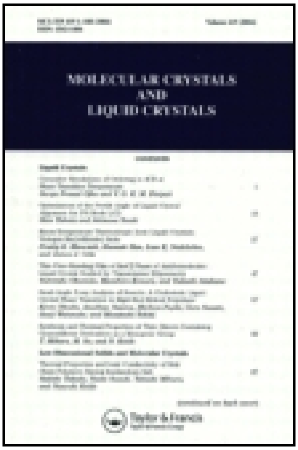

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Non-Symmetric Liquid Crystal Dimers: High Thermal Stability in Nematic Phase Enhanced by Thiophene-2-Carboxylate Moiety

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Non-Symmetric Liquid Crystal Dimers: High Thermal Stability in Nematic Phase Enhanced by Thiophene-2-Carboxylate Moiety

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Series of non-symmetric liquid crystal dimers, α-(4-benzylidenechloroaniline-4′-oxy)-ω-[4-(thiophene-2-carboxyl)benzylideneaniline-4′-oxy]alkanes incorporating a thiophene-based moiety in one of the two mesogenic units have been synthesized and characterized. The nematogenic properties of the dimers were studied wherein the flexible spacers made up by n methylene units (–CH_2-) ranging from n=5 to n=12. These dimers exhibit enantiotropic N phase with high thermal stability (>187.0°C). The N phase temperature range for the present homologues is found to be strongly dependent on the length and parity of the methylene spacer which connects the 4-benzylidenechloroaniline and 4-(thiophene-2-carboxyl)- benzylideneaniline mesogenic cores.

Keywords: enantiotropic N phase; high thermal stability; non-symmetric liquid crystal dimers; thiophene

1. INTRODUCTION

The liquid crystals derived from oligomers have attracted much attention for several reasons. Part of the growing interest resulted from the fact that the oligomers exhibit considerable differences in

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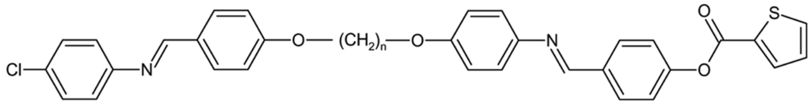
properties in comparison to the conventional low molecular mass liquid crystals [1]. Also, previous findings on the dimers and trimers have suggested that the oligomeric members can act as model compounds for the semiflexible main chain liquid crystalline polymers [2]. A striking similarity between the oligomeric and polymeric derivatives which has received great attention from researchers is the odd–even effect which refers to the spacer parity-dependent mesomorphic properties [3]. Because of higher degree of structure linearity, the members with even spacers possess higher phase transition temperatures in comparison to the odd members which are less linear [2,3]. Spacers with even parity possess more conformers which allow parallel arrangement of mesogenic cores. On the other hand, odd spacers possess more conformers which result in arrangement of cores with bent configuration. Extensive investigation on this interesting odd–even alternation of transition temperatures has been carried out by Imrie and co-workers on various systems of dimers, trimers, and tetramers such as the 4,4′-bis[ω-(4-cyanobiphenyl-4′-yloxy)alkoxy]-biphenyls [4].

Although many novel liquid crystal dimers have been reported so far but the number of dimers with non-symmetric structure has still been relatively small. Among these non-symmetric dimers, the five-membered heterocyclic rings such as furan and thiophene in the molecular structures are rare. Most of the known liquid crystals incorporating one or more five-membered rings are not liquid crystal oligomers and many of these compounds are smectogenic and nematogenic [5,6]. Previous studies have shown that heteroatoms in the heterocyclic rings may cause changes in a variety of parameters such as dielectric anisotropy [7]. Since the report on non-symmetric dimers incorporating five-membered heterocyclic rings and the potential influence of these rings on certain physical characteristics has hitherto found to be rare, the structure-property relationships of these dimers are indeed worth an exploration. In the mesophase, the presence of a heterocyclic ring in either one of the two mesogenic groups within the dimers can induce a different kind of intermolecular interaction, and hence it will be interesting if further investigation can focus on this subject.

The unconventional properties of non-symmetric dimers and our interests to examine the influence of a heterocyclic ring on the liquid crystalline properties have prompted us to prepare a novel series of thiophene-based non-symmetric dimers. This series of non-symmetric dimers contains eight homologous α-(4-benzylidenechloroaniline-4′-oxy)-ω-[4-(thiophene-2-carboxyl)benzylideneaniline-4′-oxy]alkanes with the general molecular structure as shown below.

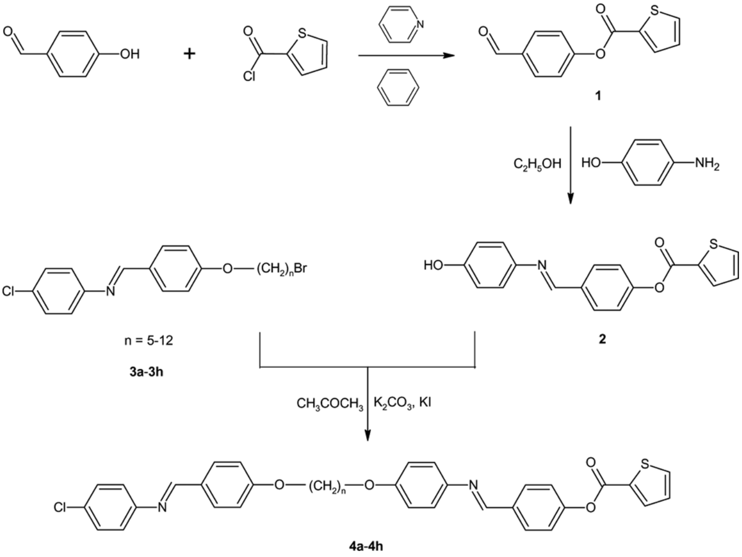


The dimers differ from one another in terms of the methylene spacer, $(CH_2)_n$ with odd and even n ranging from 5 to 12. The liquid crystalline properties of the hexyl and octyl homologues in this series are also compared with the previously reported analogous DL-α-(4-benzylidenechloroaniline-4′-oxy)-ω-[2-methylbutyl-4′-(4″-phenyl)-benzoateoxy]alkanes.

2. EXPERIMENTAL

2.1. Synthesis

All intermediates and title compounds in this series were synthesized based on the routes given in Scheme 1. Compound **1** is the product of esterification upon employment of Schotten–Baumann technique with pyridine serving as the base. The condensation between compound **1** and 4-aminophenol in an ethanolic solution led to the formation of the compound **2**. Compounds **3a**–**3h** were prepared via two-step syntheses starting from condensation reaction and then Williamson ether synthesis in the presence of potassium carbonate anhydrous as



SCHEME 1

reported elsewhere [8]. The title compounds **4a–4h** were synthesized by reacting compound **2** with compounds **3a–3h**, respectively, with potassium carbonate anhydrous and catalytic amount of potassium iodide. The labels referring to the intermediary compounds **3a–3h** and title compounds **4a–4h** with respective spacers (C_5H_{10} to $C_{12}H_{24}$) are shown in Table 1.

2.1.1. *Synthesis of Compound* 1

4-Hydroxybenzaldehyde (2.44 g, 20.0 mmole) was dissolved in 8 mL pyridine in a round-bottom flask prior to the addition of 50 mL benzene. 2-Thiophenecarbonyl chloride (2.93 g, 20.0 mmole) was then added very slowly to the stirring solution. The mixture was refluxed for 2 h. The undesired precipitate was immediately filtered off and the resulting solution was left for evaporation. The product was washed with absolute ethanol and subsequently recrystallized from the mixture of chloroform and hexane. Yield 71%. Elemental analysis (%): found, C 62.07, H 3.49; calculated ($C_{12}H_8O_3S$), C 62.06, H 3.47. IR (KBr) ν/cm^{-1}, 1726 (C=O ester), 1697 (C=O aldehyde). ^{1}H-NMR ($CDCl_3$) δ/ppm, 7.23 (dd, 1 H, Th), 7.46 (d, 2 H, Ar), 7.73 (dd, 1 H, Th), 7.98 (d, 2 H, Ar), 8.03 (dd, 1 H, Th), 10.05 (s, 1 H, CHO).

2.1.2. *Synthesis of Compound* 2

Compound **1** (2.79 g, 12.0 mmole) was dissolved in 40 mL absolute ethanol in a round-bottom flask. As the solution was heated up, an ethanolic solution of 4-aminophenol (1.31 g, 12.0 mmole) was added dropwise. The mixture was refluxed for 3 h. The resulting hot solution was subsequently cooled to 5°C for 1/2 h to precipitate out the solids. Upon filtration, the crude products were then recrystallized from the mixture of chloroform and hexane. Yield 52%. Elemental analysis (%): found, C 66.88, H 4.06, N 4.34; calculated ($C_{18}H_{13}NO_3S$),

TABLE 1 Intermediary Compounds **3a**–**3h** and Title Compounds **4a**–**4h** with Respective Spacers, $(CH_2)_n$

Intermediate	Compound	Spacer $(CH_2)_n$
3a	**4a**	C_5H_{10}
3b	**4b**	C_6H_{12}
3c	**4c**	C_7H_{14}
3d	**4d**	C_8H_{16}
3e	**4e**	C_9H_{18}
3f	**4f**	$C_{10}H_{20}$
3g	**4g**	$C_{11}H_{22}$
3h	**4h**	$C_{12}H_{24}$

C 66.86, H 4.05, N 4.33. IR (KBr) ν/cm^{-1}, 3448 (OH), 1690 (C=O ester), 1627–1600 (C=N). ^{1}H-NMR ($CDCl_3$) δ/ppm, 4.70 (s, 1 H, OH), 6.89 (d, 2 H, Ar), 7.21 (2d, 3 H, Ar and Th), 7.38 (d, 2 H, Ar), 7.69 (dd, 1 H, Th), 7.96 (d, 2 H, Ar), 8.02 (dd, 1 H, Th), 8.50 (s, 1 H, CH=N).

2.1.3. *Syntheses of Compounds* 3a-3 h

Compounds **3a–3h** were synthesized according to the previously reported method [8]. The carbon, hydrogen, and nitrogen (CHN) microanalytical results of these intermediates conform to the calculated values.

2.1.4. *Synthesis of Compound* 4a

In a round-bottom flask containing potassium carbonate anhydrous (0.14 g, 1.0 mmole), compound **2** (0.16 g, 0.5 mmole) was dissolved in 40 mL acetone and heated up. Subsequently, compound **3a** (0.19 g, 0.5 mmole) in another 40 mL acetone was added dropwise to the solution. The mixture was refluxed for 16 h. The acetone solution was then left at room temperature to evaporate off. The potassium carbonate anhydrous was removed in 50 mL water. The desired precipitate was filtered off and recrystallized twice, initially from ethyl acetate and, subsequently, from the mixture of chloroform and hexane. Yield 52%. Elemental analysis (%): found, C 69.41, H 5.04, N 4.51; calculated ($C_{36}H_{31}N_2O_4SCl$), C 69.39, H 5.01, N 4.50. IR (KBr) ν/cm^{-1}, 2943–2871 (C-H alkyl), 1729 (C=O ester), 1622–1605 (C=N), 1252 ($O\text{-}CH_2$). ^{1}H-NMR ($CDCl_3$) δ/ppm, 1.60–1.99 (m, 6 H, CH_2), 4.10 (t, 4 H, OCH_2), 7.02 (d, 4 H, Ar), 7.17 (d, 2 H, Ar), 7.22 (t, 1 H, Th), 7.27 (m, 4 H, Ar), 7.35 (d, 2 H, Ar), 7.70 (d, 1 H, Th), 7.87 (2d, 4 H, Ar), 8.02 (d, 1 H, Th), 8.38 (s, 1 H, CH=N), 8.43 (s, 1 H, CH=N).

Whilst compounds **4b, 4d, 4f,** and **4h** were recrystallized from the mixture of ethyl acetate and chloroform, compounds **4c, 4e,** and **4g** were purified by the same solvent system applied for compound **4a**.

2.1.5. *Synthesis of Compound* 4b

Yield 73%. Elemental analysis (%): found, C 69.75, H 5.24, N 4.42; calculated ($C_{37}H_{33}N_2O_4SCl$), C 69.74, H 5.22, N 4.40. IR (KBr) ν/cm^{-1}, 2940–2863 (C-H alkyl), 1738 (C=O ester), 1620–1605 (C=N), 1248 ($O\text{-}CH_2$). ^{1}H-NMR ($CDCl_3$) δ/ppm, 1.62–1.91 (m, 8 H, CH_2), 4.10 (t, 4 H, OCH_2), 6.99 (d, 4 H, Ar), 7.15 (d, 2 H, Ar), 7.20 (t, 1 H, Th), 7.26 (m, 4 H, Ar), 7.34 (d, 2 H, Ar), 7.67 (d, 1 H, Th), 7.86 (t, 4 H, Ar), 8.02 (d, 1 H, Th), 8.37 (s, 1 H, CH=N), 8.42 (s, 1 H, CH=N).

2.1.6. *Synthesis of Compound* 4c

Yield 51%. Elemental analysis (%): found, C 70.10, H 5.44, N 4.31; calculated ($C_{38}H_{35}N_2O_4SCl$), C 70.08, H 5.42, N 4.30. IR (KBr)

ν/cm^{-1}, 2938–2862 (C-H alkyl), 1723 (C=O ester), 1621–1606 (C=N), 1247 (O-CH$_2$). ^{1}H-NMR (CDCl$_3$) δ/ppm, 1.51–1.88 (m, 10 H, CH$_2$), 4.06 (t, 4 H, OCH$_2$), 7.01 (d, 4 H, Ar), 7.16 (d, 2 H, Ar), 7.20 (t, 1 H, Th), 7.28 (m, 4 H, Ar), 7.34 (d, 2 H, Ar), 7.69 (d, 1 H, Th), 7.86 (2d, 4 H, Ar), 8.01 (d, 1 H, Th), 8.37 (s, 1 H, CH=N), 8.41 (s, 1 H, CH=N).

2.1.7. *Synthesis of Compound* 4d

Yield 63%. Elemental analysis (%): found, C 70.42, H 5.63, N 4.20; calculated ($C_{39}H_{37}N_2O_4SCl$), C 70.41, H 5.61, N 4.21. IR (KBr) ν/cm^{-1}, 2937–2856 (C-H alkyl), 1738 (C=O ester), 1620–1605 (C=N), 1247 (O-CH$_2$). ^{1}H-NMR (CDCl$_3$) δ/ppm, 1.44–1.88 (m, 12 H, CH$_2$), 4.07 (t, 4 H, OCH$_2$), 7.00 (2d, 4 H, Ar), 7.15 (d, 2 H, Ar), 7.21 (dd, 1 H, Th), 7.25 (m, 4 H, Ar), 7.33 (d, 2 H, Ar), 7.66 (dd, 1 H, Th), 7.84 (2d, 4 H, Ar), 8.00 (dd, 1 H, Th), 8.37 (s, 1 H, CH=N), 8.41 (s, 1 H, CH=N).

2.1.8. *Synthesis of Compound* 4e

Yield 52%. Elemental analysis (%): found, C 70.75, H 5.82, N 4.13; calculated ($C_{40}H_{39}N_2O_4SCl$), C 70.73, H 5.79, N 4.12. IR (KBr) ν/cm^{-1}, 2932–2853 (C-H alkyl), 1731 (C=O ester), 1622–1605 (C=N), 1250 (O-CH$_2$). ^{1}H-NMR (CDCl$_3$) δ/ppm, 1.41–1.84 (m, 14 H, CH$_2$), 4.05 (t, 4 H, OCH$_2$), 6.99 (2d, 4 H, Ar), 7.16 (d, 2 H, Ar), 7.21 (dd, 1 H, Th), 7.26 (m, 4 H, Ar), 7.35 (d, 2 H, Ar), 7.68 (dd, 1 H, Th), 7.85 (t, 4 H, Ar), 8.01 (dd, 1 H, Th), 8.37 (s, 1 H, CH=N), 8.41 (s, 1 H, CH=N).

2.1.9. *Synthesis of Compound* 4f

Yield 70%. Elemental analysis (%): found, C 71.04, H 5.99, N 4.05; calculated ($C_{41}H_{41}N_2O_4SCl$), C 71.03, H 5.96, N 4.04. IR (KBr) ν/cm^{-1}, 2940–2863 (C-H alkyl), 1739 (C=O ester), 1620–1606 (C=N), 1249 (O-CH$_2$). ^{1}H-NMR (CDCl$_3$) δ/ppm, 1.39–1.87 (m, 16 H, CH$_2$), 4.06 (t, 4 H, OCH$_2$), 7.00 (2d, 4 H, Ar), 7.15 (d, 2 H, Ar), 7.19 (dd, 1 H, Th), 7.25 (m, 4 H, Ar), 7.33 (d, 2 H, Ar), 7.68 (dd, 1 H, Th), 7.82 (2d, 4 H, Ar), 7.99 (dd, 1 H, Th), 8.36 (s, 1 H, CH=N), 8.41 (s, 1 H, CH=N).

2.1.10. *Synthesis of Compound* 4g

Yield 54%. Elemental analysis (%): found, C 71.34, H 6.15, N 3.98; calculated ($C_{42}H_{43}N_2O_4SCl$), C 71.32, H 6.13, N 3.96. IR (KBr) ν/cm^{-1}, 2936–2852 (C-H alkyl), 1731 (C=O ester), 1622–1605 (C=N), 1249 (O-CH$_2$). ^{1}H-NMR (CDCl$_3$) δ/ppm, 1.35–1.85 (m, 18 H, CH$_2$), 4.05 (t, 4 H, OCH$_2$), 7.00 (2d, 4 H, Ar), 7.16 (d, 2 H, Ar), 7.21 (dd, 1 H, Th), 7.26 (m, 4 H, Ar), 7.35 (d, 2 H, Ar), 7.70 (dd, 1 H, Th), 7.85 (2d, 4 H, Ar), 8.02 (dd, 1 H, Th), 8.37 (s, 1 H, CH=N), 8.41 (s, 1 H, CH=N).

2.1.11. *Synthesis of Compound* 4h

Yield 67%. Elemental analysis (%): found, C 71.62, H 6.32, N 3.89; calculated ($C_{43}H_{45}N_2O_4SCl$), C 71.60, H 6.29, N 3.88. IR (KBr) ν/cm^{-1}, 2936–2850 (C-H alkyl), 1738 (C=O ester), 1620–1606 (C=N), 1250 (O-CH_2). ^{1}H-NMR ($CDCl_3$) δ/ppm, 1.33–1.85 (m, 20 H, CH_2), 4.04 (t, 4 H, OCH_2), 7.00 (d, 4 H, Ar), 7.16 (d, 2 H, Ar), 7.21 (t, 1 H, Th), 7.26 (m, 4 H, Ar), 7.34 (d, 2 H, Ar), 7.70 (d, 1 H, Th), 7.85 (2d, 4 H, Ar), 8.01 (d, 1 H, Th), 8.37 (s, 1 H, CH=N), 8.41 (s, 1 H, CH=N).

2.2. Characterization

The molecular structures of all intermediary and title compounds were elucidated via spectroscopic methods. The FT-IR technique was carried out on a Perkin Elmer 2000 FTIR spectrometer. The samples were prepared in the form of KBr pellets and analyzed within frequency range of 4000–400 cm^{-1}. The investigation by ^{1}H-NMR was performed on a Bruker 400 MHz Ultrashield^{TM} spectrometer. The compounds were dissolved in deuterated chloroform ($CDCl_3$) with 0.03% (v/v) TMS as internal standard. CHN microanalyses were performed using a Perkin Elmer 2400 LS Series CHNS/O analyzer. Texture observation was performed on a Carl Zeiss Axioskop 40 polarizing microscope linked to a Linkam TMS94 temperature controller and LTS350 hot-stage. In order to determine the phase transition temperatures, associated enthalpies and entropy changes for the nematic-isotropic transition, differential scanning calorimetry was carried out using a Seiko DSC6200R calorimeter with the heating and cooling rate of $\pm$ 5°C min^{-1} at Tokyo Institute of Technology, Japan. The nature of the mesophase was identified conclusively using a Bruker D8 powder X-ray diffractometer for representative compound **4f** at Warsaw University, Poland.

3. RESULTS AND DISCUSSION

3.1. Liquid Crystalline Properties

3.1.1. *The Odd–Even Effect on Phase Transition Temperatures*

All non-symmetric dimers (**4a**–**4h**) in this series are enantiotropic nematogens. The phase transition temperatures, respective enthalpies, and entropy changes for the nematic-isotropic transition are shown in Table 2. The dependence of all transition temperatures and N phase temperature ranges upon the number of methylene units, n in the spacers during heating run is shown in Fig. 1a. From the graph, it is apparent that the Cr-N and N-I transition temperatures are strongly correlated with the parity of the spacer. The alternation of the melting

TABLE 2 Phase Transition Temperatures (°C), Associated Enthalpies (kJ mol^{-1}), and Nematic-Isotropic Entropy Changes of Compounds **4a**–**4h** (• = Enantiotropic Phase; Cr = Crystal, N = Nematic, I = Isotropic)

Compound	Cr	N	I	$\Delta S_{NI}/R$
4a	• 126.3 (9.5)	• 203.1 (0.3)	•	0.06
4b	• 166.1 (13.2)	• 245.8 (0.5)	•	0.12
4c	• 135.4 (11.7)	• 202.9 (0.5)	•	0.11
4d	• 149.1 (14.7)	• 224.2 (1.3)	•	0.32
4e	• 131.9 (9.1)	• 196.7 (0.5)	•	0.13
4f	• 149.6 (15.5)	• 207.6 (1.2)	•	0.31
4g	• 134.6 (10.3)	• 187.9 (0.7)	•	0.18
4h	• 150.2 (20.2)	• 193.4 (1.3)	•	0.33

temperatures into the N phase is strong although attenuation has not been recorded. The members with even-parity spacers melt at higher temperatures as compared to the odd counterparts. Similarly, the even members also possess higher clearing temperatures (T_{NI}) than the odd members. However, as the series ascends towards the longer spacer, the difference of T_{NI} between neighbouring odd and even homologues reduces substantially. As such, the T_{NI} of compound **4h** (n=12) is only 5.5°C higher than that in compound **4g** (n=11). The strong attenuation of T_{NI} on increasing n has also been reported for other series of dimers such as the cholesterol and cyanobiphenylyl-based liquid crystals [9]. This odd–even characteristic is part of the unique features of the dimers and other oligomeric members which is not observed in the series of non-oligomeric mesogens.

Upon increasing n, the suppression of the nematogenic properties of the even members is more pronounced as compared to the odd members (Fig. 1b). Compounds **4b** and **4d** (n=6 and 8, respectively) possess larger N phase temperature range as compared to the odd compounds **4a** and **4c** (n=5 and 7, respectively). However, with the addition of more methylene units, significant decreasing trend is observed in the N phase temperature range for even members as compound **4h** (n=12) is 10.1°C smaller than that of compound **4g** (n=11). Such characteristic can be justified based on the influence of the spacers. Regardless of the spacer length, the dimers with odd spacers presumably possess less linear conformation and thus lower orientational order compared to the even counterparts [3]. Every addition of two methylene units from C_5H_{10} to $C_{11}H_{22}$ does not result in significant increase in the dilution of the cores if compared to the even members which have higher shape anisotropy. As the result, the dilution effect of the cores is more pronounced for the even members as the spacer

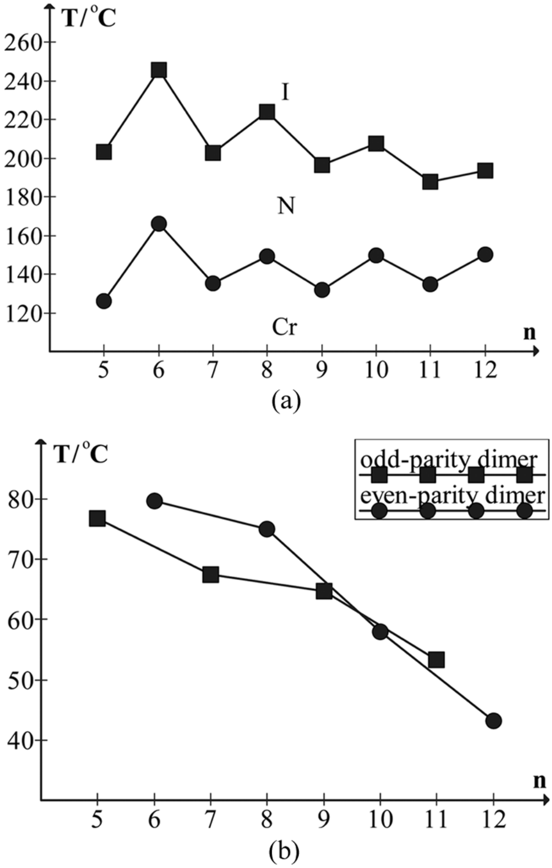
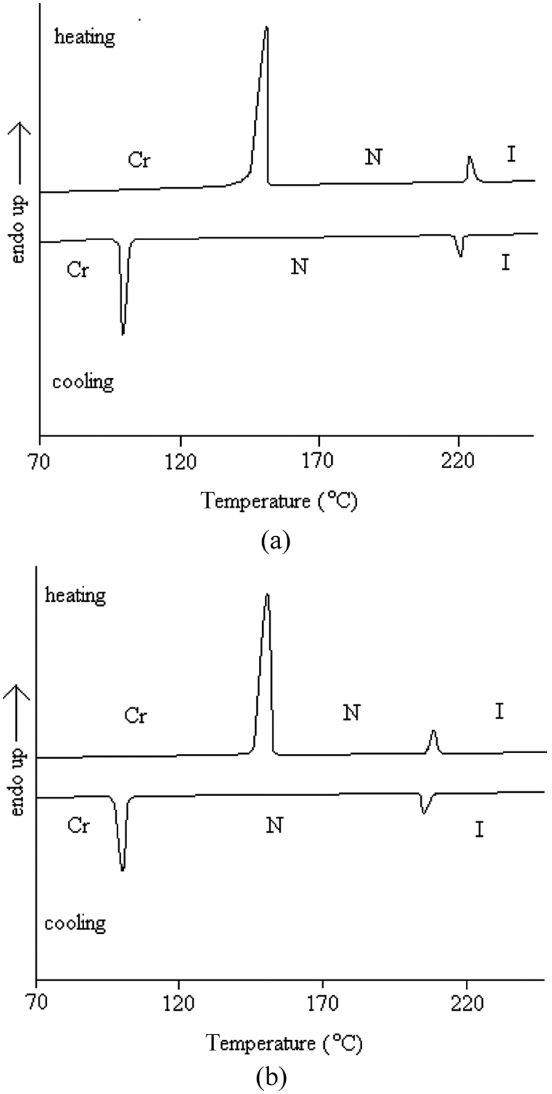


FIGURE 1 (a) The dependence of phase transition temperatures, T on the number of methylene units, *n* in the flexible spacer and (b) The comparison of N phase temperature range, T between odd and even members during heating run.

length is increased. Therefore, with the increasing spacer length, the nematogenic properties of the even dimers are reduced in greater magnitude than the odd counterparts.

3.1.2. *The Thermal and Optical Properties*

The DSC results of compounds **4a–4h** are consistent with the results obtained via polarizing microscopy in terms of transition temperatures for all heating and cooling cycles. The DSC traces of representative compounds **4d** and **4f** are given in Figs. 2a,b, respectively. Generally, the enthalpies of fusion for dimers with even-parity



(a)

(b)

FIGURE 2 The DSC traces of (a) compound **4d** and (b) compound **4f** with $\pm 5^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$ heating and cooling rates.

are higher than those detected for the odd dimers (Table 2). This characteristic suggests that the intermolecular attractive forces for the even dimers in the Cr lattice are stronger as compared to the odd members owing to the more linear conformation of the former.

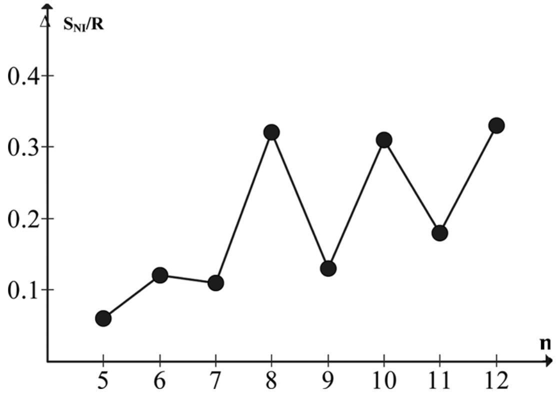


FIGURE 3 The dependence of the entropy change ($\Delta S_{NI}/R$) associated with the nematic-isotropic transition on the number of methylene units, *n* in the flexible spacer.

The nematic-isotropic (N-I) transitional entropy changes of the dimers are expressed in dimensionless quantity, $\Delta S_{NI}/R$. The dependence of the entropy change, $\Delta S_{NI}/R$ associated with the N-I transition on the number of methylene units, *n* in the flexible spacer is given in Fig. 3. The overall $\Delta S_{NI}/R$ values of the even dimers **4b, 4d, 4f,** and **4h** fall in the range of 0.12–0.33. These values are considerably lower than earlier reported dimers with even spacers such as the dimers of the *m*-O*n*O-*m* and *m*-*n*-*m* series [10]. In order to substantiate this point, a comparison in relation to the magnitude of $\Delta S_{NI}/R$ will be made later in the discussion. Despite the low entropy changes of the even members, these values are still generally higher than those detected for the odd counterparts. The $\Delta S_{NI}/R$ values of the even members are approximately 1.7–5.5 times larger than those of the odd members except compound **4b**. The $\Delta S_{NI}/R$ values for compounds **4a, 4c, 4e,** and **4g** are 0.06, 0.11, 0.13, and 0.18, respectively. The lower entropy changes of the odd dimers are, however, not uncommon as the more biaxial odd dimers tend to possess entropies of transition similar to the monomers [11]. Apart from the odd dimers, it is interesting to note that the value for compound **4b** with hexyl spacer is far lower than its even counterparts. Whilst $\Delta S_{NI}/R$ of compound **4d, 4f,** and **4h** are 0.32, 0.31, and 0.33, respectively, the $\Delta S_{NI}/R$ of compound **4b** is only 0.12. The unusually low $\Delta S_{NI}/R$ value of **4b** could be attributed to the lower shape anisotropy of **4b** as compared to the other three even members with longer spacers [10]. The overall entropy changes exhibit a dramatic alternation as *n* is increased with the exception involving *n*=6 as we mentioned earlier.

The textures of the title compounds **4a–4h** under polarized light are identified based on several characteristics. On thin samples, the N phase appears as marble texture upon heating of the Cr phase. As temperature is elevated, colour changes are observed in certain domains due to the change in birefringence [12]. As it approaches the isotropic phase, the N schlieren texture with both twofold and fourfold brushes is then observed for compound **4g** (Fig. 4). However, upon heating, compound **4f** exhibit the coexistence of homeotropic and planar region. Our observation on this microscopic sample reveals the presence of filamentary texture in the homeotropic region which resembles that of SmA and SmC phases [13]. Upon cooling at $-5°\mathrm{C\,min}^{-1}$, the filaments of compound **4f** gradually transform to compact domains as shown in Fig. 5. Such filamentary structure has yet to be reported for N phase. However, upon mechanical shearing of the sample, the occurrence of bright flashes suggests that the mesophase is indeed nematogenic in nature [12]. The flash indicates reorientation of the director and, therefore, also the optic axis of the N phase due to the applied pressure upon shearing. In order to ascertain the mesophase conclusively, the powder X-ray diffraction analysis is conducted for compound **4f**. The absence of sharp reflection at low angle confirms that layer periodicity is absent in the mesophase structure whilst the broadly diffuse signal at wide angle region indicates the short range order typical of the N phase [14].

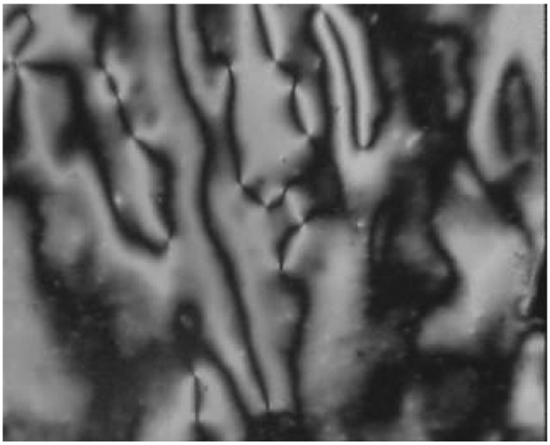


FIGURE 4 The N schlieren texture (compound **4g**) with both twofold and fourfold brushes at 186.0°C.

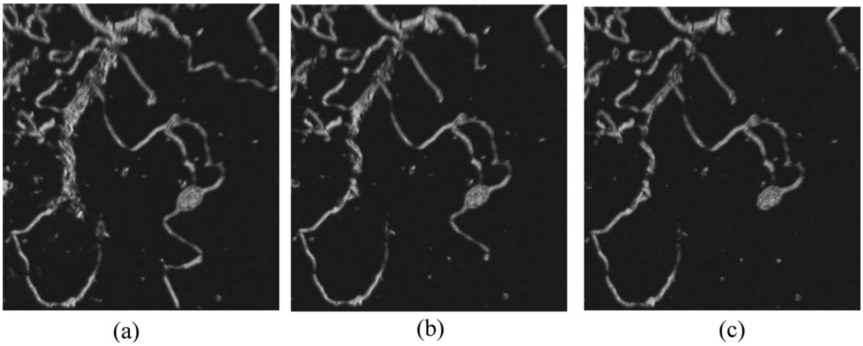
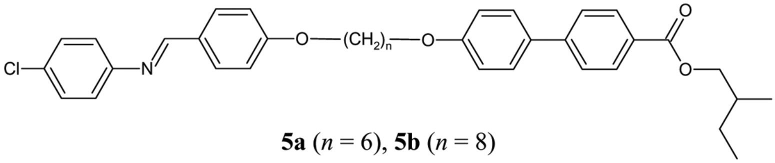


FIGURE 5 The filaments observed in the homeotropic region of N phase (compound **4f**) which initially form (left) upon cooling and gradually transform to compact domain (right).

3.1.3. *Comparison Studies Between Title Compounds and DL-α-(4-Benzylidene- Chloroaniline-4′-Oxy)-ω-[2-Methylbutyl-4′-(4″-Phenyl)benzoateoxy]alkanes*

In order to observe the changes in mesomorphic properties as the result of replacing one of the two mesogenic cores with a different core whilst another remains the same, comparison is made between the properties of the present dimers and those of the previously synthesized racemic α-(4-benzylidenechloroaniline-4′-oxy)-ω-[2-methylbutyl-4′-(4″-phenyl)benzoateoxy]alkanes [15]. These dimers are analogous with the present thiophene-based dimers in terms of 4-benzylidenechloroaniline mesogenic group. To ensure that the comparison is relevant, only compounds **4b** and **4d** from this series are chosen since the dimers mentioned above only incorporate spacers with n=6 or n=8. The general molecular structure of the reported dimers and respective phase transitions are shown below, where the dimers with the spacers made up by hexyl and octyl groups are labelled as **5a** and **5b**, respectively.



5a (n = 6), **5b** (n = 8)

5a Cr 109.8 (SmA 108.8) N 165.3 I

5b Cr 100.5 N 134.0 I

Comparison in terms of liquid crystalline properties between **5a** and **5b** and the present dimers with similar spacer length reveals that the differences are pronounced. For instance, the $\Delta S_{NI}/R$ values of **5a** and **5b** are 1.01 and 0.98, respectively. Whilst these values are within the typical range for nematic-isotropic transition of the dimers, the $\Delta S_{NI}/R$ values of **4b** and **4d**, as mentioned earlier, are several times lower than those of compounds **5a** and **5b**. Although the lower magnitude of $\Delta S_{NI}/R$ is often associated with the decreased shape anisotropy and the increased molecular biaxiality, it is premature to directly attribute the lower $\Delta S_{NI}/R$ of compounds **4b** and **4d** to the two possible factors. This is, in part, due to the fact that the melting points and mesophase thermal stability of compounds **4b** and **4d** are found to be significantly higher than those of **5a** and **5b**. By replacing the 2-methylbutyl-4′-(4″-phenyl)benzoateoxy group with 4-(thiophene-2-carboxyl)benzylideneaniline-4′-oxy group, the clearing point for compound **4b** for instance, is 80.5°C higher than that of compound **5a**.

By substituting a mesogenic group with another one, it is important to realize that a number of properties such as electronic effect, core length, rigidity and fractional residue volume are also altered at the same time. As a consequence, the differences in terms of transition temperatures between **4b, 4d** and **5a, 5b**, as stated earlier, cannot be directly justified based on the structure and chemical constitution alone, without taking into account the changes in other properties. Nevertheless, it is equally important to mention that the 4-(thiophene-2-carboxyl)benzylideneaniline group is larger in size and surface area, as compared to the biphenyl core, which results in stronger intermolecular attraction. At the same time, the presence of a thiophene ring at one of the terminals of compounds **4b** and **4d** also enhances the terminal attraction among molecules although it should not be assumed that the lateral attraction is also strengthened. This point is reflected appropriately as nematogenic properties rather than the smectogenic properties, predominate compounds **4a–4h** in this series.

3.2. Spectroscopic Results

From the FT-IR spectra of compounds **4a–4h**, the absorption band at 2943–2852 cm^{-1} is assigned to the C-H stretching of the respective methylene spacers. At lower frequency, the carbonyl group of the ester linkage between the thiophene ring and the benzylideneaniline fragment absorbs at 1739–1723 cm^{-1}. The azomethine groups give rise to a band with medium intensity at 1622–1605 cm^{-1}. The vibrations within these frequencies have also been reported for the liquid crystals derived from phthalic acid [16]. The strongest band is observed in the fingerprint region of 1252–1247 cm^{-1} which can be attributed to the presence of two ether ($O\text{-}CH_2$) groups for every dimeric structure. From the ^1H-NMR spectra, the peaks, multiplicities and respective chemical shifts are assignable to the protons of **4a–4h**. The following description is based on the ^1H-NMR spectrum of compound **4d**. At high-field, the twelve methylene protons of the C_8H_{16} spacer give rise to two sets of multiplets at δ=1.44–1.88 ppm.

A triplet at δ=4.07 ppm assignable to four methoxy protons, on the other hand, is similar to the absorption reported for 5-octylpyrimidine-2-yl oligomers [17]. Although the overall structure is non-symmetric due to two different mesogenic groups, the appearance of only one triplet owing to the two pairs of methoxy protons indicates the presence of symmetry in the flexible spacer. The appearance of six doublets, three double of doublets and one multiplet at δ=7.00–8.00 ppm can be attributed to sixteen aromatic protons and three thiophene protons. At low-field, two singlets observed at δ=8.37 and 8.41 ppm can be assigned to the azomethine protons of 4-benzylidenechloroaniline and 4-(thiophene-2-carboxyl)benzylideneaniline moieties, respectively.

4. CONCLUSIONS

Series of non-symmetric liquid crystal dimers, α-(4-benzylidenechloroaniline-4′-oxy)-ω-[4-(thiophene-2-carboxyl)benzylideneaniline-4′-oxy]-alkanes has been synthesized and characterized. The title compounds varying in terms of flexible methylene spacers (C_5H_{10} to $C_{12}H_{24}$) exhibit enantiotropic N phase with relatively high thermal stability (>187.0°C). The nematic-isotropic entropy changes of the eight homologues are considerably lower than those of the previously reported dimers. Under the polarized light, the N phase is identified based on its characteristic marble and schlieren texture as well as the flashes upon mechanical shearing. The nematogenic properties of the title compounds have been attributed to the presence of a thiophene ring at one of the terminals which induces predominant terminal intermolecular attraction rather than lateral attraction.

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