Malaysian Journal of Chemistry, 2019, Vol. 21(3), 73-85

Synthesis, Characterization and Determination of Mesophase Transition of Azo-azomethine Derivatives with Different Terminal Chain Lengths

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Six new azo-azomethine derivatives were successfully synthesized and characterized. These derivatives, **5a-f** were differentiated by a variety of different terminal lengths such as pentyl, heptyl, nonyl and dodecyl chains. The experiment started with the reaction of *p*-nitroaniline with phenol, forming 4-(4-nitrophenylazo)-phenol, **1**. Alkylation of **1** with pentyl, nonyl and dodecylbromide gave (4-nitrophenyl)-4(4-alkoxyphenyl)-diazene, **2a-c**. These nitro intermediates, **2a-c** were reduced to afford intermediates **3a-c**, 4-(4-alkoxy-phenylazo)-phenylamine. Alkylation reaction of *p*-hydroxybenzaldehyde with heptyl and dodecylbromide gave intermediates **4a-b**, 4-alkoxybenzaldehyde. Cross condensation reactions of **3a-c** and **4a-b** gave six compounds, **5a-f**, with azo and Schiff base linking units but with different chain lengths at both terminal positions. All the compounds were characterized using Fourier Transform Infrared spectroscopy (FT-IR), ^{1}H and ^{13}C Nuclear Magnetic Resonance spectroscopy (NMR) and CHN elemental analysis. The mesophase transitions of these compounds were determined using Polarized Optical Microscope (POM). It was observed that compounds **5b**, **5c**, **5d**, **5e** and **5f** were mesogenic while compound **5a** was not mesogenic. The transition temperature of the compounds having mesophase behaviour were further confirmed using DSC. All the DSC thermograms showed good agreement with the phase transition observed under POM. The study on the structure-properties relationship was conducted in order to determine the effect of the terminal group, length of the chains and linking units to the mesophase behaviour of the compounds.

Key words: Azo, azomethine, alkylation, condensation, mesophase

Received: August 2019; Accepted: November 2019

The study of liquid crystals (LCs) began in 1888 when an Austrian botanist named Friedrich Reinitzer observed cholesteryl benzoate with two distinct melting points. When Reinitzer increased the temperature of this solid sample, the crystal changed into a hazy liquid before it was transformed into a clear liquid [1]. *Liquid crystal* is a matter that has properties between solid crystal and the conventional isotropic liquid. It may flow like a liquid but its molecules may be oriented in a crystal-like lattice [2-3].

LCs of organic compounds are divided into two categories, which are thermotropic and lyotropic LCs. The thermotropic LCs show mesophase changes as the temperature changes while the lyotropic LCs are temperature and concentration dependent. The thermotropic LCs can be rod-like (calamatic LCs) or disk-like (discotic LCs) molecules while the lyotropics LCs consist of amphiphilic molecules with hydrophilic group attached to hydrophobic group [4-6].

Calamitic or rod-like molecules have structures with rigid long axes, strong dipoles and easily polarizable substituents. The distinguishing characteristic of the liquid crystal state is the tendency of the molecules to point along a common axis (director). This is in contrast to molecules in the liquid phase, which have no intrinsic order, while in the solid state molecules are highly ordered and have little translational freedom [6]. Most liquid crystal compounds exhibit polymorphism (a condition where more than one phase is observed in the liquid crystal state). The term mesophase is used to describe the "subphases" of liquid crystal, which are formed by changing the amount of order in the sample. There are many types of liquid crystal phases, depending upon the amount of order in the material [7].

These mesophases have different molecular positions and exhibit one or two dimensional orders only to display some degree of fluidity. Molecules in nematic phase have no positional order but have orientational order, whereas molecules in smectic A are arranged in layers, with long axes perpendicular to the layers. In smectic C, molecules are aligned with their long axes tilted relative to the layers in which the molecules are stacked. Increased order means that the smectic state is more "solid-like" than the nematic [8, 9].

The structure of a common calamitic molecule consists of two or more aromatic rings which are connected to the side chain or a terminal group by linking units. The influence of different elements and the extended chemical subunits on the molecules allow the construction of the targeted liquid crystal compounds. The molecular shape and the terminal chain length are the key variables in designing new liquid crystal compounds with specific types of molecular organization in a particular range of temperature [10-12]. Linking units are normally structural units that connect one core to another, which maintain the linearity of the core while being compatible with the rest of the structure. A linking unit between ring systems is to increase the length of the molecules and to alter the polarizability and flexibility of the molecules [13]. Some examples of the side chains and terminal groups are alkyl, alkoxy, nitro, bromo and cyano groups, and examples of the common linking units are Schiff base, azo, or ester [14].

In the search for improved properties, not many liquid crystal molecules with azo and Schiff base linking units have been reported. Compounds with azo linkage provide linearity to the structure and it is interesting to note that the rigid rod-like structure of the azo molecules allows them to behave as liquid crystal mesogens in many materials [15, 16]. Azo compounds are compounds bearing the functional group R–N=N–R′, in which R and R′ can be either aryl or alkyl. Azo compounds are thermally very stable and are attractive to be used in commercial applications. The azo molecules are used to induce the liquid crystal alignment [17-20]. In the development of photo-alignment technology, the liquid crystal side-chain polymer [21, 22] and photo-stable azo dye polymer [23] have been of great interest.

Schiff base, imine, or azomethine is a functional group with carbon double bond nitrogen, connected to an alkyl or aryl group but not to hydrogen atom. Schiff base has a general formula of $R_1R_2C=NR_3$ with R as a side chain [24]. Schiff base can be formed by condensation of an aldehyde with an amine. In general, Schiff base molecules provide a stepped core structure which can maintain the molecular linearity. This linearity will provide high stability which enables the mesophase formation [25]. Schiff base is very useful in liquid crystal research due to low temperature of phase transitions [26].

In this work, the synthesis of thermotropic liquid crystals and their properties were our main concern. The rod-like intermediate with an azo group underwent condensation reaction with 4-alkoxy-benzaldehyde to give calamitic molecules, whereby their mesogenicity would be determined. The correlation between the molecular structure and the mesophase behaviour is the most important aspect in liquid crystal field. In addition, there are no previous works reported on azo-azomethine derivatives with different terminal chain lengths. The interest of this research was to gain a better insight of the structure-properties relationship of these types of compounds. This new series of derivatives adds into the liquid crystal databases.

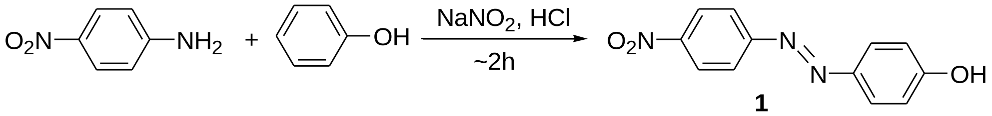
MATERIALS AND METHODS

Chemicals

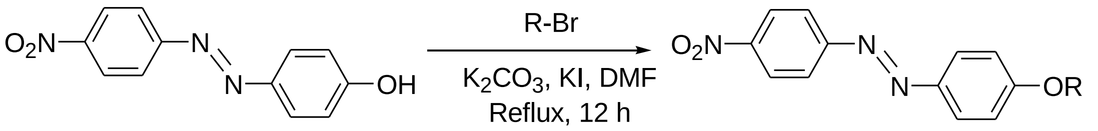
The chemicals used were 1-bromoheptane, 1-bromononane, 1-bromododecane, 4-hydroxybenzaldehyde, 4-nitroaniline, phenol, potassium iodide, potassium carbonate, sodium nitrate, sodium sulphide hydrate, dimethylformamide, dichloromethane, methanol, ethyl acetate, hexane, ethanol, glacial acetic acid, deuterated dimethylsulphoxide (DMSO-d_6) and deuterated chloroform ($CDCl_3$). All chemicals were used as received without further purification and were purchased from companies such as Sigma-Aldrich, Systerm and Merck.

Experimental

Intermediate **1** was synthesized via diazotization of 4-nitroaniline and phenol (Scheme 1). Alkylation of **1** with pentyl, nonyl and dodecylbromide gave intermediates **2a-c**, (4-nitrophenyl)-4(4-alkoxy-phenyl)-diazene (Scheme 2). These nitro intermediates, **2a-c** were reduced to afford intermediates **3a-c**, 4-(4-alkoxy-phenylazo)-phenylamine (Scheme 3). Alkylation reaction of 4-hydroxybenzaldehyde with heptyl and dodecylbromide gave intermediates **4a-b**, 4-alkoxybenzaldehyde (Scheme 4). Cross condensation reactions of **3a-c** and **4a-b** gave four compounds, **5a-f**, with an azo and Schiff base linking units but with different chain lengths at both terminal positions (Scheme 5).

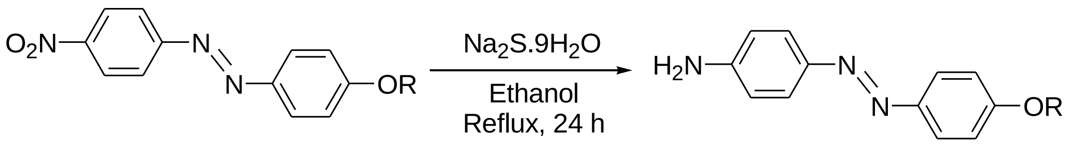


Scheme 1. Diazotization of 4-nitroaniline with phenol [27].



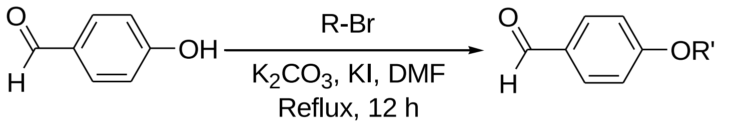
R= C_5H_{11} (**2a**); C_9H_{19} (**2b**); $C_{12}H_{25}$ (**2c**)

Scheme 2. Alkylation reaction of intermediates **2a-c** [28].



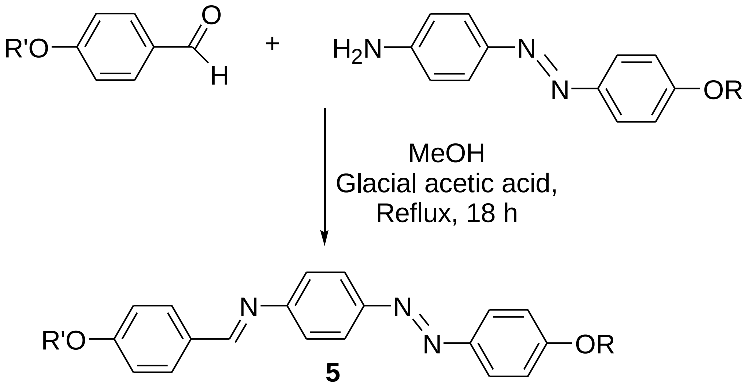
R= C_5H_{11} (**3a**); C_9H_{19} (**3b**); $C_{12}H_{25}$ (**3c**)

Scheme 3. Formation of intermediates **3a-c** [29].



R' = C_7H_{15} (**4a**); $C_{12}H_{25}$(**4b**)

Scheme 4. Alkylation reaction of intermediates **4a** and **4b** [28].



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	a	**b**	**c**	**d**	**e**	**f**
R'	C_7H_{15}	$C_{12}H_{25}$	C_7H_{15}	$C_{12}H_{25}$	C_7H_{15}	$C_{12}H_{25}$
R	C_5H_{11}	C_5H_{11}	C_9H_{19}	C_9H_{19}	$C_{12}H_{25}$	$C_{12}H_{25}$

Scheme 5. Condensation reaction of compounds **5a-f** [30].

(**1**) Synthesis of 4-(4-nitro-phenylazo)-phenol
4-nitroaniline (6.00 g, 0.022 mol) in 7 ml of water was mixed with 6.5 ml of hydrochloric acid and 25.0 ml of methanol. The solution was cooled at 0-5 °C. Sodium nitrate (1.49 g, 0.022 mol) in water was added dropwise into the solution, which was stirred in the ice bath for 30 minutes to give solution A. Sodium acetate (20.00 g, 0.22 mol) was dissolved in 100 ml of water to give sodium acetate trihydrate. Phenol (2.10 g, 0.022 mol) was added in 28 ml of sodium acetate trihydrate to give solution B. Solutions A and B were mixed and stirred for 2 hours at room temperature. The reaction progress was monitored using TLC. The precipitate formed was filtered, dried and recrystallized. The precipitate was recrystallized from methanol to yield an orange powder. Yield: 4.93 g (92.15%), brown powder, mp: 197.1-199.5°C. IR (cm^{-1}): 3370 (O-H stretching), 1507 (C=C aromatic), 844 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm: 10.66 (s, 1H, OH), 8.38 (d, J=10.0 Hz, 2H, Ar-H), 7.98 (d, J=10.0 Hz, 2H, Ar-H), 7.87 (d, J=10.0 Hz, 2H, Ar-H), 6.99 (d, J=10.0 Hz, 2H, Ar-H). ^{13}C-NMR (125 MHz, DMSO-d_6) δ, ppm: 162.37 (Ar-C), 155.55 (Ar-C), 147.73 (Ar-C), 145.37 (Ar-C), 125.73 (Ar-C), 124.95 (Ar-C), 122.93 (Ar-C), 116.21 (Ar-C).CHN elemental analysis: Calculated for $C_{12}H_9N_3O_3$: C: 59.26%, H: 3.73%, N: 17.28%. Found: C: 59.24%, H: 3.70%, N: 17.25%.

(**2a**) Synthesis of (4-nitrophenyl)-(4-pentyloxy-phenyl)-diazene
4-(4-Nitrophenylazo)-phenol (4.00 g, 0.016 mol) and 1-bromopentane (2.42 g, 0.016 mol) were dissolved in 10 ml of dimethylformamide (DMF) separately and mixed. Potassium carbonate (4.55 g, 0.033 mol) and potassium iodide (0.28 g, 0.0017 mol) were added into the mixture and was refluxed for 12 hours. The reaction progress was monitored using TLC. After 12 h, precipitate formed was filtered, dried and recrystallized. The precipitate was recrystallized from methanol to yield a dark-red powder. The same method was used to synthesise **2b-c**. Yield: 4.81 g (96.20%), brown powder, mp: 88.9-91.3°C. IR (cm^{-1}): 2943 (C_{sp3}-H stretching), 1601 (C=C aromatic), 841 (C-N stretching); ^{1}H-NMR (500 MHz, DMSO-d_6), δ (ppm): 8.34 (d, J=10 Hz, 2H, Ar-H), 7.95 (d, J=10 Hz, 2H, Ar-H), 7.24 (d, J=10.0 Hz, 2H, Ar-H), 7.01 (d, J=5 Hz, 2H, Ar-H), 4.05 (t, J=5 Hz, 2H, CH_2), 1.84-1.81 (m, 2H, CH_2), 1.45-1.38 (m, 4H, CH_2), 0.93 (t, J=5 Hz, 3H, CH_3). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (ppm): 163.19 (Ar-C), 156.31 (Ar-C), 148.44 (Ar-C), 147.03 (Ar-C), 125.82 (Ar-C), 124.97 (Ar-C), 124.89 (Ar-C), 114.97 (Ar-C), 68.75 (CH_2), 29.04 (CH_2), 28.36 (CH_2), 22.64 (CH_2), 14.19 (CH_3). CHN elemental analysis: Calculated for $C_{17}H_{19}N_3O_3$: C: 65.16%, H: 6.11%, N: 13.41%. Found: C: 65.11%, H: 6.12%, N: 13.38%.

(**2b**) (4-nitrophenyl)-(4-nonyloxyphenyl)-diazene.
Yield: 5.47 g (92.71%), brown powder, mp: 94.5-97.1°C. IR (cm^{-1}): 2921 (C_{sp3}-H stretching), 1601 (C=C aromatic), 836 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d_6), δ (ppm): 8.34 (d, J=2 Hz, 2H, Ar-H), 7.95 (d, J=10 Hz, 2H, Ar-H), 7.24 (d, J=10.0 Hz, 2H, Ar-H), 7.01 (d, J= 5 Hz, 2H, Ar-H), 4.04 (t, J=5 Hz, 2H, CH_2), 1.84-1.78 (m, 2H, CH_2), 1.48-1.45 (m, 2H, CH_2), 1.37-1.26 (m, 10H, CH_2), 0.87 (t, J=5 Hz, 3H, CH_3). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (ppm): 163.17 (Ar-C), 156.27 (Ar-C), 148.39 (Ar-C), 146.98 (Ar-C), 125.82 (Ar-C), 124.88 (Ar-C), 123.27 (Ar-C), 115.12 (Ar-C), 68.74 (CH_2), 32.07 (CH_2), 29.72 (CH_2), 29.52 (CH_2), 29.45 (CH_2), 29.42 (CH_2), 29.34 (CH_2), 26.19 (CH_2), 22.87 (CH_2), 14.30 (CH_3). CHN elemental analysis: Calculated for $C_{21}H_{27}N_3O_3$: C: 68.27%, H: 7.37%, N: 11.37%. Found: C: 68.19%, H: 7.35%, N: 11.34%.

(**2c**) (4-nitrophenyl)-(4-dodecyloxyphenyl)-diazene. Yield: 6.16 g (93.62%), brown powder, mp: 95.3-98.8°C. IR (cm^{-1}): 2848 and 2915 (Csp^3-H stretching), 1601 (C=C aromatic stretching), 1581 (N=N stretching), 1342 and 1519 (N-O stretching), 1142 (C-O stretching), 856 (aromatic C-H bending). ^{1}H-NMR (500 MHz, $CDCl_3$) δ, ppm: 8.34 (d, J=10.0 Hz, 2H, Ar-H), 7.96 (d, J=10.0 Hz, 2H, Ar-H), 7.24 (d, J=10.0 Hz, 2H, Ar-H), 7.01 (d, J=5.0 Hz, 2H, Ar-H), 4.04 (t, J=7.5 Hz, 2H, CH_2), 1.78-1.84 (m, 2H, CH_2), 1.43-1.49 (m, 2H, CH_2), 1.24-1.37 (m, 16H, CH_2), 0.86 (t, J=7.5 Hz, 3H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ, ppm: 163.17 (Ar-C), 156.26 (Ar-C), 148.39 (Ar-C), 146.99 (Ar-C), 125.80 (Ar-C), 124.85 (Ar-C), 123.25 (Ar-C), 115.12 (Ar-C), 68.74 (CH_2), 32.11 (CH_2), 29.85 (CH_2), 29.83 (CH_2), 29.78 (CH_2), 29.75 (CH_2), 29.56 (CH_2), 29.54 (CH_2), 29.33 (CH_2), 26.19 (CH_2), 22.88 (CH_2), 14.29 (CH_3). CHN elemental analysis: Calculated for $C_{24}H_{33}N_3O_3$: C: 70.04%, H: 8.08%, N: 10.21%; Found: C: 69.95%, H: 8.04%, N: 10.17%.

(**3a**) Synthesis of 4-(4-pentyloxy-phenylazo)-phenyl-amine
Compound **2a** (4.00 g, 0.012 mol) was dissolved in 30 ml of hot ethanol. Sodium sulfide nonahydrate (3.75 g, 0.048 mol) was dissolved in 5 ml of hot ethanol and 5 ml of distilled water. The solutions were mixed and refluxed for 24 hours. The reaction progress was monitored using TLC. The precipitate formed was filtered and washed with cold ethanol. The same method was used to synthesise **3b-c**. Yield: 2.92 g (91.25%), brown powder, mp: 117.4-121.6°C. IR (cm^{-1}): 3340 and 3435 (N-H stretching), 2935 (C_{sp3}-H stretching), 1601 (C=C aromatic), 833 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d_6), δ (ppm): 7.71 (d, J=10 Hz, 2H, Ar-H), 7.60 (d, J=10 Hz, 2H, Ar-H), 7.03 (d, J=10 Hz, 2H, Ar-H), 6.65 (d, J=10 Hz, 2H, Ar-H), 5.94 (s, 2H, NH_2), 4.02 (t, J= 5 Hz, 2H, CH_2), 1.76-1.70 (m, 2H, CH_2), 1.40-1.35 (m, 4H, CH_2), 0.89 (t, J=5 Hz, 3H, CH_3). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (ppm): 159.96 (Ar-C), 152.13 (Ar-C), 146.50 (Ar-C), 142.93 (Ar-C), 124.60 (Ar-C), 123.4 (Ar-C), 114.86 (Ar-C), 113.49 (Ar-C), 67.87 (CH_2), 39.01 (CH_2), 28.36 (CH_2), 27.71 (CH_2), 21.89 (CH_2), 13.91 (CH_3). CHN elemental analysis: Calculated for $C_{17}H_{21}N_3O$: C: 72.06%, H: 7.47%, N: 14.83%. Found: C: 72.00%, H: 7.44%, N: 14.78%.

(**3b**) 4-(4-nonyloxyphenylazo)-phenylamine. Yield:

3.15 g (88.73%), brown powder, mp: 126.8-131.7°C. IR (cm^{-1}): 3335 and 3445 (N-H stretching), 2918 (C$_{sp3}$-H stretching), 1604 (C=C aromatic), 841 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d$_6$), δ (ppm): 7.71 (d, J=10 Hz, 2H, Ar-H), 7.60 (d, J=10 Hz, 2H, Ar-H), 7.03 (d, J=10 Hz, 2H, Ar-H), 6.66 (d, J=5 Hz, 2H, Ar-H), 5.94 (s, 2H, NH$_2$), 4.01 (t, J=5 Hz, 2H, CH$_2$), 1.43-1.41 (m, 2H, CH$_2$), 1.39-1.37 (m, 2H, CH$_2$), 1.25-1.22 (m, 10H, CH$_2$), 0.85 (t, J=5 Hz, 3H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (ppm): 159.90 (Ar-C), 152.10 (Ar-C), 146.46 (Ar-C), 142.87 (Ar-C), 124.56 (Ar-C), 123.35 (Ar-C), 114.79 (Ar-C), 113.41 (Ar-C), 67.81 (CH$_2$), 31.25 (CH$_2$), 28.93 (CH$_2$), 28.75 (CH$_2$), 28.63 (CH$_2$), 25.47 (CH$_2$), 22.07 (CH$_2$), 13.92 (CH$_3$). CHN elemental analysis: Calculated for $C_{21}H_{29}N_3O$: C: 74.30%, H: 8.61%, N: 12.38%. Found: C: 73.90%, H: 8.59%, N: 12.32%.

(**3c**) 4-(4-Dodecyloxyphenylazo)-phenylamine.
Yield: 3.60 g (82.19%), brown powder, mp: 128.2-132.1°C. IR (cm^{-1}): 3355 and 3404 (N-H stretching), 2849 and 2917 (Csp^3-H stretching), 1600 (C=C stretching), 1628 (N-H bending), 1583 (N=N stretching), 1248 (C-N stretching), 1148 (C-O stretching), 839 (aromatic C-H bending). ^{1}H-NMR (500 MHz, DMSO-d$_6$) δ, ppm: 7.66 (d, J=10.0 Hz, 2H, Ar-H), 7.58 (d, J=10.0 Hz, 2H, Ar-H), 6.89 (d, J=10.0 Hz, 2H, Ar-H), 6.64 (d, J=5.0 Hz, 2H, Ar-H), 5.86 (s, 2H, NH$_2$), 3.84 (t, J=7.5 Hz, 2H, CH$_2$), 1.57-1.63 (m, 2H, CH$_2$), 1.27 (t, J=7.5 Hz, 2H, CH$_2$), 1.05-1.25 (m, 16H, CH$_2$), 0.77 (t, J=7.5 Hz, 3H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$) δ, ppm: 160.03 (Ar-C), 152.17 (Ar-C), 146.63 (Ar-C), 143.13 (Ar-C), 124.72 (Ar-C), 123.51 (Ar-C), 114.71 (Ar-C), 113.60 (Ar-C), 67.88 (CH$_2$), 31.54 (CH$_2$), 29.31 (CH$_2$), 29.28 (CH$_2$), 29.26 (CH$_2$), 29.24 (CH$_2$), 29.04 (CH$_2$), 28.98 (CH$_2$), 28.86 (CH$_2$), 25.69 (CH$_2$), 22.30 (CH$_2$), 13.99 (CH$_3$). CHN elemental analysis: Calculated for $C_{24}H_{35}N_3O$: C: 75.55%, H: 9.25%, N: 11.01%; Found: C: 75.43%, H: 9.13%, N: 10.95%.

(**4a**) Synthesis of 4-heptyloxybenzaldehye
4-hydroxybezaldehyde (3.00 g, 0.025 mol) and 1-bromoheptane (4.47 g, 0.025 mol) were dissolved in 5.0 ml of DMF separately. Both solutions were mixed. Potassium carbonate (5.53 g, 0.04 mol) and potassium iodide (0.42 g, 0.0025 mol) were added into the mixture. The mixture was refluxed. The reaction progress was monitored using TLC. Upon completion, the mixture was poured into cold water (500 mL) and was extracted using dichloromethane, DCM (3×30 mL). The organic layers were collected, dried over anhydrous sodium sulphate, filtered and dried overnight to form a yellowish oil. The same method was used to synthesise **4b**.Yield: 3.54 g (87.10%); yellow oil. IR (cm^{-1}): 2926 (C$_{sp3}$-H stretching), 1684 (C=O stretching), 1601 (C=C stretching). ^{1}H-NMR (500 MHz, DMSO-d$_6$), δ (ppm): 9.84 (s, 1H, CH=O), 7.83 (d, J=10 Hz, 2H, Ar-H), 7.06 (d, J=8.5 Hz, 2H, Ar-H), 4.06 (t, J=5 Hz, 2H, CH$_2$), 1.72-1.66 (m, 2H, CH$_2$), 1.38-1.33 (m, 8H, CH$_2$), 0.82 (t, J=5 Hz, 3H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (ppm): 190.79 (C=O), 163.64 (Ar-C), 131.62(Ar-C), 129.51 (Ar-C), 114.66 (Ar-C), 67.93 (CH$_2$), 31.21 (CH$_2$), 28.51 (CH$_2$), 28.44 (CH$_2$), 25.37 (CH$_2$), 22.02 (CH$_2$), 13.73 (CH$_3$).

(**4b**) 4-Dodecyloxybenzaldehyde. Yield: 5.26 g (84.58%); yellow oil. IR (cm^{-1}): 2921 (C$_{sp3}$-H stretching), 1690 (C=O stretching), 1604 (C=C aromatic). ^{1}H-NMR (500 MHz, DMSO-d$_6$), δ (ppm): 9.84 (s, 1H, CH=O), 7.83 (d, J= 5 Hz, 2H, Ar-H), 7.03 (d, J=5 Hz, 2H, Ar-H), 3.99 (t, J=6.5 Hz, 2H, CH$_2$), 1.71-1.66 (m, 2H, CH$_2$), 1.36-1.19 (m, 18H, CH$_2$), 0.81 (t, J=5 Hz, 3H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (ppm): 190.66 (C=O), 163.56 (Ar-C), 131.53 (Ar-C), 129.49 (Ar-C), 114.56 (Ar-C), 67.86 (CH$_2$), 31.30 (CH$_2$), 29.08 (CH$_2$), 29.05 (CH$_2$), 29.03 (CH$_2$), 29.01 (CH$_2$), 28.78 (CH$_2$), 28.75 (CH$_2$), 28.49 (CH$_2$), 25.40 (CH$_2$), 22.05 (CH$_2$), 13.67 (CH$_3$).

(**5a**) Synthesis of (4-heptyloxybenzylidene)-[4-(4-pentyloxyphenylazo)-phenyl]-amine
Compounds **3a** (0.20 g, 0.00071 mol) and **4a** (0.16 g, 0.00071 mol) were dissolved in 15 ml of methanol. A few drops of glacial acetate acid were added into the mixture and the solution was refluxed. The reaction progress was monitored using TLC. After 18 hours, the mixture was cooled and the precipitate formed was filtered, dried and recrystallized. The precipitate was recrystallized from ethanol to yield a red-orange powder. The same method was used to synthesise **5b-f**. Yield: 0.28 g (78.90%); orange powder, mp: 121.7-122.7°C. IR (cm^{-1}): 2938 (C$_{sp3}$-H stretching), 1601 (C=N stretching), 1582 (C=C stretching), 838 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d$_6$), δ (ppm): 8.59 (s, 1H, CH=N), 8.10 (d, J=10 Hz, 2H, Ar-H), 8.03 (d, J=10 Hz, 2H, Ar-H), 7.93 (d, J=5 Hz, 2H, Ar-H), 7.37 (d, J=10 Hz, 2H, Ar-H), 7.15 (d, J=5 Hz, 2H, Ar-H), 7.07 (d, J=5 Hz, 2H, Ar-H), 4.16-4.09 (m, 4H, CH$_2$), 1.79-1.76 (m, 4H, CH$_2$), 1.48-1.28 (m, 18H, CH$_2$), 0.94-0.91 (m, 6H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (ppm): 164.80 (C=N), 163.21 (Ar-C), 160.48 (Ar-C), 153.94 (Ar-C), 146.15 (Ar-C), 140.76 (Ar-C), 130.62 (Ar-C), 124.78 (Ar-C), 123.25 (Ar-C), 115.53 (Ar-C), 115.31 (Ar-C), 115.18 (Ar-C), 115.10 (Ar-C), 68.47 (CH$_2$), 68.43 (CH$_2$), 31.05 (CH$_2$), 28.63 (CH$_2$), 28.30 (CH$_2$), 28.20 (CH$_2$), 28.08 (CH$_2$), 27.60 (CH$_2$), 21.76 (CH$_2$), 21.62 (CH$_2$), 13.54 (CH$_3$), 13.49 (CH$_3$). CHN elemental analysis: Calculated for $C_{31}H_{39}N_3O_2$: C: 76.67%, H: 8.09%, N: 8.65%; Found: C: 76.43%, H: 8.03%, N: 8.60%.

(**5b**) (4-dodecyloxybenzylidene)-[4-(4-pentyloxyphenylazo)-phenyl]amine. Yield: 0.34 g (83.60%); orange powder, mp: 115.4-118.1°C. IR (cm^{-1}): 2917 (C$_{sp3}$-H stretching), 1605 (C=N stretching), 1570 (C=C stretching), 840 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d$_6$), *δ*(ppm): 8.89 (s, 1H, CH=N), 8.60 (d, J=5 Hz, 2H, Ar-H), 7.85 (d, J=5 Hz, 2H, Ar-H), 7.72 (d, J=5 Hz, 2H, Ar-H), 7.62 (d, J=5 Hz, 2H, Ar-H), 7.10 (d, J=10 Hz, 2H, Ar-H), 7.04 (d, J=10 Hz, 2H, Ar-H), 4.13-4.10 (m, 2H, CH$_2$), 4.09-4.01 (m, 2H, CH$_2$), 1.77-1.74 (m, 4H, CH$_2$), 1.42-1.39 (m, 24H, CH$_2$), 0.94 (t, J=6 Hz, 3H, CH$_3$), 0.90 (t, J=6 Hz, 3H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (ppm):

164.70 (C=N), 163.87 (Ar-C), 160.18 (Ar-C), 151.70 (Ar-C), 147.03 (Ar-C), 143.75 (Ar-C), 131.54 (Ar-C), 124.29 (Ar-C), 123.28 (Ar-C), 115.43 (Ar-C), 115.13 (Ar-C), 113.89 (Ar-C), 113.81 (Ar-C), 68.39 (CH$_2$), 68.32 (CH$_2$), 31.11 (CH$_2$), 28.81 (CH$_2$). 28.80 (CH$_2$), 28.74 (CH$_2$), 28.51 (CH$_2$), 28.49 (CH$_2$), 28.45 (CH$_2$), 28.33 (CH$_2$), 27.62 (CH$_2$), 25.29 (CH$_2$), 21.81 (CH$_2$), 21.62 (CH$_2$), 13.52 (CH$_3$), 13.48 (CH$_3$). CHN elemental analysis: Calculated for $C_{36}H_{49}N_3O_3$: C: 77.80%, H: 8.89%, N: 7.56%. Found: C: 77.75%, H: 8.83%, N: 7.50%.

(**5c**) (4-Heptyloxybenzylidene)-[4-(4-nonyloxyphenylazo)-phenyl]-amine. Yield: 0.16 g (79.80%); orange powder, mp: 107.2-109.7°C. IR (cm^{-1}): 2921 (C_{sp3}-H stretching), 1605 (C=N stretching), 1570 (C=C stretching), 840 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d$_6$), δ (ppm): 8.60 (s, 1H, CH=N)), 7.91-7.85 (m, 6H, Ar-H), 7.37 (d, J=10 Hz, 2H, Ar-H), 7.12-7.06 (m, 4H, Ar-H), 4.13-4.09 (m, 4H, CH$_2$), 1.78-1.76 (m, 4H, CH$_2$), 1.47-1.46 (m, 4H, CH$_2$), 1.38-1.37 (m, 16H, CH$_2$), 0.90-0.87 (m, 6H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (ppm): 164.15 (C=N), 163.31 (Ar-C), 161.62 (Ar-C), 154.88 (Ar-C), 148.96 (Ar-C), 142.64 (Ar-C), 130.60 (Ar-C), 124.26 (Ar-C), 123.23 (Ar-C), 115.35 (Ar-C), 115.14 (Ar-C), 114.78 (Ar-C), 114.49 (Ar-C), 68.4, 68.29, 33.22, 31.11, 28.83, 28.81, 28.77, 28.66, 28.58, 28.56, 25.40, 25.37, 22.35, 21.81, 14.17, 13.49. CHN elemental analysis: Calculated for $C_{36}H_{49}N_3O_3$: C: 77.59%, H: 8.74%, N: 7.76%. Found: C: 77.53%, H: 8.70%, N: 7.72%.

(**5d**) (4-Dodecyloxybenzylidene)-[4-(4-nonyloxyphenylazo)phenyl]-amine. Yield: 0.32 g (85.50%); orange powder, mp: 106.9-109.5°C. IR (cm^{-1}): 2917 (C_{sp3}-H stretching), 1601 (C=N stretching), 1570 (C=C stretching), 840 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d$_6$), δ (ppm): 8.64 (s, 1H, CH=N), 7.96-7.86 (m, 6H, Ar-H), 7.40 (d, J=15 Hz, 2H, Ar-H), 7.16-7.08 (m, 4H, Ar-H), 4.17-4.12 (m, 4H, CH$_2$), 1.83-1.41 (m, 4H, CH$_2$), 1.50-1.47 (m, 23H, CH$_2$), 1.37-1.34 (m, 6H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (ppm): 164.14 (C=N), 163.35 (Ar-C), 159.67 (Ar-C), 151.18 (Ar-C), 146.51 (Ar-C), 143.24 (Ar-C), 131.02 (Ar-C), 123.77 (Ar-C), 122.76 (Ar-C), 114.91 (Ar-C), 114.61 (Ar-C), 113.37 (Ar-C), 113.29 (Ar-C), 67.87 (CH$_2$), 67.81 (CH$_2$), 30.60 (CH$_2$), 28.86 (CH$_2$), 28.29 (CH$_2$), 28.28 (CH$_2$), 28.22 (CH$_2$), 28.18 (CH$_2$), 28.14 (CH$_2$), 28.06 (CH$_2$), 27.99 (CH$_2$), 27.97 (CH$_2$), 27.93 (CH$_2$), 27.88 (CH$_2$), 27.82 (CH$_2$), 27.10 (CH$_2$), 24.78 (CH$_2$), 21.29 (CH$_2$), 21.10 (CH$_2$), 13.00 (CH$_3$), 12.96 (CH$_3$). CHN elemental analysis: Calculated for $C_{40}H_{57}N_3O_2$: C: 78.51%, H: 9.39%, N: 6.87%. Found: C: 78.39%, H: 9.32%, N: 6.83%.

(**5e**) (4-Dodecyloxybenzylidene)-[4-(4-heptyloxyphenylazo)phenyl]-amine. Yield: 0.23 g (74.77%), yellowish-brown powder, mp: 100.5-102.7°C. IR (cm^{-1}): 2849 and 2918 (Csp^3-H stretching), 1618 (C=N stretching), 1602 (C=C stretching), 1473 (N=N stretching), 1247 (C-O stretching), 1148 (C-N stretching), 856 (aromatic C-H bending). ^{1}H-NMR (500 MHz, DMSO-d$_6$) δ, ppm: 8.59 (s, 1H, CH=N), 7.90 (d, J=10.0 Hz, 2H, Ar-H), 7.87 (d, J=10.0 Hz, 2H, Ar-H), 7.85 (d, J=10.0 Hz, 2H, Ar-H), 7.37 (d, J=10.0 Hz, 2H, Ar-H), 7.11 (d, J=5.0 Hz, 2H, Ar-H), 7.07 (d, J=10.0 Hz, 2H, Ar-H), 4.09-4.13 (m, 4H, CH$_2$), 1.70-1.85 (m, 4H, CH$_2$), 1.42-1.52 (m, 4H, CH$_2$), 1.25-1.40 (m, 22H, CH$_2$), 0.86-0.92 (m, 6H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$) δ, ppm: 164.13 (C=N), 162.54 (Ar-C), 158.42 (Ar-C), 153.96 (Ar-C), 145.61 (Ar-C), 141.10 (Ar-C), 130.62 (Ar-C), 126.52 (Ar-C), 124.19 (Ar-C), 123.23 (Ar-C), 121.57 (Ar-C), 115.35 (Ar-C), 115.14 (Ar-C), 58.36 (CH$_2$), 58.34 (CH$_2$), 31.10 (CH$_2$), 31.02 (CH$_2$), 28.80 (CH$_2$), 28.78 (CH$_2$), 28.73 (CH$_2$), 28.66 (CH$_2$), 28.61 (CH$_2$), 28.52 (CH$_2$), 28.46 (CH$_2$), 28.43 (CH$_2$), 28.31 (CH$_2$), 28.17 (CH$_2$), 25.34 (CH$_2$), 25.33 (CH$_2$), 21.78 (CH$_2$), 21.73 (CH$_2$), 13.47 (CH$_3$), 13.39 (CH$_3$). CHN elemental analysis: Calculated for $C_{38}H_{53}N_3O_2$: C: 78.17%, H: 9.15%, N: 7.20%; Found: C: 78.06%, H: 9.13%, N: 7.15%.

(**5f**) (4-Dodecyloxybenzylidene)-[4-(4-dodecyloxyphenylazo)phenyl]-amine. Yield: 0.14 g (79.95%), yellowish-brown powder, mp: 102.7-104.1°C. IR (cm^{-1}): 2849 and 2917 (Csp^3-H stretching), 1620 (C=N stretching), 1602 (C=C stretching), 1473 (N=N stretching), 1249 (C-O stretching), 1148 (C-N stretching), 854 (aromatic C-H bending). ^{1}H-NMR (500 MHz, DMSO-d$_6$) δ, ppm: 8.59 (s, 1H, CH=N), 7.90 (d, J=10.0 Hz, 2H, Ar-H), 7.87 (d, J=10.0 Hz, 2H, Ar-H), 7.85 (d, J=10.0 Hz, 2H, Ar-H), 7.37 (d, J=10.0 Hz, 2H, Ar-H), 7.11 (d, J=5.0 Hz, 2H, Ar-H), 7.07 (d, J=5.0 Hz, 2H, Ar-H), 4.09-4.14 (m, 4H, CH$_2$), 1.76-1.80 (m, 4H, CH$_2$), 1.41-1.51 (m, 4H, CH$_2$), 1.20-1.38 (m, 32H, CH$_2$), 0.86-0.90 (m, 6H, CH$_3$). ^{13}C-NMR (125 MHz, DMSO-d$_6$) δ, ppm: 163.96 (C=N), 162.15 (Ar-C), 159.35 (Ar-C), 150.25 (Ar-C), 144.85 (Ar-C), 142.29 (Ar-C), 131.86 (Ar-C), 130.61 (Ar-C), 124.21 (Ar-C), 123.25 (Ar-C), 121.60 (Ar-C), 115.31 (Ar-C), 115.09 (Ar-C), 68.43 (CH$_2$), 68.23 (CH$_2$), 31.17 (CH$_2$), 31.13 (CH$_2$), 28.85 (CH$_2$), 28.84 (CH$_2$), 28.82 (CH$_2$), 28.78 (CH$_2$), 28.75 (CH$_2$), 28.70 (CH$_2$), 28.67 (CH$_2$), 28.61 (CH$_2$), 28.60 (CH$_2$), 28.57 (CH$_2$), 28.52 (CH$_2$), 28.48 (CH$_2$), 28.45 (CH$_2$), 28.42 (CH$_2$), 25.43 (CH$_2$), 25.36 (CH$_2$), 21.86 (CH$_2$), 21.83 (CH$_2$), 13.54 (CH$_3$), 13.50 (CH$_3$). CHN elemental analysis: Calculated for $C_{43}H_{63}N_3O_2$: C: 78.97%, H: 9.71%, N: 6.43%; Found: C: 78.75%, H: 9.68%, N: 6.29%.

RESULTS AND DISCUSSION

FT-IR spectral discussion

The IR spectrum of intermediate **1** showed a broad band at 3370 cm^{-1} for the O-H stretching. The successful alkylation of **1** formed **2a-c** whereby the band at 3370 cm^{-1} dissappeared and a new band was seen at ~2900 cm^{-1} for C_{sp3}-H stretching. Reduction reaction of compunds **2a-c** succesfully converted nitro (-NO$_2$) substituent into amine (-NH$_2$) substituent in **3a-c**. The appearance of two spikes for the N-H stretching in the regions of 3335 and 3445 cm^{-1} can be observed for compounds **3a-c**. Other absorption bands remained the same for the C-H stretching (sp^3) of the aliphatic group of pentyl and nonyl chains and the

C=C stretching of the aromatic ring at 1604 cm^{-1}. Compounds **4a-b** were alkylation products of 4-hydroxybenzaldehyde. The appearance of the absorption bands at 2850 and 2921 cm^{-1} for the C-H (sp^3) stretching proved the succesful insertion of the alkyl chains in these compounds. Other bands in the regions of 1692 cm^{-1} (C=O stretching), 1602 cm^{-1} (C=C stretching) and 1201 cm^{-1} (C-O stretching) were also observed.

The cross condensation reactions of compounds **4a-b** with the amine compounds having azo units, **3a-c** gave six different compounds, **5a-f**, as shown in Figure 1. The strong band at 1692 cm^{-1} attributed to C=O stretching in compounds **4a-b** was not observed and the appearance of new absorption bands of the C=N linkage at 1620 cm^{-1} indicated that the Schiff base formation was successful. The IR spectra for all these compounds showed similar absorption bands.

^{1}H and ^{13}C-NMR spectral discussion

In the ^{1}H-NMR spectra, compound **1** showed a singlet at 10.66 ppm for the hydroxyl proton and four doublets which were close to each other in the aromatic region for four different aromatic protons. Compounds **2a-c** and **3a-c** showed similar patterns of proton and carbon peaks. Four doublets in the aromatic region referred to four different aromatic protons and peaks for the aliphatic protons and carbons in the upfield regions referred to the pentyl and nonyl chains in the related compounds.

Compounds **4a-b** showed two doublets for two different aromatic protons and peaks for the aliphatic protons and carbons in the upfield region referred to the pentyl and nonyl alkyl chains. Compounds **5a-f** with three benzene rings linked by a Schiff base and an azo unit which were attached to different alkyl chains at both terminal ends. There were six doublets in the aromatic region, referring to six different aromatic protons. The chemical shifts (^{1}H and ^{13}C) for azomethine and aromatic region of compounds **5a-f** are summarized in Table 1. The peaks in the upfield region referred to the aliphatic protons, depending on the alkyl chains (pentyl, heptyl, nonyl and dodecyl). The ^{1}H-NMR spectrum of compound **5a** is shown in Figure 2 as an example.

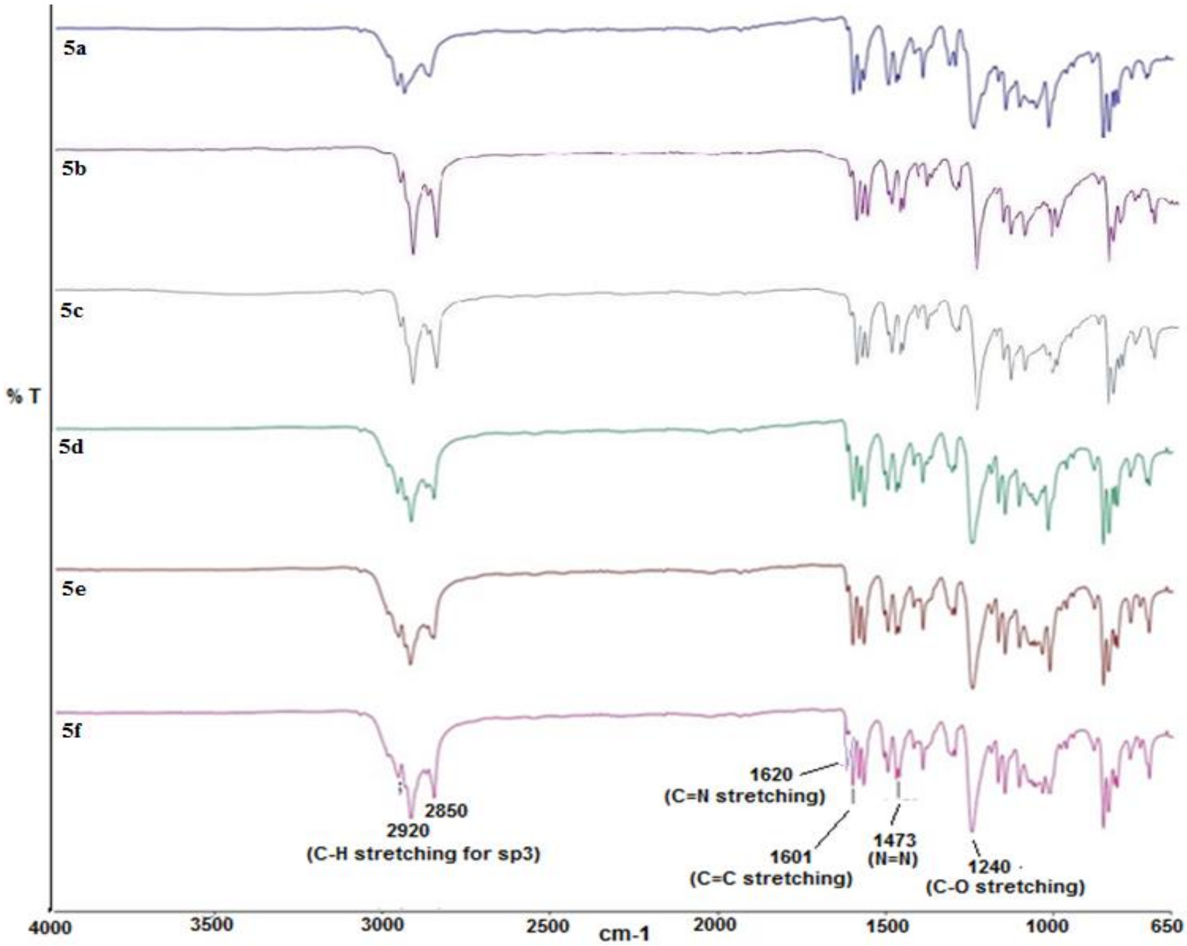

Figure 1. The FTIR overlay spectra of **5a-f**.

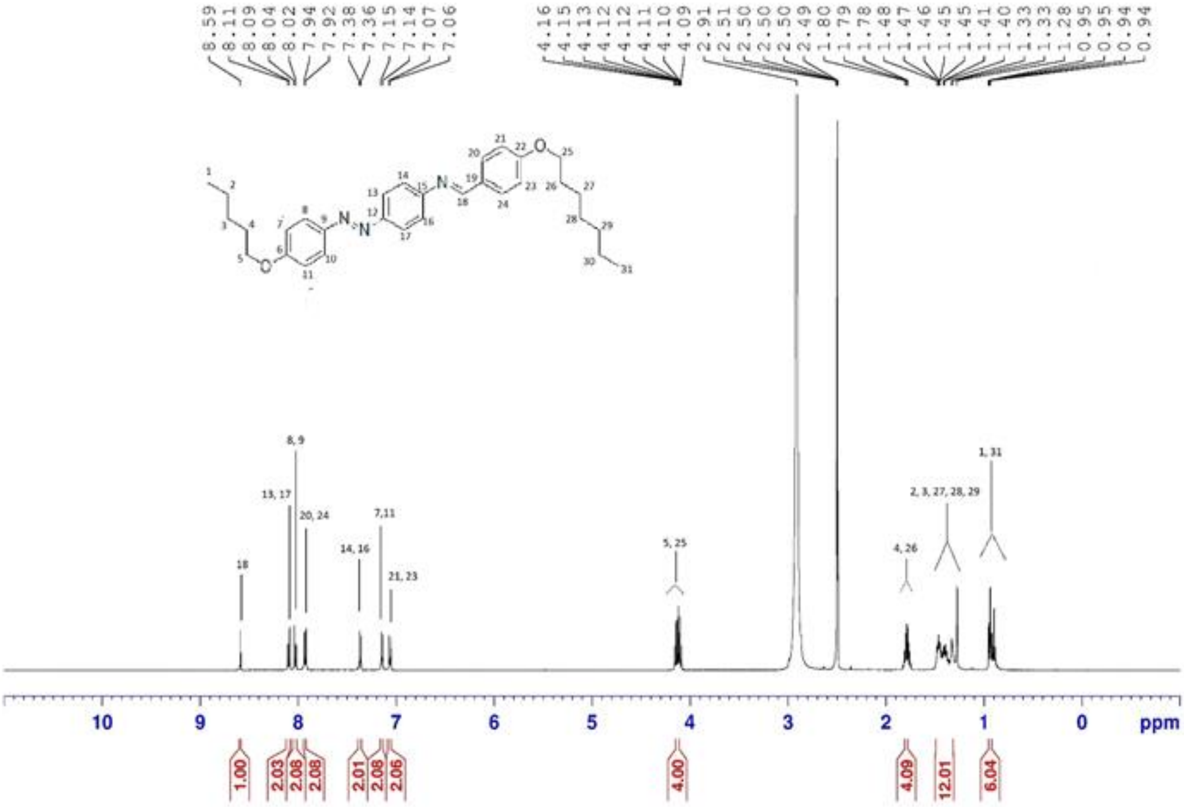

Figure 2. ^{1}H (500 MHz, DMSO-d$_6$) NMR spectrum of compound **5a**.

Table 1. The chemical shifts (^{1}H and ^{13}C) of compounds **5a-f**.

Compound	**Chemical Shift (ppm)**			
	^{1}H		**^{13}C**	
	CH=N (Schiff Base)	**Ar-H (Aromatic)**	**C=N (Schiff base)**	**Ar-C (Aromatic)**
5a	8.59 (s)	8.10 (d), 8.03 (d), 7.93 (d), 7.37 (d), 7.15 (d), 7.07 (d)	164.80	163.21, 160.48, 153.94, 146.15, 140.76, 130.62, 124.78, 123.25, 115.53, 115.31, 115.18, 115.10
5b	8.89 (s)	8.60 (d), 7.85 (d), 7.72 (d), 7.62 (d), 7.10 (d), 7.04 (d)	164.70	163.87, 160.18, 151.70, 147.03, 143.75, 131.54, 124.29, 123.28, 115.43, 115.13, 113.89, 113.81
5c	8.60 (s)	7.91-7.85 (m), 7.37 (d), 7.12-7.06 (m)	164.15	163.31, 161.62, 154.88, 148.96, 142.64, 130.60, 124.26, 123.23, 115.35, 115.14, 114.78, 114.49
5d	8.64 (s)	.96-7.86 (m), 7.40 (d), 7.16-7.08 (m)	164.14	163.35, 159.67, 151.18, 146.51, 143.24, 131.02, 123.77, 122.76, 114.91, 114.61, 113.37, 113.29
5e	8.59 (s)	7.90 (d), 7.87 (d), 7.85 (d), 7.37 (d), 7.11 (d), 7.07 (d)	164.13	162.54, 158.42, 153.96, 145.61, 141.10, 130.62, 126.52, 124.19, 123.23, 121.57, 115.35, 115.14
5f	8.59 (s)	7.90 (d), 7.87 (d), 7.85 (d), 7.37 (d), 7.11 (d), 7.07 (d)	163.96	162.15, 159.35, 150.25, 144.85, 142.29, 131.86, 130.61, 124.21, 123.25, 121.60, 115.31, 115.09

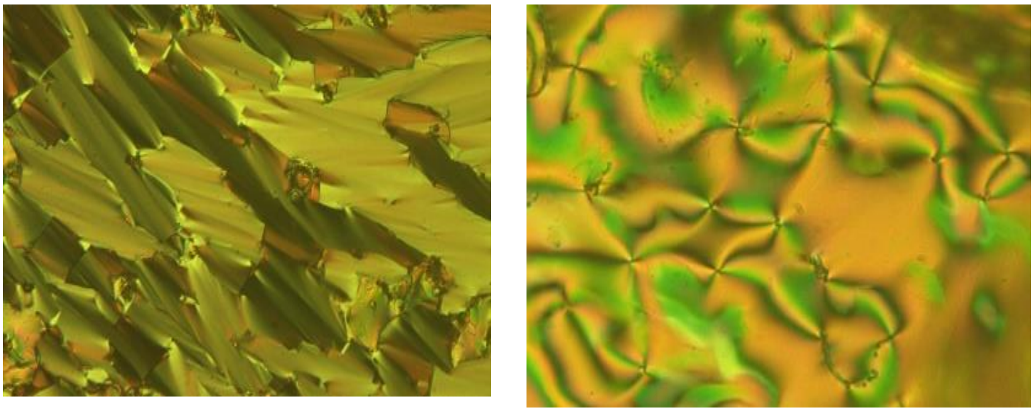
(a) (b)

Figure 3. The POM photomicrographs of compound **5b** (upon heating): (a) SmA texture of fan-shaped at 126.21 ºC; (b) nematic texture of a thread-like four point brush at 212.45 ºC with magnification: 20 × 0.40.

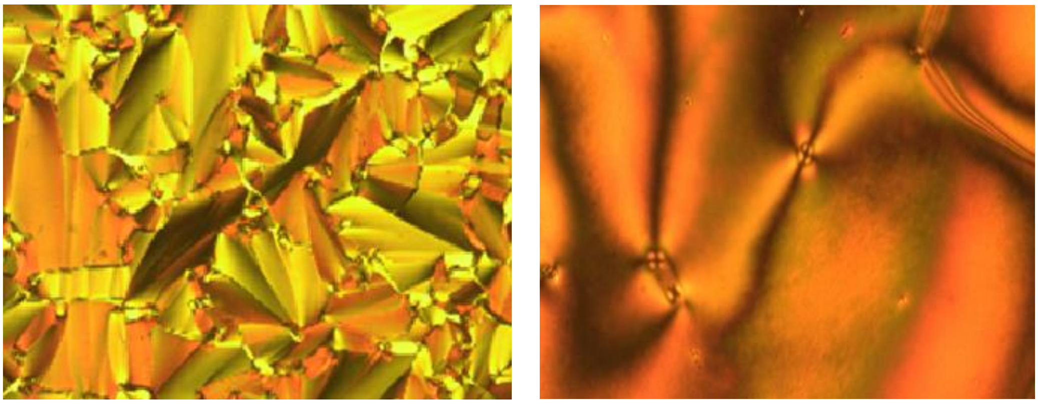
(a) (b)

Figure 4. The POM photomicrographs of compound **5c** (upon heating): (a) SmA texture of fan-shaped at 122.83 ºC; (b) nematic texture of a thread-like four point brush at 218.51 ºC with magnification: 20 × 0.40.

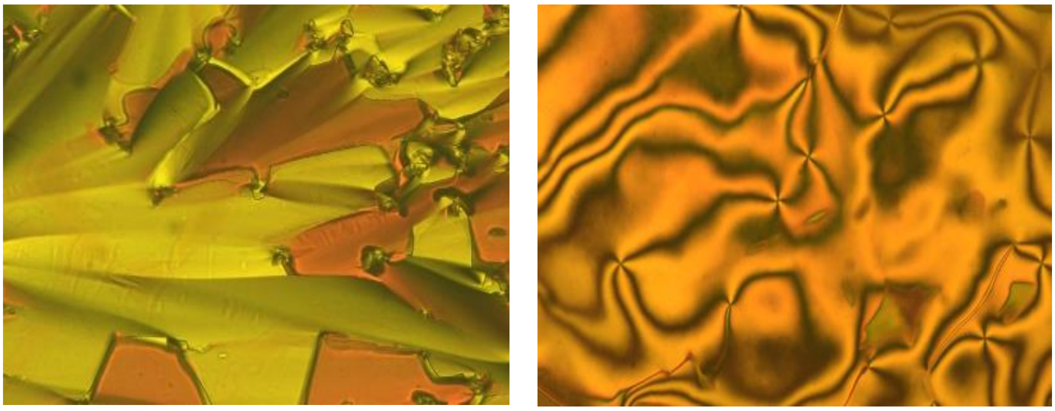
(a) (b)

Figure 5. The POM photomicrographs of compound **5d** (upon heating): (a) SmA texture of fan-shaped at 130.27 ºC; (b) nematic texture of a thread-like four point brush at 202.14 ºC with magnification: 20 × 0.40.

Determination of mesophase behaviour using POM

The texture of the mesophase transition of all compounds were observed using POM. The samples were run in the heating and cooling cycles. Observations under POM determined that compounds **1, 2a-c** and **3a-c** showed the transition phase from crystal to isotropic phase in the heating cycle and isotropic to crystal phase in the cooling cycle. No liquid crystal phase was observed for these compounds. Nevertheless, for the cross condensation products of **5a-f**, it was observed that **5a** did not show any liquid crystal phase in both the heating andcooling cycles. However, compounds **5b, 5c** and **5d** showed transition of phases from crystal to smectic A and nematic phases before entering isotropic phase in the heating cycle. In the cooling cycles it entered nematic and smectic A phases before crystal phase. While, compound **5e** exhibited smectic C phase and compound **5f** showed smectic C and nematic phases for both cycles. The mesophase textures for compounds **5b-d** are illustrated in Figures 3-5. Meanwhile, the POM photomicrographs of compounds **5e** and **5f** are shown in the Appendix Section.

Determination of thermal transitions using DSC

Compounds **5b**, **5c**, **5d**, **5e** and **5f** with liquid crystal mesophases were further determined of their thermal transitions using differential scanning calorimetry (DSC). The experiment involved the heating and cooling of the compounds and the data are summarized in Table 2 (heating cycle) and Table 3 (cooling cycle). The dots (•) in Tables 2 and 3 represent the phases which occurred in the cycles.

Table 2. DSC thermal transitions of compounds **5b-5f** (Heating cycle).

Compounds	**Transition temperature (℃)** *Enthalpy (ΔH = kJ/mol)*								
	Cr		SmC		SmA		N		I
5b	•	116.46 *34.56*	-	-	•	146.59 *1.91*	•	242.88 *2.02*	•
5c	•	108.54 *11.42*	-	-	•	135.45 *1.16*	•	247.65 *2.69*	•
5d	•	109.21 *36.19*	-	-	•	146.25 *1.97*	•	227.48 *1.62*	•
5e	•	101.36 *6.12*	•	116.62 *5.50*	-	-	-	-	•
5f	•	114.62 *25.94*	•	142.37 *1.20*	-	-	•	211.96 *4.55*	•

Note: **Cr**=crystal, **SmC**= Smectic C, **SmA**=Smectic A, **N**=Nematic, **I**=Isotropic

Table 3. DSC thermal transitions of compounds **5b-5f** (Cooling cycle).

Compounds	**Transition temperature (℃)** *Enthalpy (ΔH = kJ/mol)*								
	I		N		SmA		SmC		Cr
5b	•	238.24 *-2.03*	•	139.51 *-2.66*	•	-	-	101.35 *-10.71*	•
5c	•	240.96 *-1.60*	•	129.59 *-2.43*	•	-	-	113.60 *-5.82*	•
5d	•	222.01 *-1.82*	•	138.33 *-2.30*	•	-	-	105.54 *-9.04*	•
5e	•	107.00 *-4.41*	-	-	-	-	•	92.89 *-1.06*	•
5f	•	200.98 *-2.70*	•	138.30 *-1.22*	-	-	•	102.19 *-17.96*	•

Note: **Cr**=crystal, **SmC**= Smectic C, **SmA**=Smectic A, **N**=Nematic, **I**=Isotropic

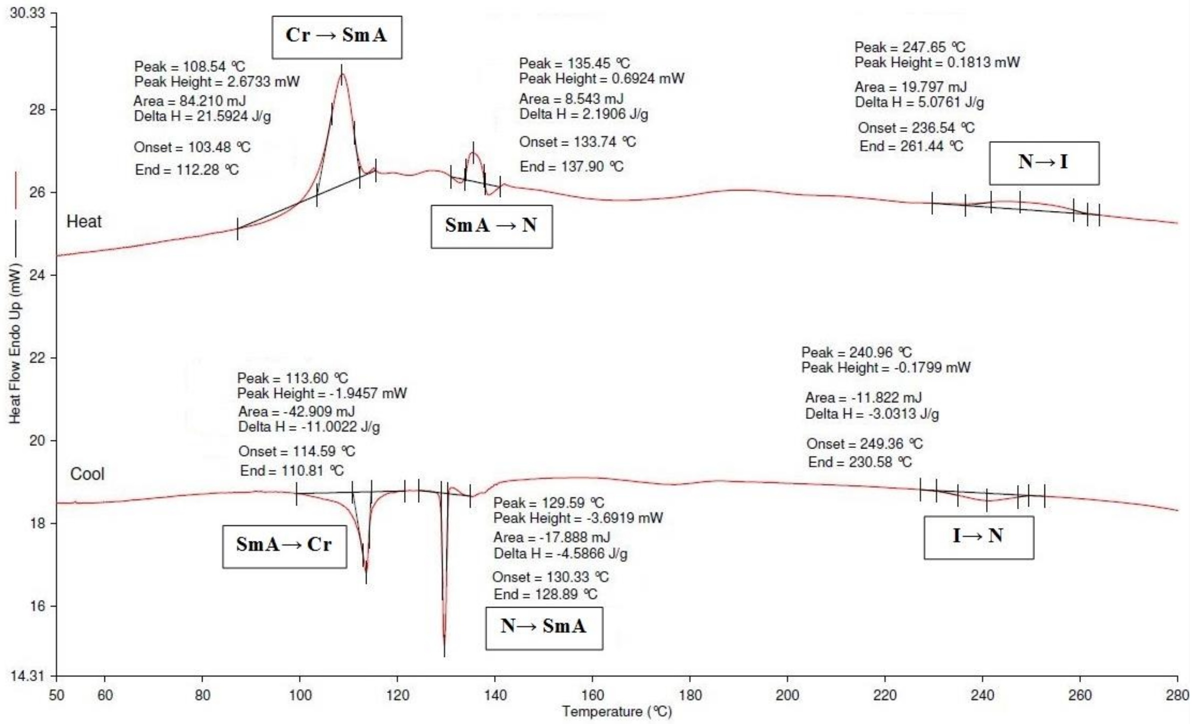

Figure 6. DSC thermogram of compound **5c**.

The DSC spectra for compounds **5b**, **5c**, **5d** and **5f** exhibited three curves in both heating and cooling cycles. These curves confirmed the phase transitions of Cr→ SmA, SmA→ N and N→ I for compounds **5b**, **5c** and **5d,** and transitions of Cr→ SmC, SmC→ N and N→ I for compound **5f**, which were observed using POM. Compound **5e** showed two curves for the phase transitions of Cr→ SmC and SmC→ I for both cycles. The thermal enthalpy for each curve was calculated from these spectra. The DSC thermogram of compound **5c** is shown in Figure 6.

Structure-properties relationship

In general, the alkoxy chain length affected the mesogenic properties. Increasing the number of carbon chains increased the flexibility, whereby the melting temperatures (T_m) were considerably reduced. As the length of the chain increased, the nematic phase stability decreased, thus leading to a decrease in the phase thermal range. On the other hand, the clearing temperatures (T_c) too dropped as the number of carbon atoms increased. A substance may form one or more liquid crystal phases if the structural conditions allowed this. The terminal attraction became weaker as the flexibility of the molecule increased, which in turn contributed to a lower stability of the phase [31, 32]. Compounds with long alkyl chain lengths in general exhibited enantiotropic mesophase which is thermodynamically stable while compounds with shorter alkyl chains showed monotropic mesophase since these compounds have the unstable behaviour [33]. As a result, compound **5a** with a shorter alkyl chain was unable to induce the mesophase formation. The formation of smectic phase might be attributed to the lamellar packing which maintained the sliding of the layered molecular arrangement in floating condition with the influence of thermal vibrations in both the heating and cooling conditions. At the definite temperature, the layered structure broke down and the magnitudes of the end-to-end side intermolecular attractions and appropriate permanent dipole moment were still maintained. This caused the homologue to arranged in a parallel orientational order to adopt a nematogenic character, either directly or via smectic phase in an enantiotropic manner [34, 35].

CONCLUSION

All the intermediates and six new azo-azomethine compounds with different terminal chain lengths were successfully synthesized and characterized. All these intermediates and final compounds were characterized by using FT-IR, ^{1}H and ^{13}C-NMR and CHN elemental analysis. The existence of azo and azomethine linkages in the spectroscopy study confirmed the successful synthesis of the final compounds. Besides, the determination of the mesophase behaviour of the intermediates and final compounds was done using POM and the transition temperatures of the compounds having mesophase behaviour were further confirmed using DSC. All the DSC thermograms showed good agreement with the phase transition observed under POM. The final compounds **5b-f** showed liquid crystal phase in both heating and cooling cycles at different temperatures. However, the compounds **1, 2a-c, 3a-c, 4a-b** and **5a** were non-mesogenic without liquid crystal behaviour. An increase in the number of carbons in the terminal chain was found to affect the melting and clearing temperatures and phase stability as indicated by the thermal mesomorphic range. The azo and Schiff base linking groups were among the factors influencing the formation of these enantitropic phase.

ACKNOWLEDGEMENT

The authors would like to thank the University Sains Malaysia (USM) to provide the lab facilities and the RUI (USM) grant (1001/PKIMIA/811332).

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