Calamitic liquid crystals of 1,2,3-triazole connected to azobenzene: synthesis, characterisation and anisotropic properties

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Azobenzene-based calamitic liquid crystals, 4-((4-(4-methoxymethyl-1,2,3-triazol-1-yl)phenyl)diazenyl)phenylalkanoates have been isolated and their structures were characterised. The structure–property correlation with respect to the different alkanoyloxy terminal chain (–COOCnH2n+1 where n adopts odd numbers ranging from 3 to 15) has also been given attention in the present study. In this series, all compounds exhibit smectogenic properties. The lower homologues shows enantiotropic SmA phase as well as monotropic SmC phase. The higher homologues exhibit homeotropic alignment of smectic phases. These compounds possess very high anisotropic inclination in which the mesomorphic region covers nearly 80°C.

Keywords: 1,2,3-triazole; calamitic liquid crystals; homeotropic alignment; SmA phase; SmC phase

1. Introduction

A considerable number of heterocyclic compounds exhibiting anisotropic properties have been synthesised and reported in the last 2–3 decades.[1–5] This research area has drawn great attention because the introduction of heteroatom seemed to induce considerable changes of polarity, polarisability and geometry in the molecules. As such, it influenced the mesophase stability, phase transition temperatures and dielectric properties of the mesogens.[6,7] In addition, the heteroatom may participate in intermolecular interaction and affect the type of mesophase. The earlier studied heterocyclic compounds used to possess either five- or six-membered rings but the five-membered heterocyclic rings were claimed to be well evaluated.[8–11]

One of the main targets in synthetic chemistry will be 1,2,3-triazole ring as this system tends to give high yield[12] and potential usage in multifield applications such as biological activity, nanochemistry and supramolecular chemistry.[13–16] At the same time, the linking group implies considerable impact on the mesomorphic transitions. It is generally understood that various types of liquid crystal systems can be constructed from different linking groups. One of these groups will be azobenzene which possesses the potential to exhibit photosensitive behaviour owing to its ability to undergo cis-trans photoisomerisation. This phenomenon has contributed to novel optical applications such as reversible optical information storage media and optical switches.[17]

Many systems reported in the literature focus on the incorporation of azobenzene molecules into polymers, dendrimers and bent-core liquid crystals.[18–21] These studies have also made an interesting remark that the liquid crystalline properties of azobenzene containing liquid crystals could be influenced by the heteroatom. The heterocyclic ring seemed to increase the dipole–dipole interaction and thus favoured the formation of smectic phase in the calamitic liquid crystals.[22] In order to explore further the extent to which the azobenzene could govern the differences with respect to the variation of molecular system, we are prompted to focus on the compounds in which one end of the terminal azobenzene molecule is directly linked to three electronegative nitrogen atom containing 1,2,3-triazole ring, and another end linked to variable alkanoyoxy group (–COOCnH2n+1 where n adopts odd numbers ranging from 3 to 15).

2. Experimental

2.1 Reagents and physical measurements

All the chemicals were obtained from Sigma Aldrich Chemicals (St. Louis, MO, USA) and Merck (Darmstadt, Germany). Silica gel (MN Kieselgel 100–200 mesh) was used for column chromatography. Diethyl ether, dichloromethane and other solvents were purified using reported procedures.

CHN microanalyses were carried out on a Perkin-Elmer 2400 LS Series CHNS/O Analyzer (Waltham, MA, USA). The infrared (IR) spectra for all compounds were recorded in the frequency range 400–4000 cm⁻¹ using a Perkin-Elmer 2000 FTIR spectrophotometer (Waltham, MA, USA).
with the samples embedded in KBr discs. Thin layer chromatography was performed with TLC sheets coated with silica. The 1H and 13C NMR spectra were obtained using a Bruker 500 MHz Ultrashield spectrometer (Karlsruhe, Germany). The CDCl₃ and DMSO-d₆ were used as solvents and TMS as the internal standard. The liquid crystalline textures were observed under a Carl Zeiss Axioskop 40 polarising optical microscope (Oberkochen, Germany) equipped with a Linkam TMS94 temperature controller (Surrey, UK) and a LTS350 hot stage. The transition temperatures and enthalpy changes were measured by Perkin Elmer Pyris 1 calorimeter (New Castle, DE, USA) coupled with Perkin Elmer intracooler 2P cooling accessory at a rate of 5°C min⁻¹ for both heating and cooling cycles.

2.2 Synthesis

The synthesis of all intermediates 1–5 and corresponding dimers 6a–6g were carried out using the experimental procedures illustrated in Scheme 1. The synthetic methods for the intermediate 1–5 were reported in the literature.[22]

2.2.1 Procedure for the synthesis of 4-((4-(4-methoxymethyl-1,2,3-triazol-1-yl)phenyl)diazenyl) phenyl butyrate (6a)

Compound 5 (3 g, 0.01 mol) and triethylamine (1.2 g, 0.012 mol) were dissolved in 50 ml dry THF. A solution of butanoyl chloride (1 mL, 0.01 mol) and 10 mL of THF was added dropwise to the reaction mixture. The reaction was performed under N₂ atmosphere for 6 h. Finally, the reaction mixture was filtered and washed with excess of THF before the solvent was evaporated off. The orange colour solid thus obtained was recrystallised from ethanol. The similar procedure was adopted for the compounds 6b–6g.

6a: Yield: 72%. C₁₉H₁₉N₅O₃: C, 62.46; H, 5.24; N, 19.17; found: C, 62.37; H, 5.29; N, 19.09. FT–IR (KBr pellet) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3142 (triazole C–H), 2948 (alkyl –CH), 1597 (aromatic C=C), 1425 (–N=N–). \(^1\)H NMR (CDCl₃, \( \delta/\text{ppm} \): 8.08 (d, 2H, ArH), 8.06 (s, 1H, triazole-H), 7.97 (d, 2H, ArH), 7.90 (d, 2H, ArH), 7.25 (d, 2H, ArH), 4.70 (s, 2H, ArOCH₂), 3.48 (s, 3H, –OCH₃), 2.59 (t, 2H, –CH₂), 1.79–1.81 (m, 2H, –CH₂), 1.37–1.40 (m, 2H, CH₂), 0.89 (t, 3H, –CH₃). \(^{13}\)C NMR (CDCl₃) \( \delta/\text{ppm} \): 171.9, 153.2, 152.0, 149.9, 146.2, 138.4, 124.3, 122.3, 120.87, 120.45, 66.0, 58.5, 34.4, 31.8, 14.1.

6b: Yield: 67%. C₂₁H₂₃N₅O₃: C, 64.11; H, 5.89; N, 17.80; found: C, 64.21; H, 5.93; N, 17.77. FT–IR (KBr pellet) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3142 (triazole C–H), 2947 (alkyl –CH), 1592 (aromatic C=C), 1425 (–N=N–). \(^1\)H NMR (CDCl₃, \( \delta/\text{ppm} \): 8.08 (d, 2H, ArH), 8.06 (s, 1H, triazole-H), 7.97 (d, 2H, ArH), 7.90 (d, 2H, ArH), 4.99 (s, 2H, ArOCH₂), 3.48 (s, 3H, –OCH₃), 2.59 (t, 2H, –CH₂), 1.79–1.84 (m, 4H, –CH₂), 1.37–1.40 (m, 2H, CH₂), 0.89 (t, 3H, –CH₃). \(^{13}\)C NMR (CDCl₃) \( \delta/\text{ppm} \): 171.9, 153.2, 152.0, 149.9, 146.2, 138.4, 124.3, 122.3, 120.87, 120.45, 66.0, 58.5, 34.4, 31.8, 29.4, 29.1, 14.1.

6c: Yield: 67%. C₂₃H₂₇N₅O₃: C, 65.54; H, 5.64; N, 16.62 found C, 65.59; H, 6.41; N, 16.66. FT–IR (KBr pellet) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3142 (triazole C–H), 2947 (alkyl –CH), 1592 (aromatic C=C), 1425 (–N=N–), 1121, 1157 (triazole –N=N–), 1186 (–OCH₃—). \(^1\)H NMR (CDCl₃, \( \delta/\text{ppm} \): 8.08, 8.06 (d, 2H, ArH), 8.06 (s, 1H, triazole-H), 7.97 (d, 2H, ArH), 7.90 (d, 2H, ArH), 7.25 (d, 2H, ArH), 4.99 (s, 2H, ArOCH₂), 3.48 (s, 3H, –OCH₃), 2.59 (t, 2H, –CH₂), 1.79–1.84 (m, 4H, –CH₂), 1.37–1.40 (m, 2H, CH₂), 0.89 (t, 3H, –CH₃). \(^{13}\)C NMR (CDCl₃) \( \delta/\text{ppm} \): 171.9, 153.2, 152.0, 149.9, 146.2, 138.4, 124.3, 122.3, 120.87, 120.45, 66.0, 58.5, 34.4, 31.8, 29.4, 29.1, 14.1.

Scheme 1. Synthesis of compounds 6a–6f. Reagents and conditions: (i) (CH₃)₂SO₄, NaOH at 60°C; (ii) HCl, NaNO₂, NaN₃; (iii) CuI, THF; (iv) Fe, NH₄Cl, ethanol reflux; (v) HCl, NaNO₂, NaOH, phenol and (vi) CₙH₂ₙ₊₁COCl, TEA, THF, r.t.
ArH), 7.90 (d, 2H, ArH), 7.25 (d, 2H, ArH), 4.99 (s, 2H, ArOCH3), 3.48 (s, 3H, –OCH3), 2.59 (t, 2H, –CH2), 1.67–1.79 (m, 2H, –CH2), 1.3–1.42 (m, 12H, CH2), 0.89(t, 3H, –CH3). 13C NMR (CDCl3) δ/ppm: 171.9, 153.2, 152.0, 149.9, 146.2, 138.4, 124.3, 122.3, 120.87, 120.45, 66.0, 58.5, 34.4, 31.8, 29.4, 29.1, 24.6, 22.4, 14.1.

6d: Yield: 67%. C27H35N5O3: C, 67.90; H, 7.39; N, 15.58 found C, 66.93; H, 6.87; N, 14.99. FT–IR (KBr pellet) νmax/cm⁻¹: 3144 (triazole C–H), 2947 (alkyl –CH), 1593 (aromatic C=C), 1425 (–N=N=–), 1221, 1157 (triazole –N=N–), 1186 (–OCH2–). 1H NMR (CDCl3), δ/ppm: 8.08, 8.06(d, 2H, ArH and s, 1H, triazole-H merged together [Figure 2]), 7.97 (d, 2H, ArH), 7.90 (d, 2H, ArH), 7.25(d, 2H, ArH), 4.99 (s, 2H, ArOCH3), 3.48(s, 3H, –OCH3), 2.59(t, 2H, –CH2), 1.67–1.79 (m, 2H, –CH2), 1.3–1.44 (m, 12H, CH2), 0.89(t, 3H, –CH3). 13C NMR (CDCl3) δ/ppm: 171.9, 153.2, 152.0, 149.9, 146.2, 138.4, 124.3, 122.3, 120.87, 120.45, 66.0, 58.5, 34.4, 31.8, 30.9, 29.4, 29.2, 29.1, 24.8, 22.6, 14.1.

6e: Yield: 67%. C25H33N3O3: C, 66.79; H, 7.39; N, 14.66 found C, 67.94; H, 7.33; N, 14.50. FT–IR (KBr pellet) νmax/cm⁻¹: 3143 (triazole C–H), 2947 (alkyl –CH), 1592 (aromatic C=C), 1425 (–N=N=–), 1222, 1157 (triazole –N=N–), 1186 (–OCH2–). 1H NMR (CDCl3), δ/ppm: 8.08, 8.06 (d, 2H, ArH and s, 1H, triazole-H merged together), 7.97 (d, 2H, ArH), 7.90 (d, 2H, ArH), 7.25 (d, 2H, ArH), 4.70 (s, 2H, ArOCH3), 3.48 (s, 3H, –OCH3), 2.59 (t, 2H, –CH2), 1.67–1.79 (m, 2H, –CH2), 1.3–1.44 (m, 16H, CH2), 0.89 (t, 3H, –CH3). 13C NMR (CDCl3) δ/ppm: 171.9, 153.2, 152.1, 150.0, 146.3, 138.4, 124.3, 122.3, 120.87, 120.45, 66.0, 58.5, 34.4, 31.9, 29.6, 29.4, 29.2, 29.1, 24.9, 23.4, 22.6, 14.1.

3. Results and discussion

The target molecule designed as the photo switchable azobenzene is connected to 1,2,3-triazole ring at one end and the other terminal was attached by variable alkanoyloxy chain. The transition temperatures and corresponding enthalpies are summarised in Table 1. The representative DSC thermogram has been shown in Figure 1. All compounds exhibit enantiotropic mesomorphism. The lower homologue 6a shows SmA phase on heating and cooling cycles (Figure 2a). On cooling from the isotropic, SmA phase formed at 199.9°C and crystallised at 107.2°C. The compounds 6b–6f exhibit enantiotropic SmA phase and monotropic SmC phase. Among these compounds, 6b shows focal conic fan texture of SmA phase on heating cycle (Figure 2b). On cooling from the isotropic, it exhibits SmA phase at 191.1°C. Further cooling entails the SmA–SmC phase transition and crystallisation at 106.5°C and 99.8°C, respectively. The curve associated with the SmA–SmC transition was not observed by the differential scanning colorimetry as it possesses very low enthalpy value. The compounds 6e and 6d show SmA and SmC phases on cooling from isotropic. The enthalpy values associated with the SmA–SmC transition in compounds 6c and 6d are 1.3 kJ mol⁻¹ and 0.2 kJ mol⁻¹, respectively. The representative photomicrographs for SmA and SmC phases for compound 6d are shown in Figures 2c and 2d. The SmA–SmC phase transition for compounds 6e and 6f are not observable in DSC thermogram. But the typical focal conic texture of SmA phase and broken focal conic texture of SmC phases can be observed by polarised optical microscopy (POM) on slow cooling rate of 2°C/min. The higher homologue 6g shows enantiotropic SmC phase on heating and cooling. It melts at 120.7°C and no birefringence was observed on further heating. On cooling from the isotropic phase the same observation is recorded. However, the dark region forms birefringence at different position in the microscopy slide.
This phenomenon is due to the homeotropic alignments of the molecules. In order to confirm the mesophase, homogeneously aligned cell was used for POM observation. It can be noticed that the compound 6g possesses focal conic fan texture surrounded by threads (Figure 4) on cooling from isotropic liquid. The smectogenic nature of the series was not affected by changing the terminal chain length from C3H7 to C15H31. Hence, we can say that in this series the lower and higher homologues are also inclined to form smectogens and this can be attributed to the presence of 1,2,3-triazole ring. From the molecular viewpoint, one end of the azobenzene possesses three electronegative N atom residing in triazole ring while the other side of azobenzene consists of one electronegative O which linked to the alkanoloxy chain. As such, it increases the polarisation of the entire molecules which in turn favours the formation of smectogen.

The correlation plot of transition temperature and terminal chain lengths (n) are summarised in Figure 5. It clearly shows that there is no drastic difference in melting temperature (Tm) and isotropic

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temperature \(T_i\) on increasing chain length from \(\text{C}_3\text{H}_7\) to \(\text{C}_{13}\text{H}_{27}\) (members with odd numbers only), whereas the isotropic temperature decreases for \(\text{C}_{15}\text{H}_{31}\) containing compound. In these homologues, the SmA phase possesses very large mesomorphic temperature range but SmC possesses very short range. The stabilisation of smectic phase for the compounds having a long chain can obviously be attributed to the weakening of the terminal intermolecular interactions.\[23–25\] The SmA-I phase transitional entropies \(\Delta S_{\text{SmA-I}}\) for compounds \(6a–6g\) are demonstrated in dimensionless quantity, \(\Delta S/R\) as listed in Table 1. The dependence of these entropy values on the number of carbon atom is illustrated in

Figure 2. Photomicrographs of the textures of (a) SmA phase of compound \(6a\) at 150°C, (b) SmA phase of compound \(6b\) at 155°C, (c) SmA phase of compound \(6d\) at 140°C, (d) SmC phase of compound \(6d\) at 108°C, (e) SmA phase of compound \(6e\) at 130°C and (f) SmC phase of compound \(6e\) at 110°C.

Figure 3. Photomicrographs of the broken fan texture of homeotropically aligned SmC phase of (a) compound \(6f\) at 115°C and compound \(6g\) at 140°C.

Figure 4. Photomicrographs of the textures observed in homogeneously aligned cell (cell thickness \(d = 5 \pm 0.2 \mu\text{m}\)): (a) SmC phase at 115°C, (b) SmC phase at 140°C.
Figure 6. It can be noticed that the change in entropy gradually increases with the lengthening of the terminal chain from C₃H₇ to C₁₃H₂₇ and the drastic decrease is observed for the analogue with C₁₅H₃₁.

A comparison between the target compounds and previously reported analogues such as 4-[(4-[4-(methoxymethyl)-1H-1,2,3-triazol-1]phenyl)-diazenyl]-1-(heptyloxy)benzene (Ib) and 4-[(4-[methoxymethyl]-1H-1,2,3-triazol-1]phenyl)-diazenyl]-1-(nonyloxy)benzene (Id) [22] has also been carried out to determine the effect of ester linkage on the mesogen. The transition temperatures of these compounds are listed in Table 2. It can be seen that the compounds Ib and Id exhibit SmA phase. The present target compounds 6c and 6d exhibit monotropic SmA and enantiotropic SmA and SmC phases, respectively. Moreover, these compounds possess homeotropic alignment.

The difference of the earlier reported compounds (Ib and Id) [22] in comparison to the present compounds (6c and 6d) can be attributed to the presence of ester linkage connecting the terminal flexible chain. The interaction between the carbonyl oxygen and the aromatic proton led to the restriction of free rotation about the flexible chain. As a result, the aspect ratios for 6c and 6d are found to be higher than the Ib and Id.[22] As such, it promotes the smectogenic behaviour of the present compounds.

4. Conclusion
A series of new azobenzene derivatives with 1, 2, 3-triazole and variable terminal chain length (CₙH₂ₙ₊₁, where n adopt 3–15 odd numbers only) was synthesised. All the compounds possess mesomorphic properties. The lower homologue (n = 3)
exhibits enantiotropic SmA phase and the other homologues \((n = 5–13)\) exhibit enantiotropic SmA phase and monotropic SmC phase. However, the higher homologue \((n = 15)\) exhibits enantiotropic SmA and SmC phases. Interestingly, the higher homologues of the series display homeotropic alignment. The length of the terminal chain is claimed as one of the determining factors towards the formation of mesophase.

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**Supplementary data**

Supplementary data for this article can be accessed here.

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