Non-symmetrical liquid crystal dimers armed with azobenzene and 1,2,3-triazole-cholesterol

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(Received 1 February 2015; accepted 16 May 2015)

New non-symmetrical dimers which contain respective side units of azobenzene and 1,2,3-triazole-cholesterol have been synthesised from the reaction between 6-azido-[4-(4-acetylphenylazo)phenoxy]alkanes and cholesterol-4-(prop-2-ynyloxy)benzoate. The results show that the derivatives of 6-bromo-[4-(4-acetylphenylazo)phenoxy]alkanes which possess the odd alkyl spacers exhibit dimesomorphism of N and SmA phases whilst the members with even numbers are non-mesogenic. However, the 6-azido-[4-(4-acetylphenylazo)phenoxy]-alkanes show N and SmA phases in a wide temperature range. On heating and cooling the target compounds cholesterol-4-[(1-(6-(4-(4-acetylphenylazo)phenoxy)alkyl)-1H-1,2,3-triazol-4-yl)methoxy]benzoate show chiral nematic (oily streak and fan-shaped texture) and focal conic texture characteristics of smectic A phases with high thermal stability. Present investigation also reveals the effect of the spacer length upon the phase transition temperature. Intercalated arrangement is favoured by the molecules in the smectic phase. The observation is well established by XRD measurement wherein the actual molecular length is smaller than the theoretical value.

**Keywords:** non-symmetrical liquid crystals; azobenzene; 1,2,3-triazole-cholesterol; smectic; chiral nematic

1. Introduction

Since the discovery of the liquid crystalline (LC) state in cholesteryl benzoate,[1] chirality has been considered as one of the most important factors contributing towards the uniqueness in liquid crystals.[2,3] Chirality can be introduced in a LC entities by the inclusion of (i) an asymmetric carbon in a molecule such as 2-(6-methoxy-2- naphthyl)propionic,[4] (ii) a chiral moiety like cholesterol as a part of the molecule,[5–7] (iii) special conformation of the molecule and/or (iv) multicomponent with chiral dopant in a binary mixture leading to several exotic chiral frustrated phases.[8]

Many cholesterol-based dimers that possess a cholesterol ester unit joined to an aromatic mesogenic moiety such as benzoate ester, Schiff’s base, azobenzene, tolan or biphenyl have been synthesised.[9–13] While Itoh et al. reported a chiral cyclic liquid crystal dimers consisting of two biphenyl mesogens connected by alkyl spacer in one side while the other side is a R-enantiomeric chiral diol,[14] Sarkar et al. reported a chiral unsymmetrical dimeric liquid crystals consisting of a cholesterol and a substituted salicylidene imine connected by different alkyl spacers.[15] These dimers usually exhibit a wide variety of mesophases, for instances, N*, SmC*, SmA, TGBA, TGB* and blue phase.[16] Dimesogenic compounds composed of a hydrogen bonding-induced straight arylamide spacer and two cholesterol groups have been designed and exhibited fluid smectic and N* phases.[17] Also, interlinking chalcone with cholesterol mesogenic entities through spacers have been reported and showed intercalated SmA, TGB* and N*.[18]

In view of the need to stabilise a variety of highly frustrated fluid structures, the introduction of heterocyclic moiety in liquid crystal dimers derived from naturally occurring cholesterol have attracted considerable attention among researchers working on LCs. This heterocyclic system can be a good candidate in the development of new materials,[19] supramolecular chemistry,[20] design of new supported organocatalysts, biotechnology area[21] and in asymmetric synthesis.[22] There are many attempts to obtain liquid crystal properties based on heterocyclic systems. For example, Majumdar et al. have reported cholesterol and oxadiazole-based liquid crystal dimers which were found to possess high thermal stability of TGBC*.[23] Umesh et al. synthesised discotic liquid crystal materials containing three pendent triphenylenes, triazine and a triazole groups which exhibit a wide-range columnar phases from room temperature up to more than 100°C.[24]

In recent years, LC dimers consisting of 1,2,3-triazole in their structure have been studied extensively due to their remarkable phase transition...
behave. The triazole core in this system can be synthesised via click reaction methodology. Sharpless and Meldal had also popularised this reaction and established a copper-catalysed azide alkyne cycloaddition version for this useful transformation with regioselectivity to yield 1,4-disubstituted 1,2,3-triazoles under mild reaction conditions as employed in ‘Click Chemistry’.\cite{25–28}

There was a diversified work reported by 1,3-dipolar cycloaddition of azides with alkynes in the literature especially for the synthesis of 1,2,3-triazole-cored liquid crystals. The first unsymmetrical dimer and trimer containing cholesterol and triazole moieties showed SmC* and N*.\cite{29} Benbayer et al. reported a series of analogues containing 1,2,3-triazole and an unsaturated carbon–carbon double bond which exhibited SmA and SmC phases.\cite{30} Calamitic liquid crystals based on azobenzene and triazole core have been synthesised and characterised by Balamurugan et al., and these compounds show SmA and SmC phases.\cite{31} Zhao et al. had synthesised triphenylene discotic dimer connected by triazole segment using click reaction procedure.\cite{32} Recently, metallomesogens incorporated with triazole moiety have been reported. The ligand and their corresponding complexes exhibited SmA and SmC phase.\cite{33,34} However, bent-shaped mesogens consisting of cholesterol unit as one of the side arms connected to a 1,2,3-triazole ring while the other arm of the triazole ring is connected to two- and three-ring aromatic systems with varying terminal chain lengths have been synthesised. These homologues exhibited SmA*, SmC* and TGB*.\cite{35} Furthermore, this bent molecular structure particularly for odd dimers may give rise to the new twist-bend nematic phase.\cite{36–38}

Our present work involves the (i) design and synthesis of new dimers based on azido-azobenzene and 1,2,3-triazole-cholesterol using click chemistry methodology and (ii) investigation on the structure–property relationship of the target compounds by increasing the flexible spacer.

2. Experimental

2.1. Materials

Cholesterol, copper sulphate pentahydrate, 1,6-dibromohexane, 1,8-dibromooctane, 1,10-dibromodecane, N,N′-dicyclohexylcarbodiimide (DCC) and sodium azide were purchased from Acros Organics (Geel, Belgium). Potassium carbonate anhydrous and potassium iodide were obtained from Fisher Scientific (Waltham, MA, USA). 1,7-Dibromohexane, 1,9-dibromononane, 1,11-dibromoundecane, 1,12-dibromododecane, sodium ascorbate and dimethylaminopyridine (DMAP) were purchased from Sigma Aldrich (St. Louis, MO, USA) while n-bromoalkanoic acid and 4-(4-hydroxyphenyl)benzoic acid were received from Tokyo Chemical Industry (Chuo, Tokyo, Japan). Propargyl bromide was purchased from Fluka (Buchs, Switzerland).

2.2. Synthesis

The first approach to generate 6a–6g is outlined in Scheme 1. The synthesis of compounds 6a–6g was started via diazonated 4-aminoacetophenone and the derivative thus obtained was coupled with phenol to form compound 1. The terminal OH was alkylated by dibromoalkane in the presence of potassium carbonate and potassium iodide using acetone as solvent to afford 2a–2g. The 2a–2g were subsequently reacted with sodium azide to result in the formation of 3a–3g. The 4-hydroxybenzoic acid was etherified using propargyl bromide and potassium hydroxide as base medium to afford 4, which would react with cholesterol under Steglich esterification in the presence of DCC and DMAP to yield compound 5. Finally, click reaction took place by reacting compounds 3a–3g with 5 in a mild condition wherein copper sulphate and sodium ascorbate were used to afford the 6a–6g.

Detailed description with respect to the syntheses of compounds 1, 2a, 3a, 4, 5 and 6a is given in the following sections.

2.2.1. Synthesis of 4-(4-hydroxyphenylazo) acetophenone (1)

Intermediary compound 1 was prepared according to the method described by Lutfor et al.\cite{39} Dilute hydrochloric acid [conc. hydrochloric acid (13.5 ml) in water (25 ml)] was added to a solution containing 4-amino-acetophenone (5.0 g, 36.99 mmol) in acetone (130 ml) and the resulting mixture was cooled to 2°C in the ice bath. Sodium nitrite (3.06 g, 44.38 mmol) dissolved in water (10 ml) was added dropwise to the cooled mixture with the temperature kept below 2°C and the diazonium salt solution thus obtained was left to stir for 1 hour. Urea (0.6 g) in water (2.5 ml) was added and the solution was stirred for further 10 minutes.

Subsequently, phenol (3.47 g, 36.99 mmol) which has earlier dissolved in a mixture of acetone/water (100 ml/50 ml) was added to the diazonated mixture wherein the pH maintained at 8 with sodium hydroxide solution (about 12.5 ml of 50%). The mixture was left at stirring for 2 hours. Finally, the resulting mixture was acidified (pH <5) with dilute hydrochloric acid (40 ml, 10%) and then 150 ml of water was added. The resulting precipitate
2.2.2. Syntheses of 6-bromo[4-(4-acetylphenylazo)phenoxy]hexane (2a)

Compounds 2a–2g were synthesised through minor modification upon earlier report.[39] Since the procedure used to synthesise the entire series of 2a–2g is unchanged, therefore, the experimental details can be described by based on a representative compound 2a.

A mixture consisting of compound 1 (2.00 g, 8.33 mmol) in dry acetone (150 ml), potassium carbonate (8.40 g, 62 mmol), a catalytic amount of potassium iodide (100 mg) and a fifth-fold excess of 1,6-dibromohexane (20.3 g, 83.3 mmol) was refluxed for 24 hours. The reaction mixture was filtered when it was still hot and the acetone was removed under reduced pressure on the water bath. Sufficient amount of hexane was added to the product for removing unreacted 1,6-dibromohexane. The insoluble material was collected by filtration and was extracted using dichloromethane and water. The organic layer was washed with dilute hydrochloric acid, sodium carbonate solution and water, respectively. The product obtained upon removal from the solvent was recrystallised from ethanol.

2a: Colour: Orange. Yield 70%. M.P: 120°C. IR (KBr) ν cm⁻¹, 3057 (C–H aromatic), 2938, 2861 (C–H alkyl), 1676 (C=O), 1602 (C=C), 1499 (C–H bending), 1473 (N=N), 1249 (C–O).

1H-NMR (500 MHz, CDCl₃) δ/ppm, 8.08 (2H, d, J = 8.5 Hz, ArH), 7.93 (4H, d, J = 9 Hz, Ar–H), 7.00 (2H, t, J = 6.5 Hz, OCH₂), 4.06 (2H, t, J = 6.5 Hz, CH₂Br), 2.66 (3H, s, CH₃), 1.93–1.84 (4H, m, CH₂), 1.55–1.53 (4H, m, CH₂). Elemental analysis Cal. for C₂₀H₂₁BrN₂O₂ (403.31): C 59.56; H 5.75; N 6.95%. Found: C 59.31; H 5.78; N 6.84%.

2.2.3. 6-Azido-[4-(4-acetylphenylazo)phenoxy]hexane (3a)

All derivatives in this series were synthesised using a similar procedure. Compound 3a is selected as a
representative compound for the experimental description. To a solution of 6-bromo-4-(4-acetylphenylazo)phenoxy]hexane (0.1 mmol) in DMF 20 ml, NaOH (0.15 mmol) was added. The reaction was left to stir at room temperature for 18 hours. The resulting mixture was then poured into cold water and extracted with ethylacetate (2 × 20 ml). The organic phase was washed by water and dried over sodium sulphate anhydrous and the solvent was removed by rotatory evaporator. The crude was recrystallised from ethanol to afford the desired compound 3a.

3a: Yield 90%. Colour: Orange. Elemental analysis Cal. for C20H32N2O2 (365.43): C 65.73, H 6.31, N 19.16%; Found C 65.52, H 6.31, N 19.16%. IR (KBr) ν cm⁻¹: 3060 (C=H bending), 2939, 2862 (C–H alkyl), 2121 (C–N), 1677 (C=O), 1604 (C=O), 1501 (C–H bending), 1474 (N=N), 1251 (C–O). ¹H-NMR (500 MHz, CDCl₃) δ/ppm: 8.08 (2H, d, J = 8.5 Hz, ArH), 7.91 (4H, d, J = 8.5 Hz, ArH), 7.02 (2H, d, J = 9 Hz, ArH), 4.06 (2H, t, J = 6.5 Hz, OCH₂), 3.30 (2H, t, J = 6.5 Hz, CH₂N₂), 2.66 (3H, s, CH₃), 1.86–1.82 (2H, m, CH₂), 1.64–1.50 (6H, m, CH₂).

2.2.4. Synthesis of 4-(prop-2-ynyloxy)benzoic acid (4)

Compound 4 was synthesised according to the method described in previous report.[40] 4-Hydroxybenzoic acid (3 g, 21.7 mmol) was dissolved in a solution of KOH (2.3 g, 43.4 mmol) in 15 ml water. The solution of propargylbromide (3.8 g, 32.6 mmol) in 10 ml of ethanol was added dropwise to the earlier prepared mixture and refluxed with stirring for 20 hours. KOH (1.2 g, 21.7 mmol) in water (5 ml) was then added and the heating was continued for 2 hours. The reaction was left to cool to room temperature before being acidified with 10 ml 4N hydrochloric acid. The precipitate was isolated by filtration and washed by water. The precipitate was recrystallised from ethylacetate.

2.2.5. Synthesis of cholesteryl 4-(prop-2-ynyloxy)benzoate (5)

Stegilsh esterification procedure was adopted to obtain homologues 18a–18f.[5] 4-(Prop-2-ynyloxy) benzoic acid (1.36 g, 7.7 mmol) was dissolved in 5 ml of dry DMF and added to a solution containing cholesterol (3 g, 7.7 mmol) in 30 ml of dry DCM. N,N′-dicyclohexylcarbodiimide (DCC) (1.49 g, 7.7 mmol) was dissolved in 10 ml of dry DCM and a catalytic amount of 4-dimethylaminopyridine (DMAP) (0.9 g, 0.77 mmol) were added to the mixture. The resulting mixture was stirred overnight at room temperature. It was filtered to remove the insoluble DCU and the solvent was evaporated. The crude product was recrystallised from ethanol whereupon the white crystal 5 was formed.

5: Colour: White. Yield: 65%. IR (KBr) ν cm⁻¹: 3056 (C–H aromatic), 2930, 2856 (C–H alkyl), 1735 (C=O ester), 2111 (C=C), 1603 (C=C), 1465 (C=C, chol.), 1251 (C–O). ¹H-NMR (500 MHz, CDCl₃) δ/ppm: 8.08 (2H, d, J = 8.5 Hz, ArH), 7.00 (2H, d, J = 9 Hz, ArH), 5.45 (1H, d, J = 3.4 Hz, HC=C chol.), 5.26 (2H, s, OCH₂), 4.84–4.79 (1H, m, chol.), 4.73 (2H, t, J = 7.1 Hz, NCH₂), 4.02 (2H, t, J = 6.2 Hz, OCH₂), 2.65 (3H, s, CH₃), 2.45 (2H, d, J = 7.7 Hz, CH₂ chol.), 2.00–0.68 (41H, 10 × CH₂, 6 × CH, 5 × CH₃).

2.2.6. Synthesis of cholesteryl 4-{1-[6-(4-(4-acetylphenylazo)phenoxy)hexyl]-1H-1,2,3-triazol-4-yl}methoxy]benzoate (6a)

Similar methodology was employed to synthesise the derivatives 6a–6g. The experimental details for this series will be based on a representative compound 6a. To a well-stirred solution of azide 3a (0.5 g, 1.36 mmol) and alkyne 5 (0.74 g, 1.36 mmol) in DMF 15 ml, a catalytic amount of CuSO₄·5H₂O (0.01 g, 20 mol%) and sodium ascorbate (0.01, 20 mol%) were added. The solution was stirred for 6 hours at room temperature whereupon the precipitate thus formed was isolated and extracted by diethyl ether and water. The organic layer was washed by water, dried over sodium sulphate and filtrated. The solvent was evaporated and the crude product was recrystallised from ethanol to afford the target compound 6a.

6a: Yield: 80%. Colour: Orange. Elemental analysis Cal. for C₇₅H₇₅N₅O₅ (910.24): C 75.21, H 8.31, N 7.69%; Found C 75.39, H 8.31, N 7.46%. IR (KBr) ν cm⁻¹: 3056 (C–H aromatic), 2937, 2866 (C–H alkyl), 1707 (C=O ester), 1681 (C=O keton), 1603 (C=C), 1502 (C–H bending), 1470 (N=N), 1251 (C–O). ¹H-NMR (500 MHz, CDCl₃) δ/ppm: 8.08 (2H, d, J = 8.4 Hz, ArH), 7.98 (2H, d, J = 8.7 Hz), 7.91 (4H, d, J = 8 Hz, Ar-H; d, J = 8.2 Hz, Ar-H), 7.60 (1H, t, Triazol), 7.00 (4H, d, J = 9 Hz, ArH), 5.40 (1H, d, J = 3.4 Hz, HC=C chol.), 5.26 (2H, s, OCH₂), 4.84–4.79 (1H, m, chol.), 4.37 (2H, t, J = 7.1 Hz, NCH₂), 4.02 (2H, t, J = 6.2 Hz, OCH₂), 2.65 (3H, s, CH₃), 2.44 (2H, d, J = 7.7 Hz, CH₂ chol.), 2.02–0.68 (49H, 14 × CH₂, 6 × CH, 5 × CH₃). ¹³C-NMR (125 MHz, CDCl₃) δ/ppm: 197.45, 165.62, 162.19, 161.79, 155.33, 147.02, 139.74, 137.90, 131.58, 129.35, 125.25, 123.92, 122.71, 122.59, 114.80, 114.34, 74.35, 68.01, 62.19, 56.72, 50.35, 50.09, 42.34, 39.53, 31.94, 30.14, 28.90, 28.01, 26.77, 24.30, 22.80, 22.55, 19.37, 18.73, 11.86. All the physical properties, elemental analysis and
spectroscopic data for the intermediate and final compounds are given in the supplementary information.

2.3. Techniques

The Fourier transform infrared (FT-IR) analyses were carried out on a Perkin Elmer 2000-FT-IR spectrophotometer (PerkinElmer, Inc., Waltham, MA, USA) at the frequency range of 4000–400 cm\(^{-1}\). \(^1\)H and \(^13\)C NMR analyses were performed by Bruker–Avance 500 MHz Ultrashield spectrometer (Bruker Biospin, Karlsruhe, Germany). CHN microanalyses were recorded using a Perkin Elmer 2400 LS Series CHNS/O analyzer. Textural analyses were inspected using a Carl Zeiss polarising microscope (Carl Zeiss AG, Oberkochen, Germany) equipped with a Linkam LTS350 hot stage and TMS94 temperature controller (Linkam Scientific Instruments Ltd., Tadworth, UK). The phase transition temperatures and associated enthalpies were measured using a Seiko DSC120 Model 5500 differential scanning calorimeter. Synchrotron powder X-ray diffraction (XRD) measurements were performed at beamline BL17A of the National Synchrotron Radiation Research Center, Taiwan, where the wavelength of X-ray was 1.33366 Å. The XRD data were collected using imaging plates (area = 20 × 40 cm\(^2\) with a pixel resolution of 100) curved with a radius equivalent to a sample-image plate distance of 280 mm, and the diffraction signals were accumulated for 3 min. The powder samples were packed into capillary tubes heated by a heat gun, whose temperature controller was programmed by a computer with a proportional, integral and differential feedback system. The scattering angle \(\theta\) was calibrated by a mixture of silver behenate and silicon.

3. Results and discussion

3.1. Evaluation of mesomorphism of intermediates 2a–2g

The phase transition temperatures and the associated enthalpy values of the monomers as inferred from the DSC are listed in Table 1. All three homologues 2b, 2d

| Compound | Heating | Cooling | Heating | Cooling | Heating | Cooling | Heating | Cooling | Heating | Cooling |
|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 2a       |         | 120\(^{a}\) | 107\(^{a}\) | 99.2 (1.8) | 104.9 (0.7) |
| 2b       |         | 95.4 (35.4) | 82.3 (33.6) | 97.3 (2.0) | 103.5 (0.7) |
| 2c       |         | 116\(^{a}\) | 105\(^{a}\) | 97.3 (2.0) | 103.5 (0.7) |
| 2d       |         | 95.7 (37.4) | 86.7 (35.8) | 94.7 (1.5) | 100.2 (0.8) |
| 2e       |         | 116\(^{a}\) | 108\(^{a}\) | 94.4 (1.0) | 98.4 (0.7) |
| 2f       |         | 90.2 (32.0) | 72.9 (33.3) | 93.0 (1.2) | 97.2 (0.9) |
| 2g       |         | 118\(^{a}\) | 105\(^{a}\) | 93.0 (1.2) | 97.2 (0.9) |
| 3a       | Cooling | 83.5 (32.4) | 103.9 (2.6) | 107.3 (0.4) |
| 3b       | Heating | 58.5 (25.7) | 102.1 (2.6) | 106.2 (0.6) |
| 3c       | Heating | 60.4 (31.2) | 100.8 (2.9) | 103.2 (0.9) |
| 3d       | Heating | 48.3 (28.4) | 98.9 (2.9) | 100.6 (0.9) |
| 3e       | Heating | 85.0 (23.7) | 93.4 (21.2) | 101.0 (2.2) | 103.5 (0.5) |
| 3f       | Heating | 75.1 (31.2) | 99.3 (2.3) | 102.3 (0.7) |
| 3g       | Heating | 60.8 (6.1) | 82.0 (30.4) | 98.2 (2.9) | 99.9 (0.7) |
| 3h       | Heating | 56.6 | 98.6 (2.8) | 98.6 (0.9) |
| 3i       | Heating | 74.9 (44.5) | 98.2 (2.9) | 99.9 (0.7) |
| 3j       | Heating | 81.1 (35.8) | 96.5 (2.5) | 98.0 (1.6) |
| 3k       | Heating | 69.7 (40.2) | 95.4 (2.7) | 97.3 (1.8) |
| 3l       | Heating | 98.3 (40.1) | 94.9 (2.3) | 96.1 (1.5) |

Notes: Cr, crystal; Cr1, crystal 1; SmA, smectic A; N, nematic; I, isotropic; values within parenthesis denote phase transition enthalpy. \(^{a}\)The phase transition temperature was assigned by polarizing optical microscope (POM).
and 2f with relatively odd alkyl terminal exhibit enantiotropic mesogenic properties of which the phase transition temperatures on heating (99.2°C, 98.3°C and 94.4°C) and cooling (97.3°C, 94.7°C and 93.0°C) have been ascribed to the SmA–N transition phases whereas the even alkyl members (2a, 2c, 2e and 2g) are not mesogenic. The mesomorphic behaviour exhibited by compounds 2b, 2d and 2f can be rationalised in term of the rigidity of the molecular long axis which will often be reduced owing to the increase of flexibility of the terminal alkyl chains, hence suppress the anisotropic shape of the molecules.[41]

Under the polarised light microscope the member 2b on cooling shows a droplet and Schlieren texture with two- and four-brush defects identified as N phase (Figure 1(a)). On further cooling, a focal conic texture characteristics of SmA phase (Figure 1(b)) was observed before it crystallised at 83°C.

A comparison between the derivatives 2a–2g with their analogues having different terminal substituents has been carried out. These analogues have similar chemical structure as 2a–2g but the terminal groups are methoxy or cyano [42,43] as shown below:

\[
X - N - O(CH_2)_nBr \quad \text{Where } X = \text{OCH}_3, \text{CN}
\]

The results show that compounds with acetyl terminal group (2b, 2d and 2f) exhibited enantiotropic SmA and N phase whereas the compounds with methoxy and cyano terminal substituents show enantiotropic N phase. Moreover, the clearing temperatures for derivatives 2a–2g are slightly higher as compared with the derivatives with methoxy and cyano terminal groups.

3.2. Evaluation of mesomorphism of intermediates 3a–3g

All homologous 3a–3f exhibit enantiotropic N and SmA phases while the highest homologue 3g behaves as monotropic mesogen. The observation using POM on compound 3c during cooling from the isotropic liquid shows the presence of Schlieren texture characteristics of N phase (Figure 2(a)). On further cooling, the Schlieren texture transformed to focal conic texture of SmA phase (Figure 2(b)).

As can be seen from Table 1, the length of alkoxy side chain also influences the type of mesophase. The odd–even effect on the mesomorphic properties was observed when the alkoxy chain is increased from 3a to 3g. However, the ΔN has apparently decreased by the increase in the length of the terminal chain from 3a (4.1°C) to 3g (1.2°C). This phenomenon is resulted

Figure 1. (colour online) Photomicrographs of compound 2b on cooling: (a) nematic Schlieren texture with two and four brushes, and (b) focal conic texture for SmA.

Figure 2. (colour online) Photomicrographs of compound 3c on cooling: (a) nematic Schlieren texture with two and four brushes, and (b) focal conic texture for SmA.
from the long terminal chain being attracted and intertwined which in turn facilitates the lamellar packing. As a result, it leads to a decrease in the N phase range. However, the temperature ranges associated with the SmA phase (ΔSmA) reached a maximum and minimum at 50.6°C and 9.4°C for respective compounds 3b and 3g. The elongation of the terminal chain length resulted in a gradual decrease of liquid crystal stability. This can be explained by the increase of the flexibility for the terminal chain. As such, the tails are not exactly aligned along the long molecular axis and are not fully stretched.[7] The figures relating to DSC and the correlation between the phase transition temperatures with alkyl spacer in the intermediates are shown in supplementary information.

3.3. Evaluation of mesomorphism of title compounds 6a–6g

The transition temperatures and associated enthalpy values from the DSC experiments for 6a–6g are listed in Table 2. All homologues in this series display enantiotropic mesomorphism. It is apparent from Table 2 that all homologues 6a–6g have very high thermal stabilities as indicated by the high clearing points.

Texture observation under POM shows in general that on first heating all 6a–6g exhibit focal conic texture of SmA which transforms to typical cholesteric oily streak as exemplified by 6g (Figure 3(a)). Compound 6g shows the phase sequence of I-N*-SmA-Cr on first cooling run in which the transition from isotropic phase lead to the formation of fan-shaped texture at 216.2°C which can be characterised as N* phase (Figure 3(b)). The fan-shaped texture, however, changed to oily streak texture on second cooling when it was subjected to mechanical stress (Figure 3(c)). On further cooling the N* phase transforms to SmA phase (Figure 3(d)). This phenomenon can be attributed to the chiral moiety present in the homologues 6a–6g. The cholesterol is considered as a chiral molecule which can be used to increase the twisting power and to shorten the pitch. The change of helical handedness may be observed also within SmC*α and N* phases. The shared mesophase thus observed within the chiral nematic phase can be attributed to the orientation of the helix which is parallel to the light beam.[44–46]

Figure 4 shows the dependence of the transition temperatures on the number of methylene units in the flexible alkyl spacers (n) on heating. It is apparent that the clearing and the melting temperatures depend on the length and parity of the flexible spacers. Specifically, the transition temperatures (TCr-SmA and TCr,SmA) exhibit an odd–even alternation in which the even members show the higher values in comparison with odd members when n was increased. Hence, the molecules with even parity favour linear structure and thus lead to more effective packing. On contrary, the compounds with odd alkyl spacer were inclined to bent shape.[47,48] Moreover, the presence of polar alkoxy groups enhances the interaction between the molecule owing to the dipole–dipole interaction which enhances the arrangement of the molecule to form smectic layer structure.[49] It can also be inferred from Figure 4 that the clearing points for all the compounds in this series were generally high and this could be due to the introduction and increase of polarity on the O and N atoms residing in the central cores which enhance the anisotropy properties.[50]

However, the odd–even effect can be inferred from the phase transition temperatures (ΔT_Cr,SmA)

| Compound | Cr | N* | I | ΔS_N*/R |
|---------|----|----|---|---------|
| 6a      | Heating | 181.1 (16.9) | 195.3 (0.3) | 240.5 (0.8) | 0.18 |
|         | Cooling | 99a | 231.7 (0.4) | 235.8 (0.4) |       |
| 6b      | Heating | 171.1 (24.6) | 181.1 (3.3) | 225.8 (1.0) | 0.22 |
|         | Cooling | 105a | 196.5 (2.7) | 218.8 (1.5) |       |
| 6c      | Heating | 178.5 (41.6) | 198.4 (0.7) | 233.3 (1.9) | 0.45 |
|         | Cooling | 84.51 (22.4) | 155.8a | 229.2 (0.3) |       |
| 6d      | Heating | 170.2 (27.4) | 206.0 (0.7) | 230.8 (1.9) | 0.44 |
|         | Cooling | 83.5 (11.0) | 190.3a | 225.6 (1.8) |       |
| 6e      | Heating | 175.4 (23.8) | 196.4 (1.5) | 237.2 (1.9) | 0.45 |
|         | Cooling | 66.1 (12.4) | 204.0 (0.6) | 234.3 (1.2) |       |
| 6f      | Heating | 159.1 (30.9) | 199.4 (0.7) | 222.5 (1.8) | 0.43 |
|         | Cooling | 70.6 (16.9) | 184.4a | 219.8 (1.2) |       |
| 6g      | Heating | 169.4 (42.7) | 191.4 (1.0) | 217.8 (2.2) | 0.53 |
|         | Cooling | 109.9 (27.4) | 184.4 (0.8) | 216.2 (2.2) |       |

Notes: Cr, crystal; SmA, smectic A; N*, chiral nematic; I, isotropic. The enthalpy was too small to be detected by DSC and the phase transition temperature was assigned by POM; values within parenthesis denote phase transition enthalpy.
of the titled compounds (6a–6g). Among these compounds, 6e has the highest thermal stability ($\Delta T_{I-Cr} = 168^\circ C$) whereas compound 6g possesses the shortest thermal stability range ($\Delta T_{I-Cr} = 106^\circ C$). The $\Delta T_{I-Cr}$ increased with the increase in the alkyl spacers from $n = 6$ ($\Delta T_{I-Cr} = 136.8^\circ C$) to $n = 10$ ($\Delta T_{I-Cr} = 168.2^\circ C$) and this contributed to the increase in the molecular length with breath ratio (L/W) ratio indicating the molecules are closely packed with each other via the Van der Waals intermolecular forces of attraction. However, the thermal stability ($\Delta T_{I-Cr}$) of homologue 6f is higher than 6g by 42.9$^\circ C$. This phenomenon can be ascribed to the rigidity of the molecular long axis which will be reduced owing to the increase of flexibility of the terminal alkyl chains leading to the suppression of anisotropic shape of the molecules.[41]

It is noteworthy that although there is an odd–even effect on the N*–I transition temperatures between the corresponding dimers, but it can still be considered as small difference. This behaviour suggests that the role of the central alkyl spacer has a weaker effect on the average molecular shape during the N*–I transition. Hence, the clearing point is not controlled just by the parity of the central spacer but also by a number of factors such as mesogens length and parity of the two outer spacers. The behaviour may be contributed by the position of the mesogenic linkage of the triazole core which introduces an aspect of non-linearity into the even membered dimers, therefore, the two innermost mesogenic units are no longer planar.[51] As a consequence, the molecular

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Figure 3. (colour online) Photomicrographs of the textures for different mesophases in compound 6g: (a) oily streak texture, (b) fan-shaped texture of N*, (c) gradual formation of N* phase amid the focal conic texture when a mechanical stress was given to the cell and (d) focal conic texture of SmA.

Figure 4. (colour online) The plots depicting the dependence of the transition temperatures on the number of methylene units in the flexible alkyl spacers on heating for 6a–6g.
arrangement for both the odd and even members can be considered as a bent shape. This phenomenon can be observed in other oligomers such as trimers and tetramers.\[52\]

It should be noted, however, that the $\Delta S_{N^*/R}$ values as shown by 6a–6g dimers are considerably lower than those are normally seen for liquid crystal dimers containing small terminal substituents or terminal linear alkyl chains. This can be attributed to the (i) two arms kinked at an angle with respect to each other and, therefore, give an overall bent shape to the molecule,\[53\] (ii) increased biaxiality of the bulky cholesteryl-based unit resulting from the decreased length-to-breadth ratio relative to conventional rod-like core such as the cyanobiphenyl, dimers containing branched terminal chains and other dimers containing cholesterol moiety,\[54,55\] (iii) in term of molecular geometry, the flexible spacer linked up two mesogenic groups by nitrogen in the triazole core and oxygen caused a bent conformation and dilutes the interaction strength parameter.\[56,57\]

### 3.4. X-ray diffraction study

To confirm the nature of the phases in intermediate (3b & 3c) and final compounds (6d & 6g), XRD experiments were performed. Table 3 represents the $d$-spacing and the distance between molecules for intermediate and final compounds. The compound 3b possesses nematic and SmA phases upon cooling cycle. X-ray pattern shows typical signals for SmA phase with Bragg reflection corresponding to 28.1 Å which is a full molecular length at small angle arising from the layered structure with sharp peak at $2\theta = 2.6^\circ$. A broad peak with a wide-angle region centred at 4.9° characteristics of the liquid-like arrangement of the molecules within the layers. From the $d/l$ ratio, it can be interpreted as monolayer SmA ordering. However, the theoretical molecular length ($d = 25.4$ Å) is shorter than the measured $d$-spacing and the molecule alternates with each other. The alternated structure would increase the molecular length in the SmA phase, and $d$-spacing is longer than the theoretical molecular length (Figure 5). Azobenzene group also alternates with each other. However, the same observation was found in homologue 3c in which the ordering for SmA phase is monolayer. The $d$-spacing is 29.6 Å and the distance between the molecules is decreased from 4.8 to 4.5 Å upon decreasing the temperature. As expected the layer spacing increases with increasing spacer length from 28.1 Å for 3b to 29.6 Å for 3c.

#### Table 3. The $d$-spacing and the distance between molecular for the intermediate and final compounds by XRD.

| Compound | Temperature °C | 2 theta (2$\theta$) | $d$-Spacing and distance between molecular (Å) |
|----------|---------------|--------------------|----------------------------------|
| 3b       | 90            | 2.69               | 15.5 28.1 4.9                   |
| 3c       | 90            | 2.56               | 16.4 29.6 4.6                   |
| 6d       | 155           | 2.76               | 14.9 27.5 5.1                   |
| 6g       | 155           | 2.56               | 14.8 29.6 5.1                   |

![Figure 5](image-url)  
Figure 5. (a) The theoretical molecular length obtained from molecular modelling and (b) the possible arrangement of the SmA phase.
The XRD profile for compounds 6d and 6g carried out at 155°C is shown in Figure 6. The XRD profile of 6d displayed a sharp diffraction peak at $2\theta = 2.75^\circ$ which corresponds to a layer spacing of 27.5 Å and suggests the existence of the SmA phase. The $d$-spacing for compound 6d is slightly increased from 27.3 to 27.5 Å upon cooling. Å. This increase can be attributed to the increasing in the orientational order parameter.[58] Moreover, the bending angle increases slightly when the temperature is decreased. Hence, the distance between molecules decreases from 5.3 to 5.1 Å. The centre of the wide diffuse outer scattering shifts towards higher angles when the temperature is lowered thus indicating an increase in the strain forces and the packing density of the molecule.[59] The fully extended molecular length is calculated by molecular modelling ($l = 54.3$ Å). The $d$-spacing determined from the XRD measurement is smaller than the calculated molecular length value. The molecular ratio is $dl/l = 0.5$, therefore, we expect an intercalated SmA phase. A schematic diagram of packing of molecules in smectic phase deduced from XRD study is presented in Figure 7.

Many researchers have synthesised different series of non-symmetrical dimers containing cholesterol in one arm.[60,61] Luckhurst et al. had proposed the molecular arrangement in non-symmetric dimers. The layer arrangement in non-symmetric dimers consists of a rather random mixture of the two types of mesogenic group, while the spacers connecting at random the mesogenic groups within different layers. Their relative stability is attributed to favourable specific interactions between the unlike mesogenic groups.[62,63] Although these models nicely explain some features, in reality the interactions may be more subtle and governed by steric and electronic interactions.[64,65]

For the even member 6g, the SmA phase was investigated on decreasing the temperature from 160°C to 130°C. The $d$-spacing for the SmA is 29.6 Å and remains constant with the increase in temperature. The layer spacing is considered smaller than the extended backbone length ($l = 56.5$ Å). Thus, 6g might also adopt a stacking pattern similar to compound 6d.

By comparing the molecular arrangement for homologous 6d and 6g, $d$-spacing for 6g remains constant when the temperature is decreased. The $d$-spacing for 6d is shorter than 6g and this can be attributed to the more elongation structure for compound 6d.

4. Conclusion

A new non-symmetric homologous have been synthesised from the reaction between 1-azido-[4-(4-acetylphenylazo)phenoxy]alkane series with cholesteryl4-prop-2-ynyloxy)benzoate to form heterocyclic triazole homologues of cholesteryl 4-((1-(3-(4-(4-acetylphenyl)diazenyl)phenoxy)alkyl)-1H-1,2,3-triazol-4-yl)methoxy)benzoate via click reaction. The results showed that series of 1-bromo-[4-(4-acetylphenylazo)phenoxy]alkane with odd alkyl spacer exhibit two LC phases while the members with even number are non-mesogenic. However, the series of 1-azido-
[4-(4-acetylphenylazo)phenoxy]-alkane show N and SmA phases in a wide temperature range. The dimers with tilting molecular arrangement exhibit chiral nematic (cholesteric and fan-shaped texture) and SmA liquid crystal phases over a wide temperature range on heating and cooling. The longer alkoxy chains facilitate the formation of the LC phases at low temperature. The XRD results show a monolayer arrangement for SmA phase in the intermediates 3b and 3c while intercalated arrangement is observed for the titled compounds 6d and 6g. The non-symmetrical dimers with even parity favour the rod-like structure in comparison to odd members which prefer bent shape.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
The main author (G.Y. Yeap) would like to thank Universiti Sains Malaysia for providing the research facilities and financial support under RU Research Grant [1001/PKIMIA/811159]. Authors are also grateful to the Malaysian Ministry of Education for the acquisition of some specialty chemicals purchased under the FRGS Grant [203/PKIMIA/6711265].

Supplemental data
Supplemental data for this article can be accessed here.

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