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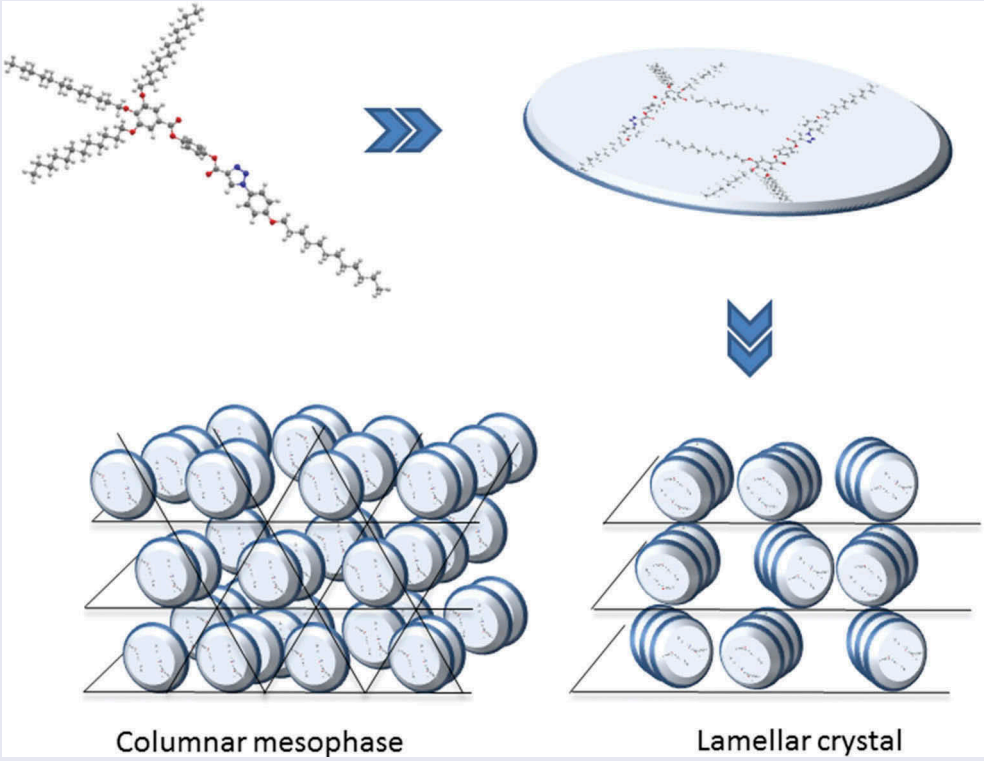
Synthesis and mesomorphic behaviour of unsymmetrical tetracatenar [1,2,3]-triazole derivatives

Soraya Benallou[a], Salima Saidi-Besbes[a], Eric Grelet[b], Ahmed Bentaleb[b], Abdelhamid Elaissari[c], Géraldine Agusti[c] and Aicha Derdour[a]

[a]Laboratoire de Synthèse Organique Appliquée (LSOA), Département de chimie, Faculté des sciences exactes et appliquées, Université Oran 1 Ahmed Benbella, BP1524 ELMnaouer, 31000 Oran, Algeria; [b]Centre de Recherche Paul-Pascal, CNRS UPR 8641, Université de Bordeaux, F-33600 Pessac, France; [c]Université Lyon-1, Villeurbanne, CNRS, UMR-5007, LAGEP-CPE, F-69622 Villeurbanne, France

ABSTRACT

New nonsymmetric four-chained and three-chained [1,2,3]-triazole derivatives were synthesised. Their phase behaviours were investigated by differential scanning calorimetry, polarised optical microscopy and X-ray diffraction analyses. The tetracatenar derivatives show a columnar mesophase and a lamellar crystalline phase. The effects of the length of the terminal alkoxy chain and the nature of the terminal group attached to the side phenyltriazole unit of the mesogenic core are discussed.



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1. Introduction

Heterocyclic mesogenic derivatives are very attractive for the achievement of thermotropic liquid crystalline phases. The polar heterocyclic core is able to induce a lateral and/or longitudinal dipole and a deviation from linearity leading to lower melting points with respect to classical 1,4-phenylene derivatives.[1–5]

CONTACT Saidi-Besbes Salima saidi.salima@univ-oran.dz; salima_saidi@yahoo.fr

Saidi-Besbes Salima designed the research, Soraya Benallou and Aicha Derdour synthesized the compounds and performed the spectroscopic characterizations, Eric Grelet and Ahmed Bentaleb performed the X-ray diffraction experiments, Eric Grelet, Abdelhamid Elaissari and Géraldine Agusti performed the DSC analyses. Saidi-Besbes Salima and Eric Grelet interpreted the experiments and wrote the paper.
Supplemental data for this article can be accessed here.

[1,2,3]-Triazole as a structural unit is gaining more and more importance for the preparation of mesomorphic compounds.[6–8] This non-natural heterocycle containing three nitrogen atoms is widely used for material and supramolecular applications and in pharmaceutical industry.[9,10] It combines multiple interesting properties including high chemical and thermal stabilities, a strong dipole moment, an aromatic character and a good hydrogen-bond-accepting ability.[11] The great revival experienced in the synthesis of [1,2,3]-triazole compounds in the form of the copper-catalysed Huisgen cycloaddition allows for obtaining various functionalized triazole derivatives in a versatile way.[12]

It was reported that the position of the triazole ring within the rigid core and the nature of the substituents attached to the latter are two main parameters governing the type and the stability of obtained mesophases.[13–15] For example, Gimeno et al. reported that 1,4-disubstituted [1,2,3]-triazole compounds, where the heterocyclic synthon is linked to a methylene or methylenoxycarbonyl group, exhibit a varied polymorphism ranging from lamellar to columnar or B4-like supramolecular liquid crystalline organisations.[16] The presence of a [1,2,3]-triazole ring promotes well-built intermolecular interactions.

Recently, we studied the effect of the connector group attached to triazole synthon on the mesomorphic behaviour of several 1,4-disubstituted [1,2,3]-triazole-based compounds. It was noted that the introduction of an ester connector group within the triazole heterocycle generates enough dipole which promotes the arrangement of molecules in stable smectic A layer structures over a wide thermal range and this is despite the linearity deviation caused by the triazole core of about 148.9°.[17]

The introduction of a double bond within the triazole core allowed us to tune both the transition temperatures and the nature of calamitic mesophases.[18] Extended conjugated systems were achieved which can potentially act as electron-transporting materials. The mesomorphic behaviour was found to be related to the nature (*E*/*Z*) of the double bond. Compounds with a trans double bond were more conductive to liquid crystalline packing and induced significantly higher stable smectic A mesophase and higher melting points.

Till date, only few polycatenar liquid crystalline derivatives containing triazole unit have been reported. For example, hexacatenar molecules based on a [1,2,3]-triazole-extended aromatic rod self-assemble into liquid crystalline hexagonal columnar structures depending on temperature.[19] If the terminal benzene rings are not directly conjugated to triazolyl groups, 2-D oblique columnar mesophase was achieved.[20]

We were interested in this work due to the design and the liquid crystalline behaviour of unsymmetrical tetracatenar triazole derivatives containing a phenyltriazole core substituted with just one alkoxy chain on one side and trialkoxy gallic acid group on the other side. These derivatives could be regarded as an intermediate of calamitic and discotic mesogens. Tricatenar homologues have also been investigated where the flexible alkoxy chain on the side of the phenyltriazole aromatic core was replaced by a polar group.

2. Experimental

2.1. Characterisation

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer (Wissembourg, France). Tetramethylsilane was used as an internal reference for chemical shifts. Infrared spectroscopies were carried out with a Jasco-4200 Fourier transform infrared spectrometer (Jasco Inc., Easton, MD, USA) using KBr pellets. Column chromatographies were carried out using Merck, Darmstadt silica gel (Kieselgel 60, 230–400 mesh) as the stationary phase (Merck Millipore, Gernsheim, Germany). Thin-layer chromatography was carried out on aluminium plates precoated with Merck silica gel $60F_{254}$ and visualised by means of ultraviolet fluorescence quenching or iodine vapour. The melting points, transition temperatures and phase transition enthalpies were determined using a differential scanning calorimetry (DSC Q200®, TA Instruments, New Castle, DE, USA) at a heating rate of 5°C/min. Mesomorphic textures were observed using a Zeiss Scope A1 polarising microscope equipped with Mettler Toledo heating stage.

X-ray diffraction (XRD) experiments were performed by using a rotating anode generator (Rigaku Nanoviewer MicroMax 007HF), coupled to a confocal Max-Flux® Osmic mirror (Applied Rigaku Technologies, Austin, TX, USA) producing beam with a wavelength of 1.54 Å together with a homemade heating stage with a thermal stability of 0.1°C. The spectra were recorded with a bi-dimensional detector (MARResearch-345, Marresearch GmbH, Norderstedt, Germany) located at 309 and 172 mm, respectively, from the sample. The latter distance at wider angles aims to hide the very intense first-order Bragg reflections in the beam stop in order to improve the contrast of higher-order Bragg reflections for determining the nature of the mesophases. All samples were introduced as a powder in glass capillary tubes (Glas, Muller, Germany) having a diameter of 1.5 mm. The spectra

were analysed using FIT2D software (ESRF; http://www.esrf.eu/).

2.2. Synthesis

All the reagents were purchased from Aldrich (Prochima Sigma, Tlemcen, Algeria) and used as received. The solvents were of commercial grade quality and were dried and distilled before use. Methylene chloride was distilled over calcium hydride.

1-*p*-Methoxyphenyl-1-H-[1,2,3]-triazole 4-carboxylic acid (5a), 1-*p*-nitrophenyl-1-H-[1,2,3]-triazole 4-carboxylic acid (5b) and 1-*p*-bromophenyl-1-H-[1,2,3]-triazole 4-carboxylic acid (5c) were prepared according to our previous study.[17] 4-(*tert*-butyldimethylsilyloxy)phenol was synthesised from hydroquinone and *tert*-butyldimethylchlorosilane (TBDSCl) as described in Reference [21].

2.2.1. N-(4-(alkyloxy)phenyl)acetamide (1a–d)

A mixture of (9.16 mmol) of 4-aminophenol, 1.1 ml of acetic anhydride and 3 ml of distilled water is stirred under reflux during 5 h (the reaction is controlled by thin layer chromatography). The reaction mixture is then cooled with an ice bath until the formation of precipitate. The solid is filtered, washed with a minimum of cold water then recrystallized in a mixture of distilled water/methanol (1/1) to give the *N*-(4-hydroxyphenyl)acetamide in the form of white crystals.

Yield: 86%, m.p. 172°C (170°C) [22], IR (KBr) ν/cm^{-1}: 3300 (O−H), 3243 (N−H), 1656 (C−O).

N-(4-hydroxyphenyl)acetamide (9.92 mmol) is then reacted with 14.6 mmol of the appropriate alkylbromide in the presence of 19 mmol of K_2CO_3 in 30 ml of butanone. After stirring for 48 h under reflux, the reaction mixture was filtered and washed 2–3 times with hot butanone. The filtrate is evaporated then purified by recrystallization from heptane to give a white powder.

N-(4-(octyloxy)phenyl)acetamide (1a)

Yield: 74%, m.p. 89°C, ^{1}H NMR ($CDCl_3$): 0.89 (t, 3H, CH_3, ^3J = 6.88 Hz), 1.30 (m, 8H, $C_2H_5(CH_2)_4$), 1.44 (m, 2H, CH_3CH_2), 1.75 (m, 2H, CH_2CH_2O), 2.09 (s, 3H, $COCH_3$), 3.91 (t, 2H, CH_2O, ^3J = 6.55 Hz), 6.82 (d, 2H, Ar–H, ^3J = 8.6 Hz), 7.35 (d, 2H, Ar–H, ^3J = 8.6 Hz), 7.58 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): 14.06, 22.68, 24.19, 26.14, 29.42, 31.88, 68.58, 115.02, 122.11, 131.19, 156.24, 168.44.

N-(4-(decyloxy)phenyl)acetamide (1b)

Yield: 73%, m.p. 92°C, ^{1}H NMR ($CDCl_3$): 0.87 (t, 3H, CH_3, ^3J = 6.96 Hz), 1.26 (m, 12H, $C_2H_5(CH_2)_6$), 1.42 (m, 2H, CH_3CH_2), 1.74 (m, 2H, CH_2CH_2O), 2.10 (s, 3H, $COCH_3$), 3.89 (t, 2H, CH_2O, ^3J = 6.59 Hz), 6.80 (d, 2H, Ar−H, ^3J = 8.97 Hz), 7.35 (d, 2H, Ar–H, ^3J = 8.97 Hz), 7.81 (s, 1H, N*H*). ^{13}C NMR ($CDCl_3$): 14.06, 22.62, 23.91, 26.96, 29.50, 31.83, 68.17, 114.57, 121.92, 130.81, 155.87, 168.57.

N-(4-dodecyloxy)phenyl)acetamide (1c)

Yield: 72%, m.p. 94°C, IR (KBr) ν/cm^{-1}: 3312 (N−H), 1640 (C=O). ^{1}H NMR ($CDCl_3$): 0.87 (t, 3H, CH_3, ^3J = 6.91 Hz), 1.25 (m, 16H, $C_2H_5(CH_2)_8$), 1.42 (m, 2H, CH_3CH_2), 1.74 (m, 2H, CH_2CH_2O), 2.11 (s, 3H, $COCH_3$), 3.89 (t, 2H, CH_2O, ^3J = 6.58 Hz), 6.80 (d, 2H, Ar−H, ^3J = 8.97 Hz), 7.35 (d, 2H, Ar−H, ^3J = 8.97 Hz), 7.68 (s, 1H, N*H*). ^{13}C NMR ($CDCl_3$): 14.17, 22.72, 24.27, 26.05, 29.44, 31.94, 68.25, 114.67, 121.98, 130.84, 155.97, 168.56.

N-(4-(tetradecyloxy)phenyl)acetamide (1d)

Yield: 80%, m.p. 98°C, ^{1}H NMR ($CDCl_3$): 0.87 (t, 3H, CH_3, ^3J = 6.92 Hz), 1.25 (m, 20H, $C_2H_5(CH_2)_{10}$), 1.42 (m, 2H, CH_3CH_2), 1.75 (m, 2H, CH_2CH_2O), 2.13 (s, 3H, $COCH_3$), 3.90 (t, 2H, CH_2O, ^3J = 6.59 Hz), 6.82 (d, 2H, Ar−H, ^3J = 9.00 Hz), 7.35 (d, 2H, Ar−H, ^3J = 9.00 Hz), 7.40 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): 14.17, 22.73, 24.34, 26.05, 29.61, 31.95, 68.26, 114.70, 121.94, 130.74, 156.00, 168.39.

2.2.2. 4-(Alkyloxy)benzenamine (2a–d)

In a round-bottom flask 6.15 mmol of the appropriate *N*-(4-(alkyloxy)phenyl) acetamide and 20 ml of distilled water were charged. The mixture is heated until reflux under stirring then 11 ml of concentrated hydrochloric acid (37%) was added. The stirring is maintained at 110°C for 48 h. After cooling to room temperature, a solution of NaOH (1 M) was added to the reaction mixture until a basic pH. The formed precipitate is filtered then washed abundantly with distilled water.

4-(Octyloxy)benzenamine (2a)

Yield: 90%, m.p. 40°C, IR (KBr) ν/cm^{-1}: 3347 (N−H), 1155 (C−O), ^{1}H NMR ($CDCl_3$): 0.90 (t, 3H, CH_3, ^3J = 6.95 Hz), 1.31 (m, 8H, $C_2H_5(CH_2)_4$), 1.44 (m, 2H, CH_3CH_2), 1.74 (m, 2H, CH_2CH_2O), 3.36 (s, 2H, NH_2), 3.88 (t, 2H, CH_2O, ^3J = 8.88 Hz), 6.62 (d, 2H, Ar−H, ^3J = 8.90 Hz), 6.74 (d, 2H, Ar−H, ^3J = 8.90 Hz). ^{13}C NMR ($CDCl_3$): 14.11, 22.75, 26.23, 29.51, 31.95, 69.11, 116.08, 116.59, 140.09, 152.68.

4-(Decyloxy)benzenamine (2b)

Yield: 94%, m.p. 52°C, ^{1}H NMR ($CDCl_3$): 0.90 (t, 3H, CH_3, ^3J = 6.82 Hz), 1.28 (m, 12H, $C_2H_5(CH_2)_6$), 1.44 (m, 2H, CH_3CH_2), 1.75 (m, 2H, CH_2CH_2O), 3.36 (s, 2H, NH_2), 3.88 (t, 2H, CH_2O, ^3J = 6.58 Hz), 6.63 (d, 2H, Ar−H, ^3J = 8.68 Hz), 6.74 (d, 2H, Ar−H, ^3J = 8.68 Hz). ^{13}C NMR ($CDCl_3$): 14.05, 21.61, 26.00, 29.00, 31.82, 68.58, 115.53, 116.41, 130.52, 152.30.

4-(Dodecyloxy)benzenamine (2c)
Yield: 92%, m.p. 58°C, ^{1}H NMR ($CDCl_3$): 0.90 (t, 3H, CH_3, ^3J = 6.95 Hz), 1.28 (m, 16H, $C_2H_5(CH_2)_8$), 1.44 (m, 2H, CH_3CH_2), 1.75 (m, 2H, CH_2CH_2O), 3.21 (s, 2H, NH_2), 3.88 (t, 2H, CH_2O, ^3J = 6.61 Hz), 6.62 (d, 2H, Ar−H, ^3J = 8.92 Hz), 6.74 (d, 2H, Ar−H, ^3J = 8.92 Hz). ^{13}C NMR ($CDCl_3$): 14.05, 22.61, 25.99, 29.36, 31.84, 68.57, 115.52, 116.31, 139.71, 152.21.
4-(Tetracyloxy)benzenamine (2d)
Yield: 91%, m.p. 60°C, ^{1}H NMR ($CDCl_3$): 0.89 (t, 3H, CH_3, ^3J = 6.84 Hz), 1.28 (m, 20H, $C_2H_5(CH_2)_{10}$), 1.44 (m, 2H, CH_3CH_2), 1.75 (m, 2H, CH_2CH_2O), 5.40 (s, 2H, NH_2), 3.89 (t, 2H, CH_2O, ^3J = 6.39 Hz), 6.76 (d, 2H, Ar−H, ^3J = 9.00 Hz), 6.88 (d, 2H, Ar−H, ^3J = 9.00 Hz). ^{13}C NMR ($CDCl_3$): 14.00, 22.65, 26.08, 29.33, 31.92, 68.84, 115.86, 119.15, 134.17, 154.87.

2.2.3. 4-Azido-1-alkyloxybenzene (3a–d)

4-Azido-1-(octyloxy)benzene (3a), 4-azido-1-(decyloxy)benzene (3b), 4-azido-1-(dodecyloxy)benzene (3c), 4-azido-1-(tetradecyloxy)benzene (3d) were prepared according to a modified Nolting and Michel method.[23]

In a general procedure, 45.2 mmol of the appropriate 4-(alkyloxy)benzenamine (2a–d), 30 ml of water and 30 ml of concentrated hydrochloric acid (35%) were placed in a two-necked round-bottom flask. The mixture is cooled at 0–5°C using an ice bath, then stirred for 20–30 min. A solution of 47.8 mmol of nitrite azide solubilized in 10 ml of distilled water is then added dropwise and the stirring is maintained for 20 min. Finally, 46.6 mmoles of sodium azide dissolved in 10 ml of water is added. The reaction mixture is vigorously stirred for an additional 1 h. The mixture is transferred to a separator funnel and the organic phase is separated. The aqueous phase is extracted four times with diethyl ether. The organic phases are gathered and dried under Na_2SO_4, then the solvent is evaporated and the obtained product is purified by flesh column chromatography using hexane as eluent.
4-Azido-1-(octyloxy)benzene (3a)
Yield: 81%, yellow oil, IR (KBr) ν/cm^{-1}: 2111 (azide function), ^{1}H NMR ($CDCl_3$): 0.88 (t, 3H, CH_3, ^3J = 6.89 Hz), 1.27 (m, 10H, $CH_3(CH_2)_5$), 1.77 (tt, 2H, CH_2CH_2O, ^3J = 6.45 Hz, ^3J = 8.19 Hz), 3.92 (t, 2H, CH_2O, ^3J = 6.45 Hz), 7.00 (m, 4H, Ar−H), ^{13}C NMR ($CDCl_3$): 14.06, 22.63, 25.79, 29.21, 31.77, 70.25, 116.09, 119.91, 132.49, 156.60.
4-Azido-1-(decyloxy)benzene (3b)
Yield: 78%, yellow oil, ^{1}H NMR ($CDCl_3$): 0.91 (t, 3H, CH_3, ^3J = 6.95 Hz), 1.30 (m, 14H, $CH_3(CH_2)_7$), 1.79 (tt, 2H, CH_2CH_2O, ^3J = 6.55 Hz, ^3J = 8.05 Hz), 3.94 (t, 2H, CH_2O, ^3J = 6.56 Hz), 6.91 (m, 4H, Ar–H),), ^{13}C NMR ($CDCl_3$): 14.10, 22.68, 26.02, 29.57, 31.90, 68.45, 115.76, 119.93, 132.11, 156.60.
4-Azido-1-(dodecyloxy)benzene (3c)
Yield: 92%, yellow oil, ^{1}H NMR ($CDCl_3$): 0.90 (t, 3H, CH_3, ^3J = 6.92 Hz), 1.28 (m, 18H, $CH_3(CH_2)_9$), 1.79 (tt, 2H, CH_2CH_2O, ^3J = 6.53 Hz, ^3J = 8.06 Hz), 3.94 (t, 2H, CH_2O, ^3J = 6.56 Hz), 6.91 (m, 4H, Ar−H). ^{13}C NMR ($CDCl_3$): 14.10, 22.68, 26.01, 29.59, 31.91, 68.45, 115.77, 119.95, 143.27, 156.59.
4-Azido-1-(tetradecyloxy)benzene (3d)
Yield: 80%, brown oil, ^{1}H NMR ($CDCl_3$): 0.90 (t, 3H, CH_3, ^3J = 6.93 Hz), 1.28 (m, 22H, $CH_3(CH_2)_{11}$), 1.73 (tt, 2H, CH_2CH_2O,^3J = 6.70 Hz, ^3J = 7.76 Hz), 3.89 (t, 2H, CH_2O, ^3J = 6.70), 6.75 (m, 4H, Ar−H). ^{13}C NMR ($CDCl_3$): 14.10, 22.69, 26.07, 29.60, 31.92, 68.75, 115.70, 116.70, 148.02, 156.64.

2.2.4. 1-(4-Alkyloxyphenyl)-1-H-[1,2,3]-triazole-4-carboxylic acid (4a–d)

In a general procedure, one equivalent (4 mmol) of 4-azido-1-alkyloxybenzene (3a–d) and 1.1 equivalents (0.31 g, 4.4 mmol) of propargyl acid dissolved in 5 ml of acetone were stirred at 60°C for 24 h. After solvent evaporation, the residue was washed with diethyl ether to yield the desired 1,4-regioisomer (4a–c). It is possible to isolate the 1,5-regioisomer by evaporation of the filtrate and trituration of the obtained solid in hexane.

We present in the following section the NMR characterisation of only the 1,4-regioisomer derivatives (4a–d) used to carry out the synthesis of the final mesogenic derivatives.
1-(4-(Octyloxy)phenyl)-1-H-[1,2,3]-triazole-4-carboxylic acid (4a)
Total yield: 72%, isomer ratio (1,4)/(1,5): 62:38, m.p. (1,4)/(1,5): 190°C/70°C. IR (KBr) ν/cm^{-1}: 3420 (O−H), 3010 (C−H), 1603 (C=C), 1691 cm^{-1} (C=O), 1315 (C−O), ^{1}H NMR (DMSO d^6): 0.84 (t, 3H, CH_3, ^3J = 6.75 Hz), 1.24 (m, 10H, $CH_3(CH_2)_5$), 1.71 (tt, 2H, CH_2CH_2O, ^3J = 6.72 Hz, ^3J = 7.67 Hz), 4.02 (t, 2H, CH_2O, ^3J = 6.72 Hz), 7.13 (d, 2H, Ar–H, ^3J = 9.06 Hz), 7.83 (d, 2H, Ar–H, ^3J = 9.06 Hz), 9.26 (s, 1H, H_5-triazole), 12.37 (s, 1H, COOH). ^{13}C NMR (DMSO d^6): 14.38, 22.53, 25.93, 29.12, 31.69, 68.43, 115.77, 122.55, 127.22, 129.86, 140.99, 159.54, 162.06.

1-(4-(Decyloxy)phenyl)-1-H-[1,2,3]-triazole-4-carboxylic acid (4b)

Total yield: 88%, isomer ratio (1,4)/(1,5): 59:41, m.p. (1,4)/(1,5): 170°C/68°C, ^{1}H NMR (300 MHz, DMSO d^6): 0.83 (t, 3H, CH_3,^3J = 6.93 Hz), 1.22 (m, 14H, $CH_3(CH_2)_7$), 1.71 (tt, 2H, CH_2CH_2O, ^3J = 7.73 Hz, ^3J = 6.71 Hz), 4.01 (t, 2H, CH_2O, ^3J = 6,71 Hz), 7.12 (d, 2H, Ar−H, ^3J = 9.08 Hz), 7.83 (d, 2H, Ar−H, ^3J = 9.05), 9.26 (s, 1H, H_5-triazole), 12.26 (s, 1H, COOH). ^{13}C NMR (DMSO d^6): 14.36, 22.55, 25.92, 29.17, 31.76, 68.41, 115.75, 122.51, 127.19, 129.86, 140.95, 159.53, 162.04.

1-(4-(Dodecyloxy)phenyl)-1-H-[1,2,3]-triazole-4-carboxylic acid (4c)

Total yield: 68%, isomer ratio (1,4)/(1,5): 68:32, m.p. (1,4)/(1,5): 165°C/74°C. ^{1}H NMR (300 MHz, DMSO d^6): 0.85 (t, 3H, ^3J = 6.75 Hz), 1.22 (m, 18H, $CH_3(CH_2)_9$), 1.72 (tt, 2H, CH_2CH_2O, ^3J = 7.04 Hz, ^3J = 6.33 Hz), 4.02 (t, 2H, CH_2O, ^3J = 6.33), 7.12 (d, 2H, Ar−H, ^3J = 9.10 Hz), 7.83 (d, 2H, Ar−H, ^3J = 9.07 Hz), 9.26 (s, 1H, H_5-triazole), 12.26 (s, 1H, COOH). ^{13}C NMR (DMSO d^6): 14.39, 22.55, 25.90, 29.48, 31.76, 68.43, 115.79, 122.57, 127.25, 129.06, 140.93, 159.55, 162.04.

1-(4-(Tetradecyloxy)phenyl)-1-H-[1,2,3]-triazole-4-carboxylic acid (4d)

Total yield: 60%, isomer ratio (1,4)/(1,5): 72:28, m.p. (1,4)/(1,5): 180°C/78°C. ^{1}H NMR (DMSO d^6): 0.85 (t, 3H, ^3J = 6.82), 1.23 (m, 22H, $CH_3(CH_2)_{11}$), 1.73 (tt, 2H, CH_2CH_2O, ^3J = 7.76 Hz, ^3J = 6.65 Hz), 4.04 (t, 2H, CH_2O, ^3J = 6.48 Hz), 7.11 (d, 2H, Ar−H, ^3J = 9.08Hz), 7.83 (m, 2H, Ar−H, ^3J = 9.04 Hz), 9.26 (s, 1H, H_5-triazole), 12.26 (s, 1H, COOH).

2.2.5. 3,4,5-Tris(dodecyloxy)benzoic acid (6)

2.2.5.1. Synthesis of methyl 3,4,5-tris(dodecyloxy) benzoate. A quantity of 24.9 g (120 mmol) of potassium carbonate was added to 5.52 g (30 mmol) of methyl 1,2,3-trihydroxybenzoate dissolved in 200 ml of DMF. After stirring for 2 h at 60°C, 22.4 g (90 mmol) of 1-bromododecane was added dropwise. The stirring is maintained at the same temperature for 8 h. The mixture is cooled at room temperature then poured into 1 L of a mixture of water and ice. The obtained solid is isolated by filtration then recrystallized from acetone to give methyl 3,4,5-tris(dodecyloxy)benzoate in the form of a solid with 85% yield, m.p. 60°C.

^{1}H NMR ($CDCl_3$): 0.89 (t, 9H, CH_3, ^3J = 6.34 Hz), 1.27 (m, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, $CH_2C_2H_4O$), 1.79 (m, 6H, CH_2CH_2O), 3.88 (s, 3H, CH_3OCO), 4.00 (m, 6H, CH_2O), 7.24 (s, 2H, Ar−H).

2.2.5.2. Synthesis of 3,4,5-tris(dodecyloxy)benzoic acid (6). KOH (1.68 g, 30 mmol) was added to a solution of previously prepared methyl 3,4,5-tris(dodecyloxy) benzoate (7.81 g, 15 mmol) solubilized in ethanol. The resulting solution is refluxed under stirring for 2 h then cooled to room temperature. The reaction mixture is poured into 1 L of distilled water and then acidified with a diluted solution of hydrochloric acid (1 N) until pH of 1 is attained. A white precipitate is formed that was isolated by filtration to give compound (6) as a white solid; yield: 90%, m.p. 54°C.

^{1}H NMR ($CDCl_3$): 0.89 (t, 9H, CH_3, ^3J = 6.34 Hz), 1.27 (m, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, $CH_2C_2H_4O$), 1.79 (m, 6H, CH_2CH_2O), 4.00 (m, 6H, CH_2O), 7.30 (s, 2H, Ar–H), 10.93 (s, 1H, COOH). ^{13}C NMR ($CDCl_3$): 14.09, 22.69, 26.09, 29.64, 30.34, 31.93, 69.22, 73.56, 106.62, 123.67, 143.22, 152.86, 171.82.

2.2.6. Tricatenar alcohol (7)

*2.2.6.1. Synthesis of 4-(*tert*-butyldimethylsilyloxy)phenyl (3,4,5-tris(dodecyloxy)benzoate).* A two-necked round-bottom flask was charged with one equivalent (4.4 mmol) of 3,4,5-tris(dodecyloxy)benzoic acid (**6**), 1.1 equivalent (4.8 mmol) of 4-(*tert*-butyldimethylsilyloxy)-phenol, 1.1 equivalent (0.99 g, 4.8 mmol) of dicyclohexylcarbodiimide DCC and 0.1 equivalent (54 mg, 0.44 mmol) of 4-dimethylamino pyridine DMAP. The mixture was dissolved in a minimum of dichloromethane then stirred for 48 h at room temperature under nitrogen atmosphere. The crude mixture was filtered, washed with dichloromethane and then the filtrate was evaporated. The residual product was purified by column chromatography using dichloromethane as eluent. The *tert*-butyldimethylsilyloxy protected form of compound 7 is obtained as viscous yellow oil; yield: 81%.

^{1}H NMR ($CDCl_3$): 0.24 (s, 6H, CH_3Si), 0.91 (t, 9H, CH_3, ^3J = 6.83 Hz), 1.02 (s, 9H, *tert*-but), 1.30 (m, 54H, $CH_3(CH_2)_9$), 1.80 (m, 6H, CH_2CH_2O), 4.00 (t, 6H, CH_2O, ^3J = 6.42 Hz), 6.90 (d, 2H, Ar−H, ^3J = 8.95 Hz), 7.00 (d, 2H, Ar−H, ^3J = 8.95 Hz), 7.43 (s, 2H, Ar−H). ^{13}C NMR ($CDCl_3$): 0.4, 14.16, 18.19, 22.7, 25.67, 26.12, 29.32, 31.97, 69.18, 73.55, 108.41, 120.62, 122.43, 124.07, 142.08, 144.90, 152.93, 153.29, 165.29.

2.2.6.2. Deprotection. The deprotection of alcohol function of the previous synthesised product was carried out as follows: to 0.865 g (1 mmol) of 4-(*tert*-butyldimethylsilyloxyphenyl) 3,4,5-tris(dodecyloxy)benzoate was added 3 ml of methanol, then 11 µl (0.1 mmol) of acetyl chloride. The mixture was stirred at room temperature for 5 days (the reaction is controlled by TLC). Afterwards 20 ml of dichloromethane, 1 ml of $NaHCO_3$ (10%) and 10 ml of water were added. The organic phase was separated then dried under Na_2SO_4. The product is purified by column chromatography using dichloromethane then ethyl acetate

as eluents to give the compound (7) in the form of a yellow solid; yield: 65%, m.p. 87°C.

^{1}H NMR ($CDCl_3$): 0.89 (t, 9H, CH_3, ^3J = 6.79 Hz), 1.28 (m, 54H, $CH_3(CH_2)_9$), 1.82 (m, 6H, CH_2CH_2O), 4.00 (t, 6H, CH_2O, ^3J = 6.5 Hz), 6.00 (s, 1H, OH), 6.82 (d, 2H, Ar−H, ^3J = 8.85 Hz), 7.00 (d, 2H, Ar−H, ^3J = 8.85 Hz), 7.42 (s, 2H, Ar−H). ^{13}C NMR ($CDCl_3$): 14.15, 22.72, 18.19, 26.72, 29.73, 31.95, 69.22, 73.64, 106.43, 116.18, 122.57, 123.88, 142.83, 144.24, 152.9, 153.63, 165.88.

2.3. Synthesis of tetracatenar compounds (8a–d)

About 0.11 mmol of the appropriate triazole acid (4a–d), 0.12 mmol of tricatenar alcohol (7), 25 mg (0.12 mmol) of DCC and 1.2 mg (0.01 mmol) of DMAP were solubilized in the minimum of dry dichloromethane and then stirred for 2–3 days at room temperature under nitrogen atmosphere. The precipitate urea was removed by filtration, then the solvent was evaporated and the residual product was purified by column chromatography using a mixture of dichloromethane/ethyl acetate (20/0.5) as eluent.

8a. Yield: 38%, ^{1}H NMR ($CDCl_3$): 0.89 (t, 12H, CH_3, ^3J = 8.04 Hz), 1.28 (m, 64H, $CH_3(CH_2)_9$ of tridodecyloxy chain and $CH_3(CH_2)_5$ of octyloxy chain), 1.87 (m, 8H, OCH_2 $\underline{CH_2}$), 4.07 (t, 8H, OCH_2, ^3J = 6.67 Hz), 7.00 (d, 2H, Ar−H, ^3J = 9.07 Hz), 7.20 (m, 4H, Ar−H), 7.43 (s, 2H, Ar−H), 7.70 (d, 2H, Ar−H, ^3J = 9.03 Hz), 8.60 (s, 1H, H_5-triazole). ^{13}C NMR ($CDCl_3$): 14.15, 22.72, 26.10, 29.66, 31.95, 69.23, 73.00, 106.49, 115.49, 122.40, 122.60, 122.83, 123.60, 126.44, 129.34, 139.65, 143.02, 147.61, 148.70, 156.19, 164.88. ESI–HRMS [M + Cl]$^-$: calculated for $C_{66}H_{103}ClN_3O_8$: 1100.7439; found 1100.7401.

8b. Yield: 50%, ^{1}H NMR ($CDCl_3$): 0.89 (t, 12H, CH_3, ^3J = 8.04 Hz), 1.34 (m, 68H, $CH_3(CH_2)_9$ of tridodecyloxy chain and $CH_3(CH_2)_7$ of decyloxy chain), 1.86 (m, 8H, OCH_2-CH_2); 4.06 (t, 8H, OCH_2, ^3J = 6.67 Hz), 7.06 (d, 2H, Ar−H, ^3J = 9.07 Hz), 7.28 (d, 2H, Ar−H, ^3J = 9.18 Hz), 7.35 (d, 2H, Ar−H, ^3J = 9.20 Hz), 7.42 (s, 2H, Ar−H), 7.68 (d, 2H, Ar−H, ^3J = 9.03 Hz), 8.61 (s, 1H, H_5-triazole). ^{13}C NMR ($CDCl_3$): 14.15, 22.72, 26.10, 29.66, 31.95, 68.55, 73.60, 106.49, 115.48, 122.48, 122.61, 122.82, 123.65, 126.43, 129.34, 139.65, 143.02, 147.61, 148.7, 158.98, 164.88. ESI–HRMS [M + Cl]$^-$: calculated for $C_{68}H_{107}ClN_3O_8$: 1128.7752; found 1128.7758.

8c. Yield: 55%, ^{1}H NMR ($CDCl_3$): 0.90 (t, 12H, CH_3, ^3J = 8.04 Hz), 1.28 (m, 72H, $CH_3(CH_2)_9$ of tridodecyloxy chain and $CH_3(CH_2)_9$ of dodecyloxy chain), 1.87 (m, 8 H, OCH_2CH_2), 4.07 (t, 8H, OCH_2, ^3J = 6.67 Hz), 7.05 (d, 2H, Ar−H, ^3J = 9.07 Hz), 7.28 (d, 2H, Ar−H, ^3J = 9.16 Hz), 7.35 (d, 2H, Ar−H, ^3J = 9.18 Hz), 7.42 (s, 2H, Ar–H), 7.68 (d, 2H, Ar−H, ^3J = 9.03 Hz), 8.60 (s, 1H, H_5-triazole). ^{13}C NMR ($CDCl_3$): 14.15, 22.72, 26.10, 29.66, 31.95, 69.23, 73.00, 106.49, 115.49, 122.40, 122.60, 122.83, 123.60, 126.44, 129.34, 139.65, 143.02, 147.61, 148.7, 156.19, 164.88. ESI–HRMS [M + Cl]$^-$: calculated for $C_{70}H_{111}ClN_3O_8$: 1156.8065; found 1156.8071.

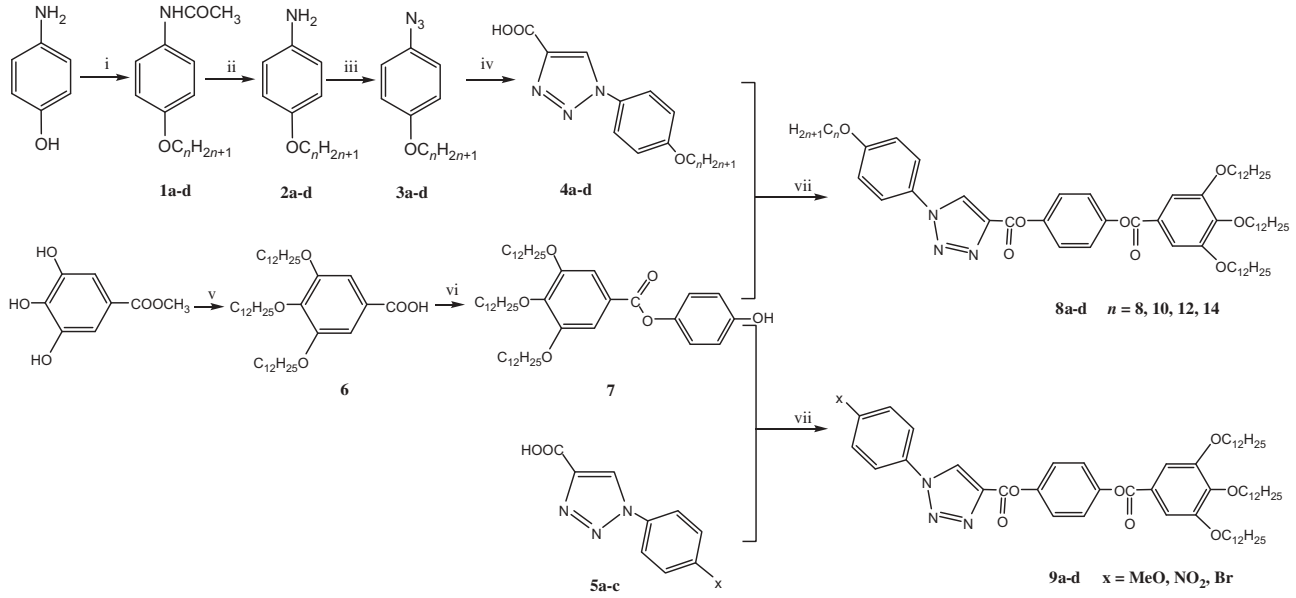
8d. Yield: 46%, ^{1}H NMR ($CDCl_3$): 0.90 (t, 12H, CH_3, ^3J = 8.04 Hz), 1.28 (m, 76H, $CH_3(CH_2)_9$ of tridodecyloxy chain and $CH_3(CH_2)_{11}$ of tetradecyloxy chain), 1.86 (m, 8H, OCH_2CH_2), 4.07 (t, 8H, OCH_2, ^3J = 6.67 Hz), 7.06 (d, 2H, Ar−H, ^3J = 9.07 Hz), 7.28 (d, 2H, Ar−H, ^3J = 9.19 Hz), 7.34 (d, 2H, Ar−H, ^3J = 9.17 Hz), 7.43 (s, 2H, Ar−H), 7.68 (d, 2H, Ar−H, ^3J = 9.03 Hz), 8.60 (s, 1H, H_5-triazole). ^{13}C NMR ($CDCl_3$): 14.15, 22.72, 26.10, 29.66, 31.95, 69.24, 73.60, 106.49, 115.49, 122.40, 122.60, 122.83, 123.60, 126.44, 129.34, 139.65, 143.02, 147.61, 148.7, 156.19, 164.88. ESI–HRMS [M + Cl]$^-$: calculated for $C_{72}H_{115}ClN_3O_8$: 1184.8378; found 1184.8416.

2.4. Synthesis of tricatenar compounds (9a–d)

These compounds were prepared by a similar procedure to that described for compounds (**8a–d**) from tricatenar alcohol (**7**) and triazole 4-carboxylic acid derivatives (**5a–c**)

9a. Yield: 43%, ^{1}H NMR ($CDCl_3$): 0.91 (t, 9H, CH_3, ^3J = 6.66 Hz), 1.28 (m, 54H, $CH_3(CH_2)_9$), 1.86 (m, 6H, OCH_2CH_2), 3.91 (s, 3H, CH_3), 4.07 (t, 6H, OCH_2, ^3J = 6.85 Hz), 7.07 (d, 2H, Ar−H, ^3J = 9.09 Hz), 7.28 (d, 2H, Ar−H, ^3J = 9.19 Hz), 7.34 (d, 2H, Ar−H, ^3J = 9.20 Hz), 7.42 (s, 2H, Ar−H), 7.70 (d, 2H, Ar−H, ^3J = 9.07 Hz), 8.61 (s, 1H, H_5-triazole). ^{13}C NMR ($CDCl_3$): 14.15, 22.70, 26.10, 29.70, 31.90, 55.70, 69.24, 73.61, 106.49, 115.03, 122.50, 122.60, 122.83, 123.64, 126.46, 139.70, 143.02, 148.02, 148.56, 152.96, 160.52, 164.02. ESI–HRMS [M + Cl]$^-$: calculated for $C_{59}H_{89}ClN_3O_8$: 1002.6344; found 1002.6305.

9b. Yield: 58%, ^{1}H NMR ($CDCl_3$): 0.9 (t, 9H, CH_3, ^3J = 6.63 Hz), 1.28 (m, 54H, $CH_3(CH_2)_9$), 1.86 (m, 6H, OCH_2CH_2), 4.07 (t, 6H, OCH_2, ^3J = 6.36 Hz), 7.30 (m, 4H, Ar−H), 7.43 (s, 2H, Ar−H), 8.00 (d, 2H, Ar−H, ^3J = 7.07 Hz), 8.46 (d, 2H, Ar−H, ^3J = 9.18 Hz), 8.87 (s, 1H, H_5-triazole). ^{13}C NMR ($CDCl_3$): 14.11, 22.69, 26.09, 29.64, 31.93, 69.29, 73.61, 106.59, 121.09, 122.47, 123.55, 125.74, 126.44, 140.00, 140.65, 143.17, 147.93, 148.95, 153.01, 158.46, 164.88. ESI–HRMS [M + Cl]$^-$: calculated for $C_{58}H_{86}ClN_4O_8$: 1017.6089; found 1017.6105.



Scheme 1. Reagents for the synthesis of triazole derivatives: (i) 1. Acetic anhydride, H_2O, 2. $C_nH_{2n+1}Br$ (n = 8, 10, 12, 14), K_2CO_3, butanone; (ii) HCl, H_2O; (iii) 1. HCl, $NaNO_2$, H_2O, 2. NaN_3, H_2O; (iv) propargylic acid, acetone; (v) $C_{12}H_{25}Br$, K_2CO_3, DMF; (vi) 1. 4-(*tert*-butyldimethylsilyloxy)phenol, DCC, DMAP, DCM, 2. Acetyl chloride, methanol; (vii) DCC, DMAP, DCM.

9c. Yield: 40%, ^{1}H NMR ($CDCl_3$): 0.90 (t, 9H, CH_3, ^3J = 6.66 Hz), 1.28 (m, 54H, $CH_3(CH_2)_9$), 1.85 (m, 6H, OCH_2CH_2), 4.07 (t, 6H, OCH_2, ^3J = 6.43 Hz), 7.30 (m, 4H, Ar−H), 7.42 (s, 2H, Ar−H), 7.74 (d, 4H, Ar−H, ^3J = 9.00 Hz), 8.66 (s, 1H, H_5-triazole).

3. Results and discussion

3.1. Synthesis

The triazole mesogens were synthesised according to the synthetic pathway illustrated in Scheme 1. The triazole acid derivatives bearing a long alkyloxy chain **4a–d** were prepared in four-stage process. The initial step involves the etherification of paracetamol with the appropriate alkylbromide compound in the presence of potassium carbonate. The amine group of compounds **1a–d** is then deprotected in a concentrated chlorhydric acid solution at reflux. The azido group was subsequently introduced using the Nolting and Michel method by the reaction of the *para*(oxyalkyl)aniline **2a–d** with sodium nitrite in HCl to accede to diazonium salts which were then transformed into the arylazide **3a–d** by the addition of sodium azide.

1H-[1,2,3]-triazole-4-carboxylic acids **4a–d** were obtained through an 1,3-dipolar cycloaddition of azides **3a–d** with propargylic acid in acetone at 60°C. Two regioisomers were obtained corresponding to the anti (1,4-triazole) and syn(1,5-triazole) with different proportions. The former compounds were easily separated by washing the reaction residues with diethyl ether. The evaporation of filtrates and the trituration of the obtained solid in hexane afford the 1,5-isomer.

The same reaction was also conducted in click reaction conditions in the presence of CuI and a catalytic amount of triethylamine in a mixture of water and ethanol as solvent at 70°C. Unfortunately, the reaction affords moderate yield and was not regioselective.

The tricatenar alcohol **7** was prepared by the reaction of methyl 3,4,5-trihydroxy benzoate with dodecylbromide in DMF in the presence of potassium carbonate. After hydrolysis, the resulting acid was reacted with 4-(*tert*-butyldimethylsilyloxy)phenol in the presence of DCC and DMAP. The deprotection of the alcohol function was then carried out with acetyl chloride in methanol at room temperature.

Finally the desired triazole-based mesogenic derivatives **8a–d** were obtained in moderate yields by an esterification reaction between **4a–d** and **7**.

Homologous triazole compounds **9a–c** with different polar groups (methoxy, nitro or bromo group) attached to the heterocyclic unit were also prepared from the corresponding triazole acid **5a–c** reported in a previous study.[17]

3.2. Mesomorphic properties

The mesomorphic behaviour of mesogenic compounds **8a–d** and **9a–c** was investigated by polarised optical microscopy (POM), DSC and X-ray scattering. The

Table 1. Transition temperatures (°C) and transition enthalpies Δ*H* (kJ/mole) of compounds **8a–d** and **9a–c** determined by DSC (heating rate: 5°C/min) during the second cycle.

Compound	R	Transitions temperatures (°C) [transition enthalpies Δ*H* (kJ/mole)]
8a	OC_8H_{17}	Cr (64.43)[99.89] I
8b	$OC_{10}H_{21}$	Cr (17.08)[21.17]Cr′ (75.15)[41.27] Col (84.03) [1.81] I
8c	$OC_{12}H_{25}$	Cr(18.58)[2.76]Cr′ (83.24)[45.91] Col (92.12)[3.061] I
8d	$OC_{14}H_{29}$	Cr(13.03)[15.82]Cr′(52.33)[17.05]Cr″ (81.07) [61.95] Col (98.99) [3.27] I
9a	OCH_3	Cr (81.62)[11.33] I
9b	NO_2	Cr (75.44)[28.34] Cr′(97.94)[10.97] Cr″(141.97) [42.67] I
9c	Br	Cr (74.27)[8.48] Cr′ (93.55)[64.02] I

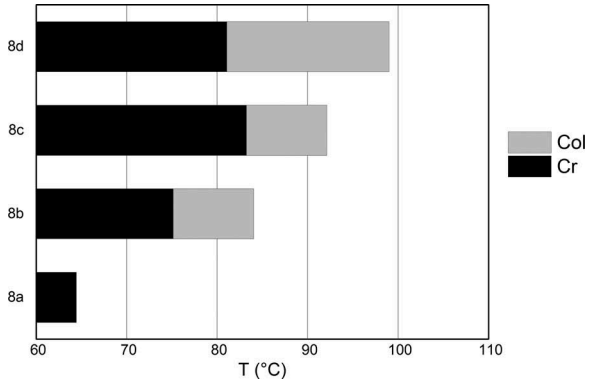


Figure 1. Comparative thermal behaviour of the final compounds **8a–d**.

phase transitions and thermodynamic data are summarised in Table 1 and in the bar-graph chart (Figure 1).

These data show that compounds with long alkyloxy chain (**8b–d**) exhibit an enantiotropic liquid crystalline mesophase. On cooling compounds **8b** and **8d** from the isotropic liquid (0.5°C/min), dendritic-like growth aggregates are formed leading to pseudo-focal conic fan-shaped textures or mosaic textures reminiscent of a columnar mesophase (Figure 2a–c and g–h). The low birefringence observed between two glass slides suggests homeotropic alignments. However, by pressing with a needle on the microscopic cover glass, it is possible to observe birefringence, although the molecules quickly reorient to the homeotropic alignment. Birefringence was also observed for samples prepared without a coversheet, suggesting in this case a planar or hybrid alignment.

The compound **8c** exhibits a distinct behaviour. Indeed, tiny batonnets developed from the isotropic liquid (Figure 2d) and grew up to the focal conic fan-shaped texture that can be regarded either as a lamellar or a columnar organisation. However, the fact that no growth of planar aligned columns was observed from the lamellar phase points rather to a columnar mesophase.

Homologous lollipop-shape structure, reported by Choi et al., containing two 1,3,4-oxadiazole moieties where the tricatenar part was directly attached to the rigid mesogenic core, having the general formula [2-(4-(dodecyloxy)phenyl)-5-(4-(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)-1,3,4-oxadiazole], showed a monotropical columnar mesophase.[24]

The mesomorphic temperature range tends to become wider with increasing alkoxy chain length (of about 9°C for **8b** and **8c** and around 18°C for **8d** on heating). This trend in liquid crystalline properties is commonly observed. An increase of the terminal chain length favours dipole–dipole interactions between those chains leading to more stable liquid crystalline phase of aligned molecules.

The clearing points are also influenced by the length of the flexible aliphatic chain. An increase of temperature transitions was observed for long alkoxy chains.

The homologous structures with shorter alkoxy chain (methoxy for **9a** and octyloxy for **8a**) or with polar terminal group (**9b** and **9c**) did not exhibit mesomorphic properties. The lack of liquid crystallinity indicates that a long alkoxy chain attached at the extremity of mesogen is essential of liquid crystalline phase formation probably through dipole–dipole interaction.

DSC analysis confirms the enantiotropic mesomorphic behaviour. The thermogram of compound **8d** is presented as an example in Figure 3 on the second heating and cooling run at a scanning rate of 5°C/min. DSC spectra of compounds **8b–d** during the first and second cycles with enthalpy values are given in the supplementary material. No crystallisation was observed for compounds **8b–d** when they were cooled to 25°C. Further cooling to −50°C allows for the detection of the crystallisation process. On subsequent heating, the liquid crystalline transitions were reversible, however a complex thermal behaviour was observed below the liquid crystalline transition. Beside the two sharp endothermic peaks corresponding to melting temperature (75.1°C for **8b**, 83.2°C for **8c** and 81.1°C for **8d**) with the higher enthalpy value and the isotropic transition with the lower enthalpy (84.0°C for **8b**, 92.1°C for **8c** and 100°C for **8d**), two exothermic processes were observed.

Upon heating compound **8b**, an exothermic peak centred at 2.8°C, followed by an endothermic peak at 17.1°C (21.16 kJ/mol) then an exothermic peak (62.7°C), partially overlapped with the melting transition peak at 75.1°C (41.27 kJ/mol) were observed.

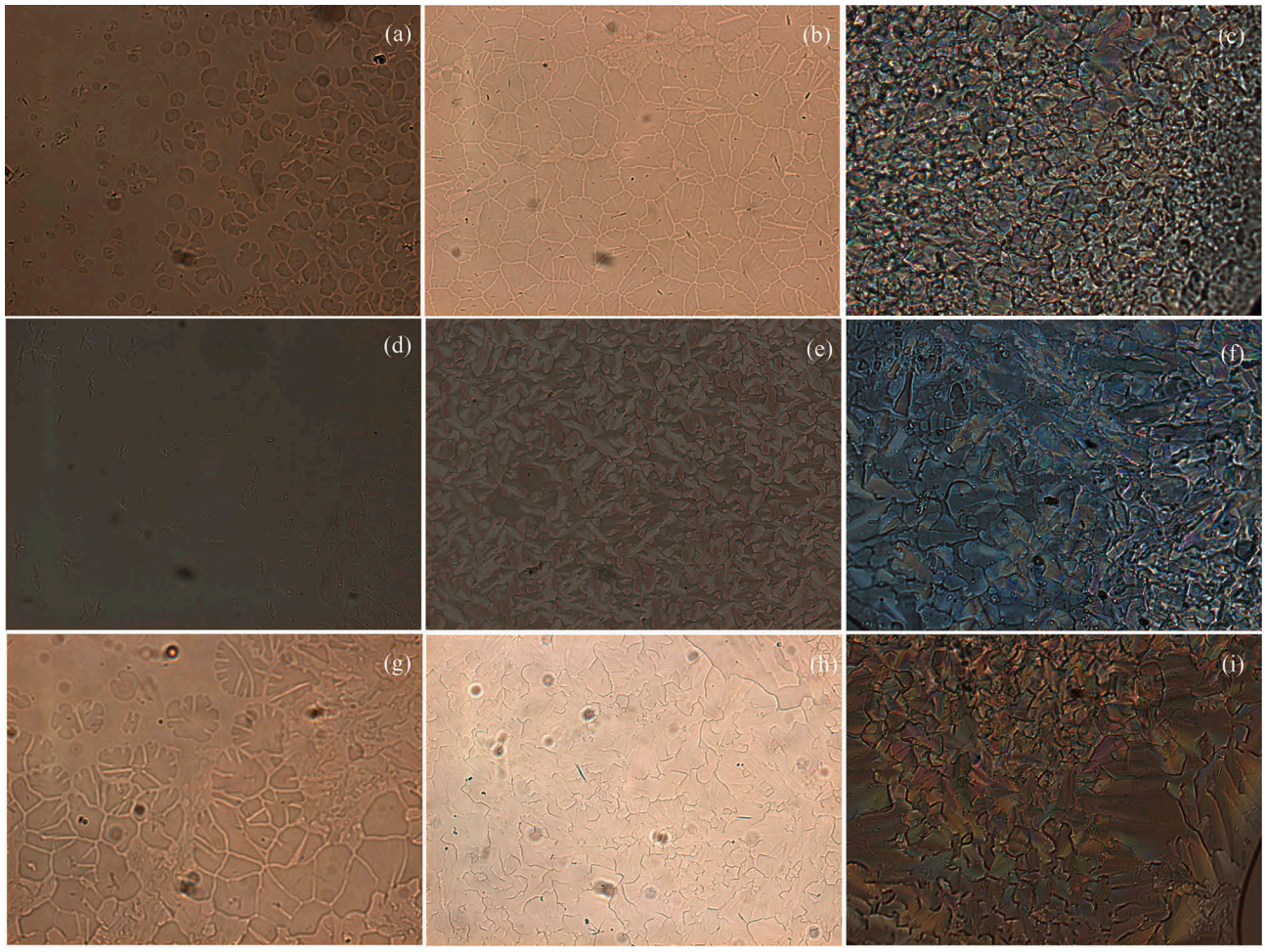


Figure 2. (colour online) Optical textures observed on cooling (5°C/min) between two glass substrates by bright field for (a) **8b** at 84°C, (b) **8b** at 82.2°C, (g) **8d** at 90.8°C, (h) **8d** at 96°C and by polarised microscopy for (c) **8b** at 83.1°C (open film), (d) **8c** at 90°C, (e) **8c** at 88.9°C, (f) **8c** at 83.3°C (open film), (i) **8d** at 88.6°C (open film). The image size is 350 µm × 450 µm.

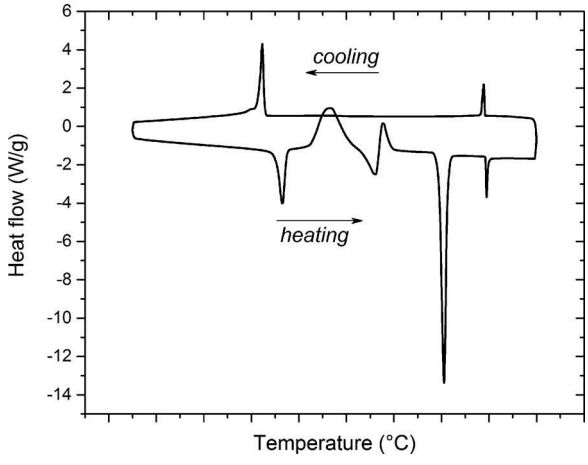


Figure 3. Thermogram of compound **8d** during the second cycle. The heating and cooling rates are 5°C/min.

The same behaviour was observed for compounds **8c** and **8d**: the exothermic peak was observed at 7.0°C for compound **8c** followed by an endothermic one at 18.6°C then a second exothermic peak at 71.0°C overlapped with the melting peak at 83.2°C. Compound **8d** presents an endothermic peak at 13.0°C, and three overlaps of consecutive exothermic– endothermic–exothermic peaks at 33.3°C, 52.33°C and 55.84°C, respectively.

It should be mentioned that the overall processes are reproducible for the three compounds during the third heating run and that the peaks below the melting transition were not detected when the cooling run was carried out until 25°C (the melting and isotropic temperature values are similar to the ones of the first heating run). These results indicate that different crystallization processes took place during heating which are related to the cooling temperature.

X-ray scattering measurements were performed on the three compounds, **8b, 8c** and **8d**, for which very similar results have been obtained: a columnar ordering (Col) appears between a lamellar crystalline state (Cr) and the isotropic liquid phase (Iso). The

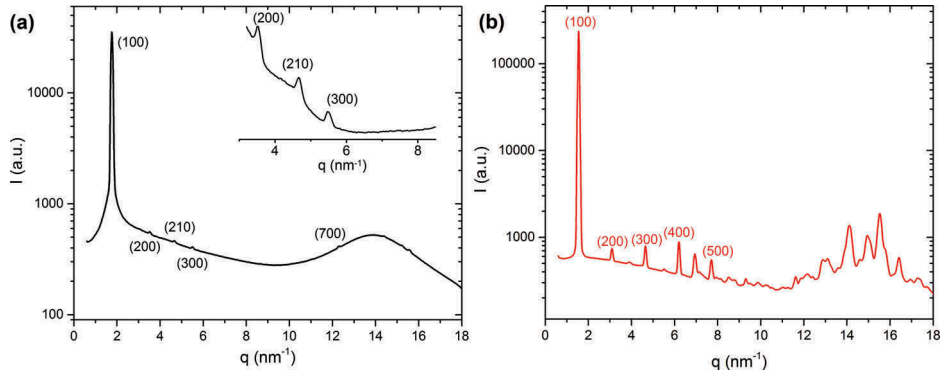
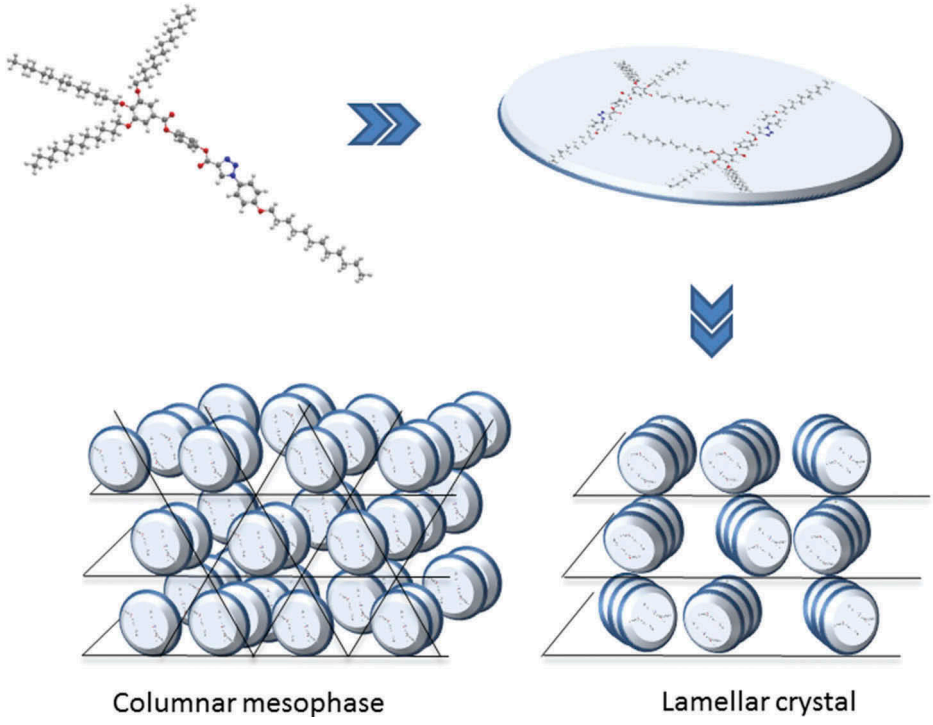


Figure 4. (colour online) Powder X-ray diffraction spectra of compound **8d** obtained (a) on cooling at the temperature of 77°C corresponding to a hexagonal columnar mesophase, and (b) at a temperature of 40°C corresponding to a lamellar crystalline phase.

corresponding diffractograms are shown in Figure 4 for the compound **8d**, whereas the ones corresponding to **8b** and **8c** are shown in the supporting information file.

In the mesophase, the Bragg reflections (hk0) indicate a two-dimensional lattice, characteristic of a columnar ordering. More specifically, the presence of the (210) peak is the signature of a hexagonal symmetry of the columnar structure. The corresponding lattice parameter given by $d = 4\pi/\sqrt{3}q_{100}$ can be calculated (d = 4.7 nm) and is found to be very consistent with the molecular length of 5.2 nm (compound **8c**). The latter one has been estimated using semi-empirical Hartree–Fock AM1 (Austin Model 1) level (Scheme 2) based on the energy-minimised structure, and provides also an average molecular width of w = 2.8 nm.

The comparison with the XRD data seems therefore to indicate a dimeric structure as building block (Scheme 2) formed by a disc-like structure composed of two molecules lying side by side. In this case, two parallel molecules have a diameter of about $2w$ = 5.6 nm, very close to their length of 5.2 nm, supporting therefore the disc-shaped approximation. The discs form a 2D arrangement and generate a hexagonal columnar organisation. Note that no intramolecular signature ((00l) peak) has been found in the



Scheme 2. (colour online) Simulation of the molecular structure and schematic representation of the molecular organisation proposed in hexagonal columnar mesophase and lamellar crystal for compounds **8b–d**.

XRD spectra indicating the very weak correlation of the molecules within the columns.

The crystalline structure found in this series of compounds **8b–d** has a specific feature shown in Figure 4b. This is the presence of a main Bragg peak (100) and many high-order reflections (h00) indicating a strong lamellar organisation, as depicted in Scheme 2. Note that crossed Bragg reflections (hkl) appear at wider angles. If the determination of the detailed symmetry of the crystal is beyond the scope of this paper, it nevertheless indicates the presence of lamellar crystal of low dimensionality.

4. Conclusion

Four unsymmetrical tetracatenar compounds containing [1,2,3]-triazole derivatives have been synthesised by an efficient synthetic pathway based on the esterification of 1H-[1,2,3]-triazole-4-carboxylic acid compounds bearing a long alkoxy chain (4a–d) with a tricatenar alcohol (7). Decyloxy, dodecyloxy and tetradecyloxy chain are more helpful in forming a liquid crystalline organisation. A hexagonal columnar mesophase was evidenced from XRD analyses, whereas a lamellar ordering was maintained in the solid structure.

The stability of the mesophase was influenced by the length of this terminal chain. A short octyl chain was detrimental to the liquid crystalline packing. The same trend was noted when the alkoxy chain was replaced by a polar methoxy, nitro or bromo group. Electrostatic interactions between the carbonyl functions and the aromatic units and dipole–dipole interactions between the terminal chains should be the main parameters governing the stability of the columnar organisation.

Disclosure statement

No potential conflict of interest was reported by the authors.

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