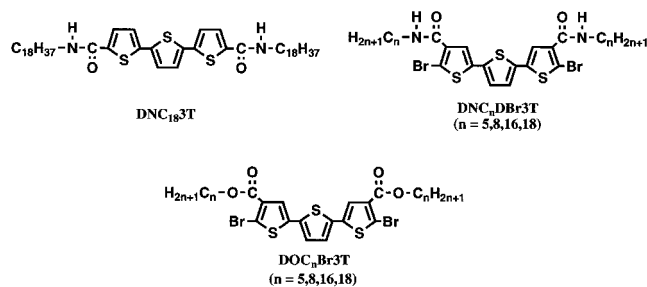
Recently, several reports on the liquid crystalline properties of oligothiophene derivatives have appeared [62–65]. It has been reported that terthiophenes substituted with long alkyl or alkanoyl groups at the terminal α - and α'' -positions, e.g. 5-alkyloxycarbonyl-5''-alkyl-2,2':5,2''-terthiophenes and 5,5''-dialkyl-2,2':5,2''-terthiophenes, exhibit a smectic liquid crystalline phase [63]. 5-Substituted and 5,5''-disubstituted quaterthiophenes have also been reported to exhibit smectic and nematic liquid crystalline phases [65]. In addition, unsubstituted sexithiophene [62] and tetrahexyl-substituted diformyl-octithiophene [64] have also been reported to form smectic and nematic liquid crystals, respectively. However, examples of oligothiophene-based liquid crystals are still scarce.

In the present study aimed at developing new liquid crystalline materials based on oligothiophenes, we were interested in the role played by intermolecular hydrogen bonding in liquid crystal phase formation. Apart from oligothiophenes, there are some examples of liquid crystalline compounds containing an amido group which readily form intermolecular hydrogen bonding [66, 67]; however, the role of hydrogen bonding in mesophase formation is not clear. To clarify this situation, we have designed and synthesized novel 2,2':5,2''-terthiophene

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(3T) derivatives containing an alkylamide group either at the α - and α' -positions or at the β - and β' -positions of 3T, *N,N'*-distearyl-2,2':5,2''-terthiophene-5,5''-dicarboxamide (DNC₁₈3T) and *N,N'*-dialkyl-5,5''-dibromo-2,2':5,2''-terthiophene-4,4''-dicarboxamide (DNC_nDBr3T, $n = 5, 8, 16, 18$), and examined their thermal behaviour. Because of the synthetic difficulty of introducing the alkylamido group at the β - and β' -positions of 3T in the absence of substituents at its α - and α' -positions, we have incorporated two bromo substituents at the α - and α' -positions of 3T; we also expected that they may enhance the mesogenic behaviour of the compounds due to their high polarizability. In addition, the thermal behaviour of 5,5''-dibromo-2,2':5,2''-terthiophene (DBr3T) and that of the corresponding ester derivatives, 4,4''-bis-(alkyloxycarbonyl)-5,5''-dibromo-2,2':5,2''-terthiophenes (DOC_nDBr3T, $n = 5, 8, 16, 18$), was examined to gain information on the rôle of the bromo substituent and the amido group in liquid crystal phase formation.

We report here the mesogenic properties of the DNC_n-DBr3T compounds and discuss the relationship between molecular structure and liquid crystalline behaviour, and the involvement of intermolecular hydrogen bonding in liquid crystal phase formation.



Scheme. Synthesis of DNC₁₈3T, DNC_nDBr3T ($n = 5, 8, 16, 18$), and DOC_nDBr3T ($n = 5, 8, 16, 18$).

2. Experimental

2.1. Synthesis

2-Bromothiophene, 2,5-dibromothiophene, [1,3-bis-(diphenylphosphino)propane]nickel(II) chloride (NiCl₂(dppp)), magnesium, diisopropylamine, butyllithium (hexane solution), thionyl chloride, triethylamine, monoalkylamines ($\text{C}_n\text{H}_{2n+1}\text{NH}_2$, $n = 5, 8, 16, 18$), and 1-iodoalkanes ($\text{C}_n\text{H}_{2n+1}\text{I}$, $n = 5, 8, 16, 18$) were commercially available and used without further purification. Synthetic procedures are illustrated in the scheme.

2.1.1. Synthesis of *N,N'*-distearyl-5,5''-(2,2':5,2''-terthiophene)dicarboxamide (DNC₁₈3T)

An ether solution (50 ml) of 2-bromothiophene (19.5 g, 0.12 mol) in the presence of magnesium (2.95 g, 0.12 mol) was stirred for 5 h at room temperature under a nitrogen atmosphere to give the Grignard reagent. This solution was added to an ether solution (20 ml) of 2,5-dibromothiophene (9.74 g, 40.2 mmol) in the presence of NiCl₂(dppp) (0.625 g, 1.2 mmol), and was heated at reflux for 10 h to give crude 2,2':5,2''-terthiophene (3T), which was purified by silica gel column chromatography using hexane as an eluent, followed by recrystallization from hexane (yield 2.8 g, 29%).

A hexane solution of butyllithium (33 mmol) was added to a THF solution (30 ml) of diisopropylamine (3.3 g, 33 mmol) at -78°C under a nitrogen atmosphere to give lithium diisopropylamide (LDA). To the solution of LDA was added 3T (1.6 g, 6.5 mmol) at -78°C and the solution was stirred for 1 h. Excess dry ice was added and the reaction mixture stirred for 8 h, and then allowed to warm to room temperature. The solution was then treated with aqueous hydrochloric acid and resulting

solid was collected and washed with hot acetonitrile to give 2,2':5,2''-terthiophene-5,5''-dicarboxylic acid (**1**) (yield 80% based on 3T).

A 1,2-dichloroethane solution (80 ml) of **1** (0.25 g, 0.74 mmol) and SOCl₂ (0.18 g, 1.5 mmol) was heated at reflux for 5 h under a nitrogen atmosphere. After the solvent was removed under reduced pressure, the resulting solid was added to a dichloromethane solution (50 ml) of stearylamine (0.39 g, 1.5 mmol) in the presence of triethylamine (1 ml) at 0°C, and stirred for 5 h under a nitrogen atmosphere to give *N,N'*-distearyl-5,5''-(2,2':5,2''-terthiophene)dicarboxamide (DNC₁₈3T); this was purified by recrystallization from 1,4-dioxan (yield 83% based on **1**). ¹H NMR (400 MHz, DMSO-d₆, 110°C, ppm): δ = 8.04 (t, 2H, NH), 7.62 (d, 2H, ArH), 7.31 (s, 2H, ArH), 7.27 (d, 2H, ArH), 3.20 (t, 4H, stearyl α-CH₂), 1.57 (tt, 4H, stearyl β-CH₂), 1.40–1.16 (m, 60H, stearyl CH₂), 0.85 (t, 6H, CH₃). IR (KBr, cm⁻¹): 3640 (ν_{N-H}), 2955, 2919, 1851 (ν_{C-H}), 1662 (ν_{C=O}). MS (EI): *m/z* 838 (M⁺). Elemental analysis: found C 71.24, H 9.83, N 3.41, S 11.33; calc. for C₅₀H₈₂N₂S₃O₂ C 71.54, H 9.85, N 3.34, S 11.46%.

2.1.2. Synthesis of *N,N'*-dialkyl-5,5''-dibromo-2,2':5,2''-terthiophene-4,4''-dicarboxamide (DNC_{*n*}DBr3T, *n* = 5, 8, 16, 18)

5,5''-Dibromo-2,2':5,2''-terthiophene (DBr3T) was prepared by the reaction of 3T (2.8 g, 11.3 mmol) with *N*-bromosuccinimide (4.2 g, 22.6 mmol) in chloroform (200 ml) at room temperature for *c.* 3 h and purified by silica gel column chromatography using chloroform as eluent, followed by recrystallization from a benzene/hexane mixture (1:2 v/v).

DBr3T (2.0 g, 4.9 mmol) was added to a THF solution (30 ml) of LDA (19.6 mmol) at -78°C and the solution stirred for 1 h. Excess dry ice was added to the solution and the resulting mixture stirred for 2 h. The solution was allowed to warm to room temperature and aqueous hydrochloric acid was added. After stirring for 5 h, the resulting solid was collected and washed with hot acetonitrile to give 5,5''-dibromo-2,2':5,2''-terthiophene-4,4''-dicarboxylic acid (**2**) (yield 60% based on DBr3T).

A dichloromethane solution (80 ml) of **2** (0.5 g, 1.0 mmol) and SOCl₂ (0.24 g, 2.0 mmol) was heated at reflux for 8 h. After the solvent was removed under reduced pressure, the resulting solid was added to a THF solution (80 ml) of amylamine (0.17 g, 2.0 mmol) in the presence of triethylamine (2 ml) at 0°C and the solution stirred for 5 h at 0°C. The solvent was removed under reduced pressure to give *N,N'*-dipentyl-5,5''-dibromo-2,2':5,2''-terthiophene-4,4''-dicarboxamide (DNC₅DBr3T). The product was purified by silica gel column chromatography

using chloroform as the eluent (yield 70% based on **2**). ¹H NMR (600 MHz, THF-d₈, ppm): δ = 7.35 (s, 2H, ArH), 7.32 (t, 2H, NH), 7.28 (s, 2H, ArH), 3.36 (dt, 4H, pentyl α-CH₂), 1.60 (tt, 4H, pentyl β-CH₂), 1.45–1.33 (m, 8H, pentyl CH₂), 0.88 (t, 6H, CH₃). IR (KBr, cm⁻¹): 3388 (ν_{N-H}), 2958, 2927, 2859 (ν_{C-H}), 1625 (ν_{C=O}). MS (EI): *m/z* 632 (M⁺). Elemental analysis: found C 45.65, H 4.44, N 4.47; calc. for C₂₄H₂₈N₂S₃O₂Br₂ C 45.57, H 4.46, N 4.43%.

The *N,N'*-dialkyl-5,5''-dibromo-2,2':5,2''-terthiophene-4,4''-dicarboxamides (DNC_{*n*}DBr3T, *n* = 8, 16, 18) were synthesized using analogous procedures involving octylamine, cetylamine, or stearylamine (yields 54–62%).

DNC₈DBr3T. ¹H NMR (600 MHz, THF-d₈, ppm): δ = 7.36 (s, 2H, ArH), 7.31 (t, 2H, NH), 7.28 (s, 2H, ArH), 3.38 (dt, 4H, octyl α-CH₂), 1.61 (tt, 4H, octyl β-CH₂), 1.46–1.23 (m, 20H, octyl CH₂), 0.88 (t, 6H, CH₃). IR (KBr, cm⁻¹): 3302 (ν_{N-H}), 2958, 2923, 2853 (ν_{C-H}), 1625 (ν_{C=O}). MS (EI): *m/z* 716 (M⁺). Elemental analysis: found C 50.38, H 5.60, N 3.96; calc. for C₃₀H₄₀N₂S₃O₂Br₂ C 50.28, H 5.63, N 3.91%.

DNC₁₆DBr3T. ¹H NMR (600 MHz, THF-d₈, ppm): δ = 7.35 (s, 2H, ArH), 7.32 (t, 2H, NH), 7.29 (s, 2H, ArH), 3.34 (dt, 4H, cetyl α-CH₂), 1.58 (tt, 4H, cetyl β-CH₂), 1.48–1.15 (m, 52H, cetyl CH₂), 0.88 (t, 6H, CH₃). IR (KBr, cm⁻¹): 3328 (ν_{N-H}), 2948, 2921, 2850 (ν_{C-H}), 1619 (ν_{C=O}). MS (EI): *m/z* 941 (M⁺). Elemental analysis: found C 58.74, H 7.64, N 3.01; calc. for C₄₆H₇₂N₂S₃O₂Br₂ C 58.71, H 7.71, N 2.98%.

DNC₁₈DBr3T. ¹H NMR (600 MHz, THF-d₈, ppm): δ = 7.35 (s, 2H, ArH), 7.31 (t, 2H, NH), 7.28 (s, 2H, ArH), 3.38 (dt, 4H, stearyl α-CH₂), 1.60 (tt, 4H, stearyl β-CH₂), 1.45–1.22 (m, 60H, stearyl CH₂), 0.88 (t, 6H, CH₃). IR (KBr, cm⁻¹): 3312 (ν_{N-H}), 2956, 2918, 2849 (ν_{C-H}), 1619 (ν_{C=O}). MS (EI): *m/z* 997 (M⁺). Elemental analysis: found C 60.36, H 8.00, N 2.79; calc. for C₅₀H₈₀N₂S₃O₂Br₂ C 60.22, H 8.09, N 2.81%.

2.1.3. Synthesis of 4,4''-bis(alkyloxycarbonyl)-5,5''-dibromo-2,2':5,2''-terthiophene (DOC_{*n*}DBr3T, *n* = 5, 8, 16, 18)

5,5''-Dibromo-2,2':5,2''-terthiophene-4,4''-dicarboxylic acid (**2**) (0.5 g, 1.0 mmol) was reacted with 1-iodopentane (0.40 g, 2.0 mmol) in the presence of potassium carbonate (0.20 g, 1.5 mmol) in hexamethylphosphorotriamide (20 ml) at room temperature for 24 h under a nitrogen atmosphere. The resulting solid was collected to give 4,4''-bis(pentoxycarbonyl)-5,5''-dibromo-2,2':5,2''-terthiophene (DOC₅DBr3T). The product was purified by silica gel column chromatography using chloroform as the eluent (yield 91%). ¹H NMR (400 MHz, THF-d₈, ppm): δ = 7.45 (s, 2H, ArH), 7.40 (s, 2H, ArH), 4.29 (t, 4H, pentyl α-CH₂), 1.64–1.27 (m, 12H, pentyl CH₂), 0.93

(t, 6H, CH₃). IR (KBr, cm⁻¹): 2953, 2935, 2862 (ν_{C-H}), 1683 ($\nu_{C=O}$). MS(EI): m/z 634 (M⁺). Elemental analysis: found C 45.44, H 4.00; calc. for C₂₄H₂₆S₃O₄Br₂ C 45.43, H 4.13%.

The 4,4''-bis(alkyloxycarbonyl)-5,5''-dibromo-2,2':5',2''-terthiophenes (DOC_{*n*}DBr3T, *n* = 8, 16, 18) were synthesized using analogous procedures involving 1-iodooctane, 1-iodohexadecane, or 1-iodooctadecane (yields 91 ~ 93%).

DOC₈DBr3T. ¹H NMR (400 MHz, THF-d₈, ppm): δ = 7.45 (s, 2H, ArH), 7.40 (s, 2H, ArH), 4.28 (t, 4H, octyl α -CH₂), 1.59–1.13 (m, 24H, octyl CH₂), 0.89 (t, 6H, CH₃). IR (KBr, cm⁻¹): 2958, 2924, 2852 (ν_{C-H}), 1707 ($\nu_{C=O}$). MS(EI): m/z 718 (M⁺). Elemental analysis: found C 50.19, H 5.32; calc. for C₃₀H₃₈S₃O₄Br₂ C 50.13, H 5.33%.

DOC₁₆DBr3T. ¹H NMR (400 MHz, THF-d₈, ppm): δ = 7.45 (s, 2H, ArH), 7.39 (s, 2H, ArH), 4.20 (t, 4H, cetyl α -CH₂), 1.55–1.05 (m, 56H, cetyl CH₂), 0.86 (t, 6H, CH₃). IR (KBr, cm⁻¹): 2955, 2917, 2848 (ν_{C-H}), 1688 ($\nu_{C=O}$). MS(EI): m/z 943 (M⁺). Elemental analysis: found C 58.82, H 7.47; calc. for C₄₆H₇₀S₃O₄Br₂ C 58.58, H 7.48%.

DOC₁₈DBr3T. ¹H NMR (400 MHz, THF-d₈, ppm): δ = 7.45 (s, 2H, ArH), 7.39 (s, 2H, ArH), 4.28 (t, 4H, stearyl α -CH₂), 1.57–0.99 (m, 64H, stearyl CH₂), 0.88 (t, 6H, CH₃). IR (KBr, cm⁻¹): 2956, 2918, 2849 (ν_{C-H}), 1689 ($\nu_{C=O}$). MS(EI): m/z 999 (M⁺). Elemental analysis: found C 60.82, H 8.06; calc. for C₅₀H₇₈S₃O₄Br₂ C 60.11, H 7.87%.

2.2. Characterization

Differential scanning calorimetry (DSC) was performed using a SSC/5200 (SEIKO I&E) calorimeter. Polarizing microscopy was carried out with an OPTIPHOT X2 (Nikon) microscope, fitted with a TH-600PM hot stage (Linkam) and crossed polarizers.

3. Results and discussion

Novel families of oligothiophene derivatives containing an alkylamide group either at the α - and α' -positions or the β - and β' -positions of 3T, DNC₁₈3T and DNC_{*n*}DBr3T (*n* = 5, 8, 16, 18), were synthesized according to the procedures shown in the scheme. The corresponding ester derivatives, DOC_{*n*}DBr3T (*n* = 5, 8, 16, 18), were also synthesized. All compounds were characterized by IR and ¹H NMR spectroscopy, mass spectrometry, and elemental analysis.

DSC and polarized light microscopy performed on DNC₁₈3T and DNC₁₈DBr3T revealed that DNC₁₈3T, containing two alkylamide groups at the α - and α' -positions of 3T, did not exhibit liquid crystalline behaviour either on heating or cooling, showing only melting and crystallization transitions at 213 and 207°C,

respectively. By contrast, DNC₁₈DBr3T, containing two alkylamide groups at the β - and β'' -positions of 3T, formed a smectic A (SmA) phase. Figure 1 shows the DSC curves for DNC₁₈DBr3T. When the crystalline sample of DNC₁₈DBr3T was heated, an endothermic peak was observed at 110°C to give a smectic A phase. On further heating, the onset of the transition from the SmA phase into the isotropic liquid was observed at 121°C, and the peak at 123°C. When the isotropic liquid was cooled, the onset of the transition into the SmA phase was observed at around 123°C and the peak at 121°C; the SmA phase crystallized at 107°C. The trace was reproducible. The formation of a SmA phase by DNC₁₈DBr3T was also evidenced by polarized light microscopy. Figure 2 shows the polarizing micrograph of the DNC₁₈DBr3T SmA phase formed from the isotropic liquid at around 120°C in the cooling process. A focal-conic fan texture typical of the SmA phase was clearly observed.

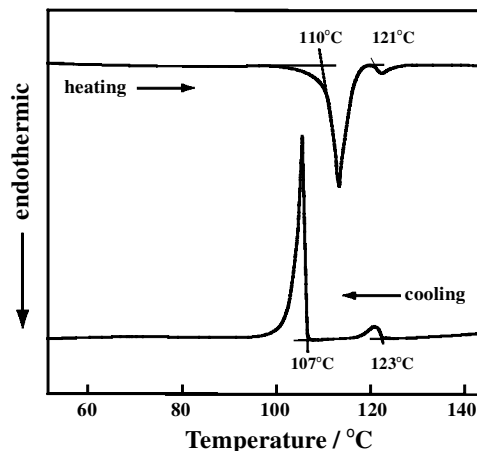


Figure 1. DSC curves for DNC₁₈DBr3T.

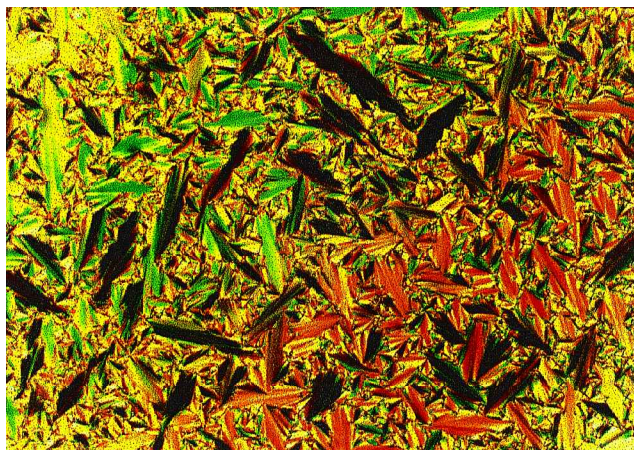


Figure 2. Photomicrograph of the texture of the SmA phase of DNC₁₈DBr3T at 120°C obtained on cooling the melt.

The results show that the position of the amido group greatly affects liquid crystal phase formation. CPK models of these molecules show that while $\text{DNC}_{18}\text{3T}$ is almost linear, with all the carbon atoms of the alkyl-amido group and the atoms of the amido moiety in the $\text{DNC}_{18}\text{3T}$ molecule lying in the same plane as the central terthiophene moiety, $\text{DNC}_{18}\text{DBr3T}$ is more or less V-shaped. The atoms of the alkylamido group in $\text{DNC}_{18}\text{DBr3T}$ do not lie in the same plane as the terthiophene moiety due to steric hindrance between the bromo atoms in the α - and α' -positions and the amido groups in the β - and β' -positions. It is thought that the linear and planar molecular structure of $\text{DNC}_{18}\text{3T}$ may favour molecular packing more readily than found for $\text{DNC}_{18}\text{DBr3T}$, so promoting crystallization. There may also be a possibility that the increased polarizability of the $\text{DNC}_{18}\text{DBr3T}$ molecule, due to the bromo substituents, facilitates liquid crystal phase formation.

The effects of the alkyl chain length in the alkylamido group on liquid crystalline behaviour were investigated. Like $\text{DNC}_{18}\text{DBr3T}$, $\text{DNC}_{16}\text{DBr3T}$ was found to form a SmA phase. In addition, $\text{DNC}_{16}\text{DBr3T}$ exhibited crystal polymorphism, showing two different crystal forms. Figure 3 shows the DSC curves for $\text{DNC}_{16}\text{DBr3T}$. When the crystalline sample (CrX) was heated, an endothermic peak due to a solid–solid phase transformation was observed at 109°C , to give a second crystal form (CrY). On further heating, an endothermic peak due to the phase transition from crystal Y into a SmA phase was observed at 120°C , followed by the phase transition from SmA into the isotropic liquid at 127°C . When the isotropic liquid was cooled, the phase transition to the SmA phase was observed at around 127°C , and on further cooling, the SmA was directly transformed into CrX at 110°C without the intervention of CrY. The DSC trace was reproducible.

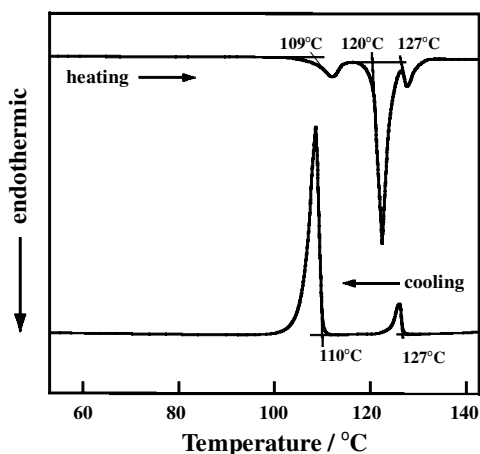


Figure 3. DSC curves for $\text{DNC}_{16}\text{DBr3T}$.

The schematic free energy–temperature curves for $\text{DNC}_{16}\text{DBr3T}$ are shown in figure 4. In the heating process, the phase transformation takes place according to arrow 1. Thus, the SmA phase appears at *c.* 120°C after CrX was transformed into CrY at 109°C . The SmA phase undergoes a transition into the isotropic liquid at 127°C . On cooling from the melt, the SmA phase is directly transformed into CrX via a supercooled smectic A phase, as indicated by arrow 2.

With regard to $\text{DNC}_8\text{DBr3T}$, the formation of a liquid crystalline phase did not occur on heating; however, a SmA phase appeared on cooling in the temperature range from about 126 to 109°C as observed by polarized light microscopy (figure 5). DSC curves showed,

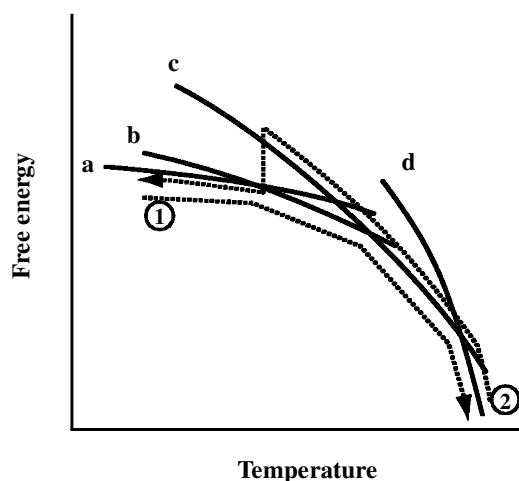


Figure 4. Schematic free energy–temperature curves for $\text{DNC}_{16}\text{DBr3T}$: (a) CrX; (b) CrY; (c) SmA phase; (d) isotropic liquid.

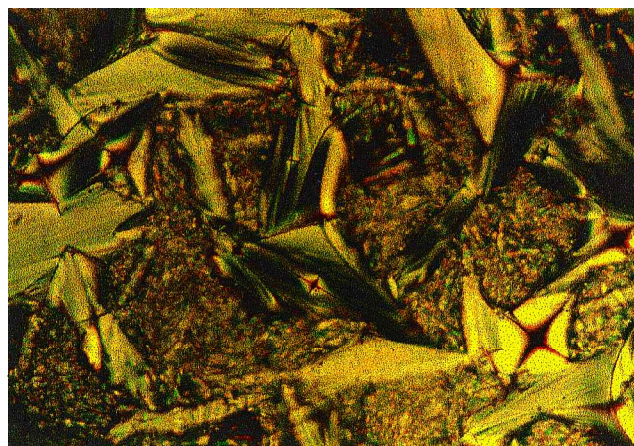


Figure 5. Photomicrograph of the texture of the SmA phase of $\text{DNC}_8\text{DBr3T}$ at 126°C formed on cooling the melt.

however, only the phase transition phenomena between the crystal and the isotropic liquid with an endothermic peak at 141°C on heating and an exothermic peak at 122°C on cooling. It is suggested that the SmA phase observed by polarized light microscopy is a metastable state, and that the isotropic liquid of DNC₈DBr3T tends readily to crystallize in the aluminum pan used for the DSC measurement. On the other hand, the isotropic liquid of DNC₈DBr3T on a glass substrate used for polarized light microscopy forms the SmA phase via a supercooled liquid, on further cooling, the metastable SmA phase transforms into the thermodynamically more stable crystal.

These phenomena are explained in terms of the free energy–temperature curves as shown in figure 6. On heating, the crystalline sample is directly transformed into the isotropic liquid as indicated by arrow 1. On cooling from the melt, the phase transition behaviour depends on the environment of the sample. In an environment such as an aluminum pan where the crystallization is induced relatively easily, the isotropic liquid is directly transformed into the crystal as indicated by arrow 2. On the other hand, in an environment such as a glass substrate where crystallization does not take place readily, the liquid crystal phase is formed via a supercooled liquid, followed by crystallization, as indicated by arrow 3.

It is noteworthy that while DNC_{*n*}DBr3T with *n* = 8, 16, and 18 formed liquid crystal phases, DNC₅DBr3T did not, showing only the phase transition between the crystal and the isotropic liquid, as revealed by DSC and polarized light microscopy. The absence of any liquid crystalline phase for DNC₅DBr3T is thought to be due to the short alkyl chain length, which may favour

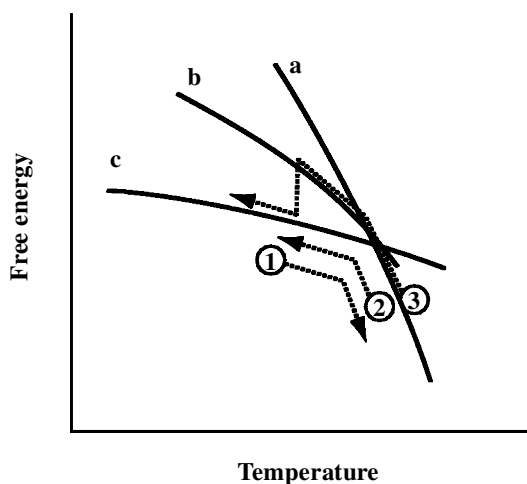


Figure 6. Schematic free energy–temperature curves for DNC₈DBr3T: (a) isotropic liquid; (b) SmA phase; (c) Cr.

stronger intermolecular interactions through the hydrogen bond, leading to ready crystallization. The results indicate that the alkyl chain length plays an important role in the formation of liquid crystal phases in the DNC_{*n*}DBr3T system.

In order to gain information on the role of the bromo substituent and the amide group in the formation of liquid crystal phases, the thermal behaviour of DBr3T and the corresponding ester compounds, DOC_{*n*}DBr3T (*n* = 5, 8, 16, 18) was examined. Neither DBr3T nor DOC_{*n*}DBr3T exhibited liquid crystallinity, showing only melting and crystallization behaviour on heating and cooling. These results show that the alkylamide groups in the β- and β'-positions of 3T play an important role in the formation of liquid crystal phases in the DNC_{*n*}DBr3T system.

It is suggested that intermolecular hydrogen bonding through the amido groups is involved in liquid crystal phase formation. The presence of intermolecular hydrogen bonding was evidenced by infrared (IR) absorption spectroscopy. Figure 7 shows the IR absorption spectra of DNC₁₈DBr3T in its crystalline and liquid crystalline phases in the wavelength region of the N–H stretching vibration mode. The crystalline sample showed only a broad absorption around 3300 cm⁻¹, which is attributable to the stretching vibration of the hydrogen-bonded N–H, figure 7(a). The liquid crystalline sample obtained by heating the crystalline sample showed both the hydrogen-bonded absorption band and a sharp absorption peak

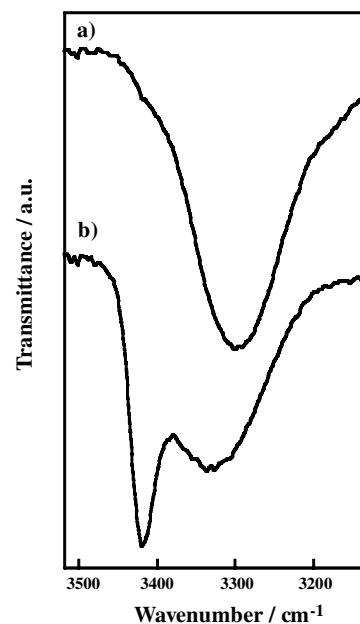


Figure 7. Infrared absorption spectra of DNC₁₈DBr3T: (a) crystal at 100°C; (b) SmA phase at 120°C formed on heating the crystal.

Table. Transition temperatures and enthalpy changes of DNC₁₈3T, DNC_nDBr3T (*n* = 5, 8, 16, 18), DOC_nDBr3T (*n* = 5, 8, 16, 18), and DBr3T. Cr = crystal, CrX = crystal X, CrY = crystal Y, SmA = smectic A liquid crystal, I = isotropic liquid.

Compound	Transition temperature/°C; enthalpy change (in parentheses)/kJ mol ⁻¹						
DNC ₁₈ 3T ^a	Cr			209 (67)	I		
DNC ₅ DBr3T ^a	Cr			119 (30)	I		
DNC ₈ DBr3T ^a	Cr			141 (47)	I		
DNC ₈ DBr3T ^b	Cr		109 (-)	SmA	126 (-)	I	
DNC ₁₆ DBr3T ^a	CrX	109 (5.1)	CrY	120 (-)	SmA	127 (-)	I
DNC ₁₆ DBr3T ^c	CrX			110 (46)	SmA	127 (3.6)	I
DNC ₁₈ DBr3T ^c	Cr			107 (56)	SmA	123 (3.7)	I
DOC ₅ DBr3T ^a	Cr					88 (58)	I
DOC ₈ DBr3T ^a	Cr					70 (90)	I
DOC ₁₆ DBr3T ^a	Cr					76 (110)	I
DOC ₁₈ DBr3T ^a	Cr					66 (86)	I
DBr3T ^a	Cr					158 (30)	I

^a Transition temperatures and enthalpy changes were determined by DSC on heating.

^b Transition temperatures were determined by polarized light microscopy on cooling.

^c Transition temperatures and enthalpy changes were determined by DSC on cooling.

at 3419 cm⁻¹ attributable to the free N-H, figure 7(b). The spectrum of the isotropic liquid was almost the same as that of the liquid crystal. The change in the IR absorption spectra between the crystal and the liquid crystal during both heating and cooling was reproducible. This indicates that the molecules in the SmA phase only partly form intermolecular hydrogen bonds, whereas in the crystal all the molecules are fixed tightly by the intermolecular hydrogen bonding. Partial intermolecular hydrogen bonding interactions may play a role in the formation of liquid crystal phases in the DNC_nDBr3T system.

The absence of liquid crystalline behaviour for both DOC_nDBr3T and DBr3T suggests that the presence of the two bromo substituents at the α- and α''-positions of 3T in DNC_nDBr3T is not directly responsible for liquid crystal phase formation in the DNC_nDBr3T system, although it may contribute to the enhancement of liquid crystal-forming properties. The elucidation of the role of the bromo substituent, if any, in liquid crystal phase formation in the DNC_nDBr3T system now requires further studies.

The table summarizes the transition temperatures of DNC₁₈3T, DNC_nDBr3T (*n* = 5, 8, 16, 18), DOC_nDBr3T (*n* = 5, 8, 16, 18), and DBr3T together with the enthalpy changes (Δ*H*) associated with the phase transitions. The temperature range in which the SmA phase exists for DNC_nDBr3T (*n* = 8, 16, 18) is more or less similar to those of the reported terthiophene derivatives that form SmA phases, e.g. 5-alkyloxycarbonyl-5''-alkyl-2,2':5',2''-terthiophenes (7–26°C) [63]. The Δ*H* values associated with the phase transition from the SmA phase into the isotropic liquid for DNC₁₆DBr3T and DNC₁₈DBr3T (3.6 and 3.7 kJ mol⁻¹, respectively) are slightly smaller

than those reported for the 5-alkyloxycarbonyl-5''-alkyl-2,2':5',2''-terthiophenes (6–11 kJ mol⁻¹), while the Δ*H* values associated with the phase transition from the crystal to the SmA phase for DNC₁₆DBr3T and DNC₁₈DBr3T (46 and 56 kJ mol⁻¹, respectively) are larger than those for the 5-alkyloxycarbonyl-5''-alkyl-2,2':5',2''-terthiophenes (15–26 kJ mol⁻¹). This is probably because the effect of hydrogen bonding on the stabilization of the crystalline phase is stronger than that on the liquid crystal phase.

4. Conclusion

In order to develop new oligothiophene-based liquid crystals involving intermolecular hydrogen bonding, new families of oligothiophene derivatives, DNC₁₈3T and DNC_nDBr3T (*n* = 5, 8, 16, 18), were designed and synthesized. DNC_nDBr3T (*n* = 8, 16, 18) were found to form SmA phases, so constituting a new class of oligothiophene-based liquid crystals. It was shown that the position of the alkylamido group and the alkyl chain length greatly affect liquid crystal phase formation. The absence of liquid crystallinity for DOC_nDBr3T and changes in the IR spectra suggest that intermolecular hydrogen bonding through the alkylamide group is involved in liquid crystal phase formation in the DNC_nDBr3T system.

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