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Mesogenic Schiff's base ether with dimethylamino end group

Sie-Tiong Ha^{a*}, Lay-Khoon Ong^a, Joanna Pik-Wan Wong^{a†}, Guan-Yeow Yeap^b,
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A series of Schiff base ethers comprising a dimethylamino group at one terminal position and an even number of carbons at the other along the molecular axis was studied. The dimethylamino unit, acting as a charge-transfer donor in the formation of conjugative interactions, contributes to the molecule's polarizability and in turn affecting its intermolecular interactions, leading to the formation of less-ordered mesophase. The mesomorphic properties were studied using polarizing optical microscopy and differential scanning calorimetry. Whilst the *n*-butyloxy to *n*-hexadecyloxy derivatives exhibited nematic phase, the *n*-ethyloxy, *n*-propyloxy and *n*-octadecyloxy derivatives were not mesogenic. Their phase transitions during heating and cooling run were presented. The title compounds were compared with other structurally related series to establish their chemical structure–mesomorphic property relationships.

Keywords: Schiff base; *p*-*n*-(dimethylamino)benzylidene-*p*-alkyloxyanilines; nematic; structure–property relationships

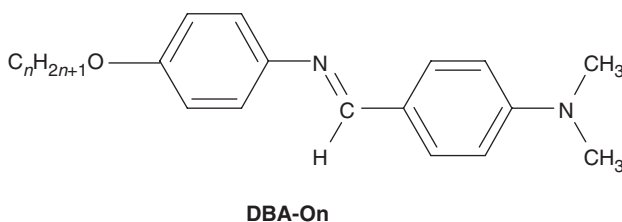
1. Introduction

The discovery of 4-methoxybenzylidene-4'-butylaniline (MBBA) and its application in displays owing to its existence in nematic phase at room temperature sparked a renewed interest in liquid crystals and prompted research in establishing structure–property relationships [1]. These relationships are elemental in selecting molecular modifications for the synthesis of mesogens with desirable properties for future applications [2].

Intermolecular interactions play a major role in generating the parallel molecular arrangement which gives rise to the liquid crystalline phase. In charge-transfer (CT) liquid crystals, the electron donor–acceptor interactions enhance the orientational cohesive forces between molecules, thus producing sufficient order in molecular arrangement for

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Where $n = 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18$

Figure 1. Molecular structure of *p*-*n*-(dimethylamino)benzylidene-*p*-alkyloxyanilines.

the generation of a mesophase [3–7]. Thus, the synthesis of electron-donor and -acceptor molecules is a prerequisite for constructing mesogenic CT complexes [8].

In the present study, we report the liquid crystalline properties of a homologous series of Schiff bases comprising a dimethylamino donor unit. The general structure of the members of this homologous series is depicted in Figure 1 and referred to as **DBA-On** (where $n = 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18$) in which n denotes the number of carbons of the terminal alkoxy group.

In addition, they were compared to structurally related compounds to establish the chemical structure–mesomorphic property relationships of thermotropic liquid crystals containing a dimethylamino group. These compounds may also serve as mesogenic CT donors for binary systems with electron acceptor molecules in future studies.

2. Experimental

4-Aminophenol, 1-bromoalkanes, 4-(dimethylamino)benzaldehyde, potassium hydroxide and potassium iodide were obtained commercially. 4-Dimethylaminobenzaldehyde was coupled with 4-aminophenol by heating under reflux in ethanol for about 3 h. The Schiff base intermediate was subsequently subjected to Williamson etherification with the suitable 1-bromoalkanes in the presence of potassium hydroxide and potassium iodide. The crude products were purified by repeated crystallisation from ethanol. The purity of the compounds was checked by thin layer chromatography and further confirmed by elemental analysis using Perkin Elmer 2400 LS Series CHNS/O analyzer. The structures of the products were further ascertained by means of IR (Figure 2), NMR (Figure 3) and EI-MS spectroscopic techniques. IR spectra were recorded using a Perkin-Elmer System 2000 FT-IR Spectrometer via KBr disc procedure. ^1H NMR (300 MHz) spectra were recorded in CDCl_3 using a Bruker Avance 300 MHz Spectrometer with TMS as the internal standard. EI-MS (70 eV) were measured with a Mass Spectrometer Finnigan MAT95XL-T at a source temperature of 200°C. The prominent molecular ion peak at m/z 408 in the mass spectrum of **DBA-O12** (Figure 4), establishing a molecular formula of $\text{C}_{27}\text{H}_{40}\text{N}_2\text{O}$, which supports the proposed structure. The analytical data, IR and ^1H NMR spectral data for the representative compounds, **DBA-On** (where $n = 8, 10, 14, 16, 18$) are summarized as follows.

DBA-O8: IR (KBr) ν_{max} cm^{-1} : 2852–2950 (C–H aliphatic); 1611 (C=N); 1592, 1502 (C=C aromatic). ^1H NMR (300 MHz, CDCl_3): δ /ppm 0.91 (t, 3H, $J = 6.6$ Hz, CH_3), 1.26–1.48 (m, 10H, $\text{CH}_3\text{-(CH}_2\text{)}_5\text{-CH}_2\text{-CH}_2\text{-O-}$), 1.81 (qt, 2H, $J = 6.9$ Hz, $\text{-CH}_2\text{-CH}_2\text{-O-}$), 3.07

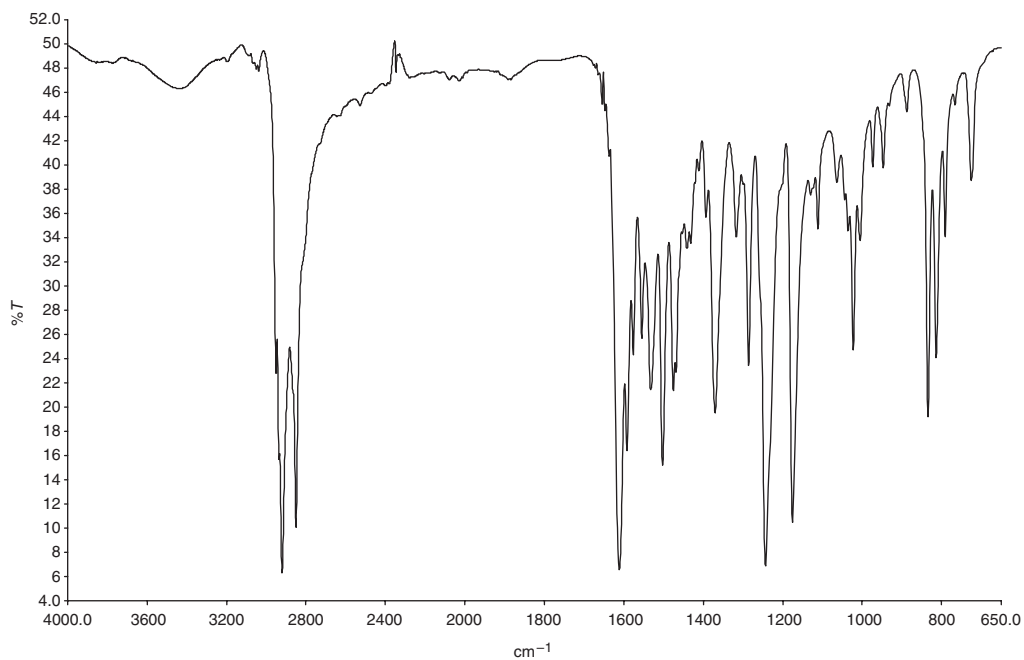


Figure 2. FTIR spectrum of **DBA-O12**.

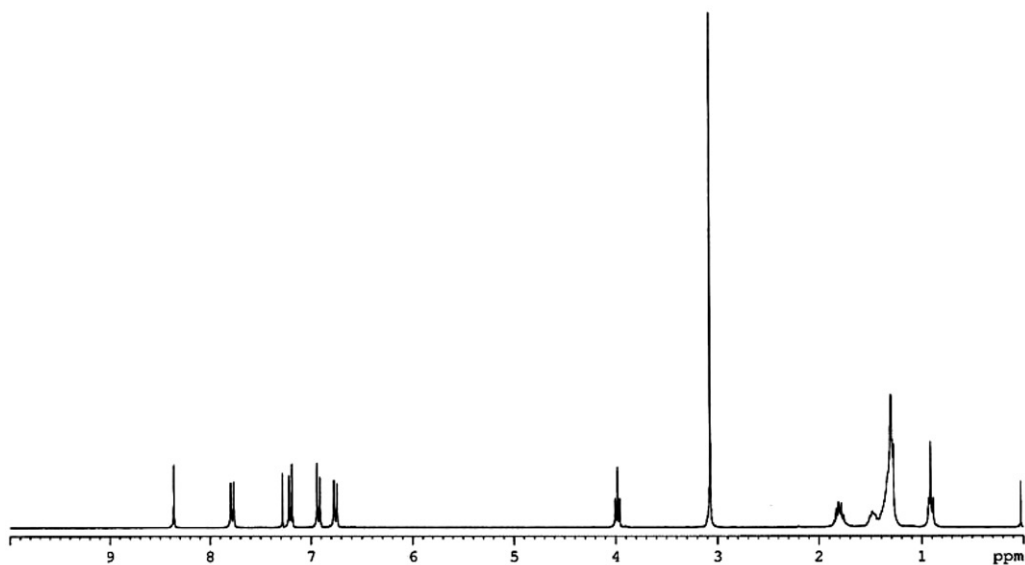


Figure 3. ^1H NMR spectrum of **DBA-O10**.

{s, 6H, $2 \times \text{N}(\text{CH}_3)_2$ }, 3.98 (t, 2H, $J = 6.6$ Hz, $-\text{CH}_2-\text{O}-$), 6.74 (d, 2H, $J = 8.9$ Hz, Ar-H), 6.91 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.19 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.76 (d, 2H, $J = 8.9$ Hz, Ar-H), 8.36 (s, 1H, CH=N). Elemental analysis: Calculated for $\text{C}_{23}\text{H}_{32}\text{N}_2\text{O}$: C, 78.36%, H, 9.15%, N, 7.95%; Found: C, 78.45%, H, 9.18%, N, 7.87%.

DBA-O10: IR (KBr) ν_{\max} cm^{-1} : 2852–2950 (C–H aliphatic); 1610 (C=N); 1591, 1502 (C=C aromatic). ^1H NMR (300 MHz, CDCl_3): δ/ppm 0.91 (t, 3H, $J=6.7$ Hz, CH_3), 1.28–1.48 (m, 14H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.80 (qt, 2H, $J=7.0$ Hz, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 3.07 {s, 6H, $2 \times \text{N}(\text{CH}_3)_2$ }, 3.98 (t, 2H, $J=6.6$ Hz, $-\text{CH}_2-\text{O}-$), 6.73 (d, 2H, $J=8.9$ Hz, Ar–H), 6.91 (d, 2H, $J=8.9$ Hz, Ar–H), 7.19 (d, 2H, $J=8.9$ Hz, Ar–H), 7.76 (d, 2H, $J=8.9$ Hz, Ar–H), 8.36 (s, 1H, CH=N). Elemental analysis: Calculated for $\text{C}_{25}\text{H}_{36}\text{N}_2\text{O}$: C, 78.90%, H, 9.53%, N, 7.36%; Found: C, 78.98%, H, 9.60%, N, 7.29%.

DBA-O14: IR (KBr) ν_{\max} cm^{-1} : 2850–2951 (C–H aliphatic); 1611 (C=N); 1591, 1502 (C=C aromatic). ^1H NMR (300 MHz, CDCl_3): δ/ppm 0.90 (t, 3H, $J=6.7$ Hz, CH_3), 1.28–1.47 (m, 22H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.80 (qt, 2H, $J=7.0$ Hz, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 3.07 {s, 6H, $2 \times \text{N}(\text{CH}_3)_2$ }, 3.98 (t, 2H, $J=6.5$ Hz, $-\text{CH}_2-\text{O}-$), 6.74 (d, 2H, $J=8.8$ Hz, Ar–H), 6.91 (d, 2H, $J=8.6$ Hz, Ar–H), 7.19 (d, 2H, $J=8.6$ Hz, Ar–H), 7.76 (d, 2H, $J=8.7$ Hz, Ar–H), 8.36 (s, 1H, CH=N). Elemental analysis: Calculated for $\text{C}_{29}\text{H}_{44}\text{N}_2\text{O}$: C, 79.76%, H, 10.16%, N, 6.42%; Found: C, 79.85%, H, 10.21%, N, 6.33%.

DBA-O16: IR (KBr) ν_{\max} cm^{-1} : 2850–2948 (C–H aliphatic); 1611 (C=N); 1592, 1502 (C=C aromatic). ^1H NMR (300 MHz, CDCl_3): δ/ppm 0.89 (t, 3H, $J=6.6$ Hz, CH_3), 1.27–1.47 (m, 26H, $\text{CH}_3-(\text{CH}_2)_{13}-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.80 (qt, 2H, $J=7.0$ Hz, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 3.06 {s, 6H, $2 \times \text{N}(\text{CH}_3)_2$ }, 3.99 (t, 2H, $J=6.6$ Hz, $-\text{CH}_2-\text{O}-$), 6.73 (d, 2H, $J=8.8$ Hz, Ar–H), 6.90 (d, 2H, $J=8.8$ Hz, Ar–H), 7.18 (d, 2H, $J=8.8$ Hz, Ar–H), 7.76 (d, 2H, $J=8.8$ Hz, Ar–H), 8.36 (s, 1H, CH=N). Elemental analysis: Calculated for $\text{C}_{31}\text{H}_{48}\text{N}_2\text{O}$: C, 80.12%, H, 10.41%, N, 6.03%; Found: C, 80.20%, H, 10.49%, N, 5.92%.

DBA-O18: IR (KBr) ν_{\max} cm^{-1} : 2849–2945 (C–H aliphatic); 1612 (C=N); 1591, 1502 (C=C aromatic). ^1H NMR (300 MHz, CDCl_3): δ/ppm 0.90 (t, 3H, $J=6.6$ Hz, CH_3), 1.27–1.48 (m, 30H, $\text{CH}_3-(\text{CH}_2)_{15}-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.80 (qt, 2H, $J=7.0$ Hz, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 3.07 {s, 6H, $2 \times \text{N}(\text{CH}_3)_2$ }, 3.98 (t, 2H, $J=6.6$ Hz, $-\text{CH}_2-\text{O}-$), 6.74 (d, 2H, $J=8.9$ Hz, Ar–H), 6.91 (d, 2H, $J=8.8$ Hz, Ar–H), 7.19 (d, 2H, $J=8.8$ Hz, Ar–H), 7.76 (d, 2H,

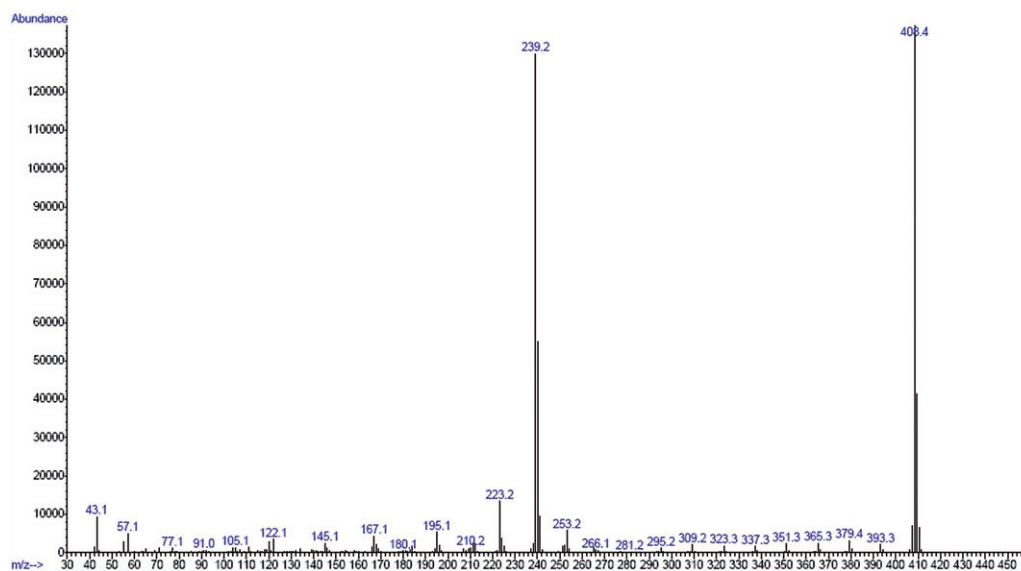


Figure 4. EI-MS spectrum of **DBA-O12** showing $[\text{M}]^+$ at m/z 408.

$J = 8.9$ Hz, Ar–H), 8.36 (s, 1H, CH=N). Elemental analysis: Calculated for $C_{33}H_{52}N_2O$: C, 80.43%, H, 10.64%, N, 5.68%; Found: C, 80.52%, H, 10.69%, N, 5.59%.

The liquid crystalline textures and phase transition temperatures were determined by means of a *Carl Zeiss* polarizing microscope equipped with a *Linkam LTS360* hotstage and a *TMS 94* temperature regulator. Phase identification was made by comparing the observed textures with those reported in the literature [9,10]. Transition temperatures were measured using a *Mettler Toledo DSC 823* differential scanning calorimeter. All measurements were conducted under a flow of nitrogen gas to prevent decomposition of the sample.

3. Results and discussion

3.1. Liquid crystallinity of DBA-On

Whilst the phase transition temperatures and enthalpy values are summarized in Table 1, the representative DSC thermogram of **DBA-O9** is shown in Figure 5. As observed

Table 1. Transition temperatures and associated enthalpy changes of **DBA-On** during heating and cooling cycles.

Compound	Transition temperatures, °C (ΔH , kJmol ⁻¹)
DBA-O2	Cr 146.7(27.9) I <i>I 115.7(27.5) Cr</i>
DBA-O3	Cr 121.3(27.1) I <i>I 99.1(27.3) Cr</i>
DBA-O4	Cr 112.9(36.6) I <i>I 96.4(2.1) N 86.8(32.4) Cr</i>
DBA-O5	Cr 93.5(29.1) I <i>I 82.8(1.3) N 72.0(24.8) Cr</i>
DBA-O6	Cr 111.3(34.1) I <i>I 85.7(0.58) N 80.8(32.7) Cr</i>
DBA-O7	Cr 104.3(31.1) I <i>I 83.2(1.1) N 69.8(27.1) Cr</i>
DBA-O8	Cr ₁ 80.4(6.5) Cr ₂ 93.0(26.5) I <i>I 91.2(1.2) N 82.6(24.3) Cr</i>
DBA-O9	Cr ₁ 66.7(7.8) Cr ₂ 87.4(29.7) N 90.3(1.3) I <i>I 89.6(1.3) N 81.3(28.9) Cr</i>
DBA-O10	Cr 89.3(50.4) I <i>I 81.5(0.12) N 79.2(47.9) Cr</i>
DBA-O12	Cr 94.5(41.8) I <i>I 88.6(1.03) N 85.7(39.8) Cr</i>
DBA-O14	Cr 98.7(62.2) I <i>I 94.8^a N 90.0(61.1) Cr</i>
DBA-O16	Cr 101.2(63.7) I <i>I 92.5^a N 91.2(62.2) Cr</i>
DBA-O18	Cr 92.8(46.9) I <i>I 83.1(40.2) Cr</i>

Notes: The values in *italics* were taken during cooling cycle. Cr=Crystal, N=Nematic, I=Isotropic liquid.

^aPOM data was used. The I–N transition was untraceable under DSC studies although this transition was observed under microscope studies.

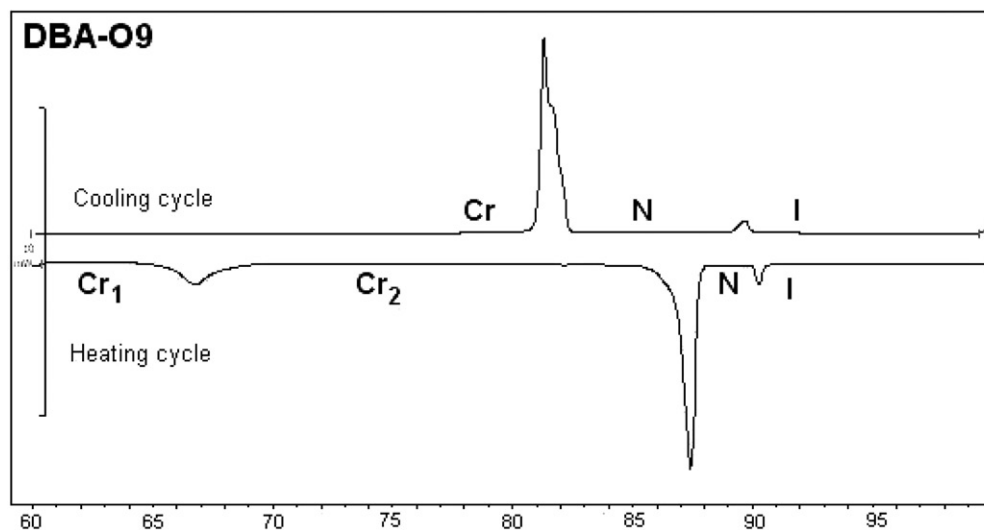


Figure 5. DSC thermogram of **DBA-O9**.

from Table 1, in contrast to all the compounds exhibiting an endotherm corresponding to the direct melting of the crystal phase to the isotropic liquid phase during the heating cycle, **DBA-O8** and **DBA-O9** exhibited two and three endotherms, respectively. The first endotherm in **DBA-O8** was corresponded to the crystalline solid subphase transition (Cr_1 – Cr_2) at 80.4°C as reported for benzylideneaniline derivatives [11–14] while the second endotherm at 93.0°C was due to the phase transition of the Cr_2 phase to the isotropic liquid phase. Similar crystalline solid subphases (Cr_1 , Cr_2) were also observed for **DBA-O9** (Figure 5) and the third endotherm appeared at 90.3°C was attributed to the phase transition of nematic to isotropic.

Upon cooling, all the compounds except **DBA-O2**, **DBA-O3** and **DBA-O18** exhibited exotherms characteristic of the isotropic–mesophase and mesophase–crystal transitions, indicating monotropic properties. The melting points of the monotropic mesogens were always equal to or higher than the clearing points, hence causing them to exhibit supercooling properties [15]. Under the polarizing microscope, the mesophases were identified by the nematic droplets, *Schlieren* and marble-like textures. Brownian flashes, characteristic of the nematic phase were also observed just before recrystallisation [16]. As a representative illustration, the optical photomicrograph of **DBA-O9** is depicted in Figure 6.

The appearance of the monotropic nematic phase was found to conform with that observed for the analogous *p*-*n*-hexyloxybenzylidene-*p*-(dimethylamino)aniline, **6OBDA** [6]. The transition temperature of **DBA-O6** (Cr 111.3 I) was observed to be higher than that of **6OBDA** (Cr 106.4 I), presumably due to the reversal of imine linkage. The similar effect of the imine linking pattern was also reported for 4-*n*-alkyloxybenzoic acid 4-[(4-dimethylaminobenzylidene)amino]phenyl esters and 4-*n*-alkyloxybenzoic acid 4-[(4-dimethylaminophenylimino)methyl]phenyl esters [8].

A plot of the melting temperatures against the number of carbons in the alkoxy chain is shown in Figure 7. Based on the plot, it can be deduced that the mesophase behaviours were greatly influenced by the length of the terminal chain. The melting temperatures exhibited a descending trend as the length of the terminal alkoxy chain

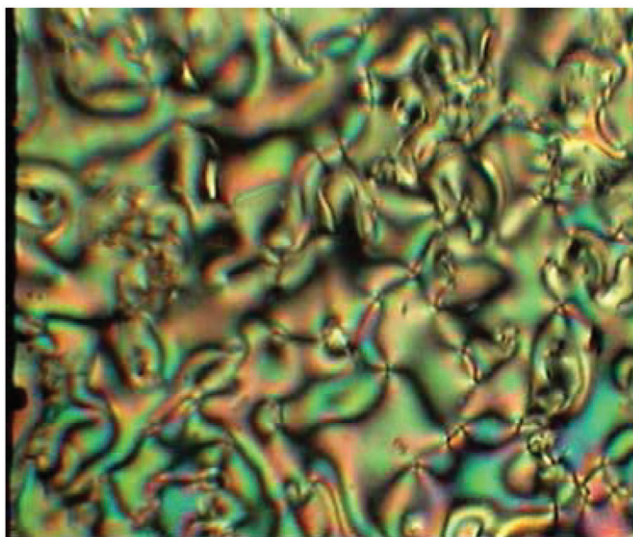


Figure 6. Optical photomicrograph of **DBA-O9** exhibiting nematic phase at 88.6°C during cooling run.

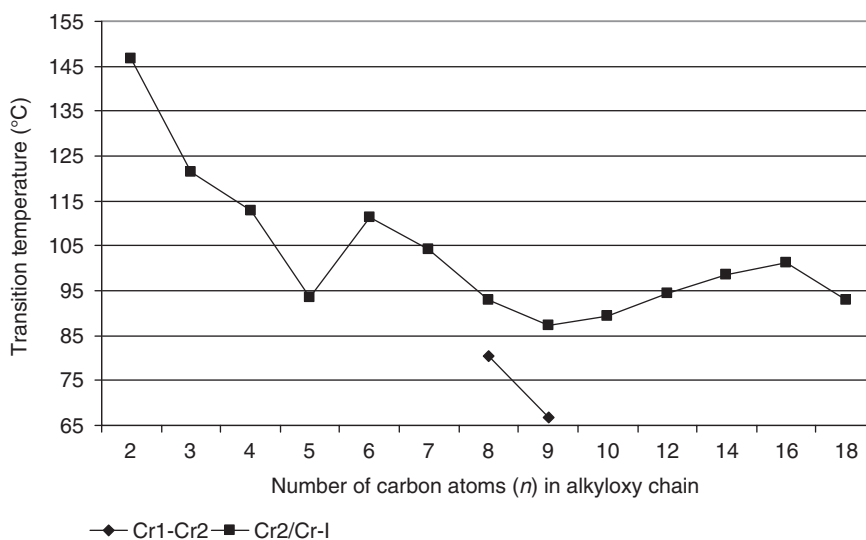


Figure 7. Plot of transition temperatures vs. the number of carbons (n) in the alkoxy chain of **DBA-On** during heating cycle.

of the derivatives increased from C2 to C10 except for C5 which showed a strong fall off. However, the lengthening of the carbon chain from the n -decyloxy to the n -hexadecyloxy derivatives revealed an ascending trend in the melting temperatures. This phenomenon can be attributed to the increase in the intermolecular Van der Waals attraction as the length of the alkoxy chain increased [17]. However, a decrease in the melting point was observed when proceeding from the C16 derivative to the

derivative with the longest terminal chain, C18, arising from the dilution of its core system [17].

3.2. Structure–liquid crystal property relationships

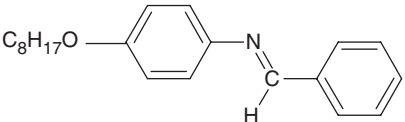
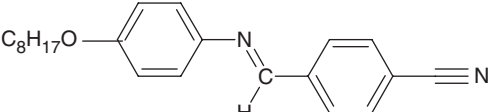
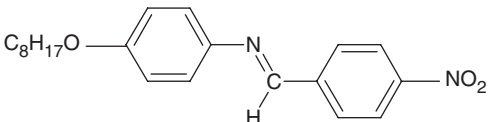
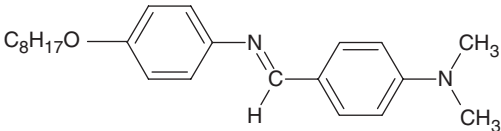
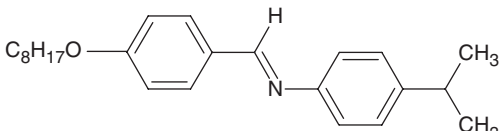
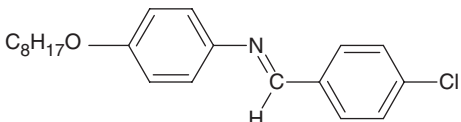
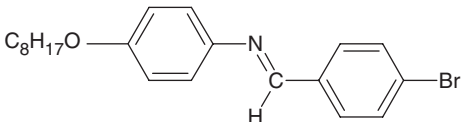
There is a close relationship between the mesomorphic properties and the molecular structure of organic compounds. Comparison of the compounds in the present study with the properties of structurally related systems has become a common practice in many studies in order to establish chemical structure–property relationships of the system involved [18–24]. Terminal groups are one of the important features in causing compounds to exhibit liquid crystal properties. There are different terminal substituents; polar substituents, medium polar substituents, alkyl or alkoxy chains. In our previous studies, we investigated the influence of terminal substituents such as *p*-H, *p*-CH₃, *p*-C₂H₅, *p*-OCH₃, *p*-F, *p*-Cl, *p*-Br, *p*-SH, *p*-OH, *p*-NO₂ and *p*-CN of *o*-*n*-hydroxy-*p*-*n*-hexadecanoyloxybenzylidene-*p*-substituted-anilines on its mesomorphic properties [11,12]. In the present work, the influence of the dimethylamino group was compared to other terminal substituents. The compounds of interest and their liquid crystalline data are tabulated in Table 2 [8,25–27].

Table 2 indicates the tendency of liquid crystal formation being strongly enhanced in homologous compounds with terminal groups compared to the unsubstituted ones (**H-O8**). The polar dimethylamino group, acting as a CT donor in the formation of conjugative interactions, contributes to the molecule's polarizability and in turn affecting its intermolecular interactions, leading to the formation of the nematic phase in **DBA-O8**. This is consistent with the properties of other polar substituents such as cyano and nitro which stabilises the nematic phase in **CN-O8** and **NO-O8**. This is further supported by the destabilisation and loss of the nematic phase for moderately polar substituents like Cl and Br in **CL-O8** and **BR-O8**.

Generally, a lateral substituent introduced into a mesogen can cause considerable depression on its thermal stability [17]. The presence of two lateral methyl groups at the terminal position in **DBA-O8** and **IP-O8** depressed its thermal stabilities and therefore having lower transition temperatures than those compounds without lateral substituents (**CN-O8**, **CL-O8** and **BR-O8**). The higher electronegativity of N atom in **DBA-O8** led to a stronger terminal intermolecular interaction which favored the formation of nematic phase. Despite the broadening effect, the less electronegative carbon in isopropyl group still possess greater lateral interaction and thus preferred lamellar arrangements of smectic phase [2]. Thermal stability of **DBA-O8** was also greatly enhanced when compared to **IP-O8**. It is because the more polar N atom enhanced the molecular polarizability and finally increased the transition temperatures in **DBA-O8**. The observed structure–property relationships are in accordance with the properties shown by their three rings analogous compounds, **DBBA-O8** and **BIP-O8** whereby the dimethylamino compound exhibited purely nematic phase, while isopropyl compound exhibited both nematic and smectic phases. In addition, **DBBA-O8** also showed higher transition temperatures than **BIP-O8**.

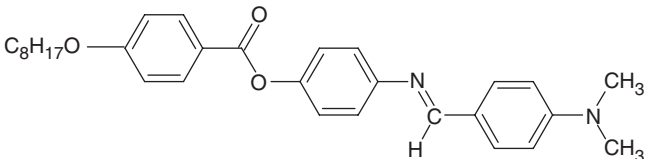
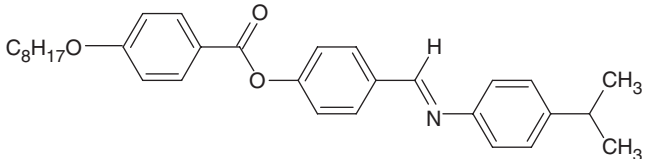
With reference to Table 2, **DBBA-O8** possesses a higher phase stability compared to **DBA-O8**. The molecular length of **DBBA-O8** is longer than **DBA-O8** due to the additional aromatic ring and the central ester linkage. Gray [17] explained the increase in the length of the molecule and the resulting enhanced anisotropy of the polarizability, increases the intermolecular cohesive forces responsible for the higher nematic phase transition temperatures of **DBBA-O8**.

Table 2. Comparison of liquid crystalline properties of **DBA-O8** with structurally related compounds.

Compound	Structure and phase transition (°C)	Ref.
H-O8	 <p>Cr 69.7 I</p>	[25]
CN-O8	 <p>Cr₁ 66.9 Cr₂ 74.0 SmA 83.2 N 109.1 I</p>	[25]
NO-O8	 <p>Cr 63.0 SmA 74.5 N 84.0 I</p>	[26]
DBA-O8	 <p>Cr₁ 80.4 Cr₂ 93.0 N (91.2)^a I</p>	[Present studies]
IP-O8	 <p>Cr 56.5 SmA 59.0 I</p>	[27]
CL-O8	 <p>Cr 90.3 SmB 97.4 SmA 108.4 I</p>	[25]
Br-O8	 <p>Cr 92.5 SmB 111.8 SmA 115.2 I</p>	[25]

(Continued)

Table 2. Continued.

Compound	Structure and phase transition (°C)	Ref.
DBBA-O8	 <p>Cr 150.7 N 223.0 I</p>	[8]
BIP-O8	 <p>Cr 114.0 SmC 126.0 N 176.0 I</p>	[27]

Note: ^aIndicates monotropic phase.

4. Conclusion

In this article, we have reported the mesomorphic properties of homologues series of *p-n*-(dimethylamino)benzylidene-*p*-alkyloxyanilines. Whilst the *n*-butyloxy to *n*-hexadecyloxy derivatives are nematogens, the *n*-ethyloxy, *n*-propyloxy and *n*-octadecyloxy derivatives are non-mesomorphic. For the effects of terminal polar substituents, stabilisation of the N phase by strong polar substituents and of the SmA phase by moderately polar substituents, were confirmed via comparison with the related systems. The presence of the dimethylamino group renders this system to be suitable components for building CT-based liquid crystals with an appropriate choice of acceptor molecules.

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