



Novel liquid crystal trimers with a wide mesophase range

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ABSTRACT

Novel liquid crystal (LC) trimers with a flexible tris(2-aminoethyl)amine (TREN) core and cyanobiphenyl arms have been designed. These non-traditional mesogens form nematic mesophase over a broad temperature range depending on the alkyl chain length. Their chemical structures were confirmed by the combination of ^1H NMR, ^{13}C NMR, APT, COSY and FT-IR spectra. The mesophases were characterized by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Thermogravimetric analysis showed that LC trimers are highly thermal stable both in the range of the mesophase and above the clearing point.

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1. Introduction

Nematic LC phase is characterized by molecules that are oriented along one vector determined by the director axis, but with the molecular arrangement in random positional order [1]. It has a relatively low viscosity [2–4]. Because of the orientational long-range order, they exhibit many anisotropic properties. Nematic LCs have attracted a great deal of attention due to their optical properties which enable one to monitor minute changes in temperature and mechanical stress, for their ability to orient in electric and magnetic fields in some research fields such as electronics [5–8], the construction of liquid crystal displays [9–11] or as anisotropic conductors [12,13].

Over the last decades, numerous LC compounds, which exhibit nematic phase, have been synthesized and investigated [1,14]. Traditional LC materials are mainly constituted by rod-like or disc-like molecules having rigid core with flexible chains. The construction of new thermotropic liquid crystals as innovative functional materials includes selection of the proper fragments. Numerous structure–property relationships for designing specific properties are constituted [15,16]. Modification of the fragments of the core group, linking groups and lateral functions are all ways of adapting the properties and a systematic alteration of the alkyl chain length is known to generate a miscellaneous of mesophases and property tendencies [17]. Though, anisometric rod-like or disk-like molecules used to be a principle requirement for

traditional thermotropic liquid crystal formation, because steric packing aspects have an essential place in this interesting state of soft matter [1,18,19].

The physical properties of LC trimers are dissimilar to those of classical calamitic and discotic liquid crystals. They present a number of mesophase and some trimers could form glass phase like polymers [20–22]. LC trimers are composed of molecules including three mesogenic units interconnected through flexible spacers. These structural constituents may be combined in a number of differing ways to form, for example: linear trimers [23,24], cyclic trimers based on 1,3,5-trisubstituted benzene [25], hydrogen bonded trimers [26], discotic trimers [27], cholesterol-based trimers [28]. LC trimers could be classified as symmetric or non-symmetric. The non-symmetry may be introduced in a number of ways including by having differing mesogenic units by using alkyl chains of differing lengths or by using differing terminal groups or indeed some combination of all these differences [29,30]. Stebani and co-workers described TREN derivatives as dendritic. They prepared metal complexes using various metal ions and first- or second-generation ethyleneimine dendrimers and a Cu(II) complex displayed a hexagonal columnar phase [31]. Combination of three promesogenic units with a salicylideneimine unit produced LC phases with additional attractive intermolecular forces provided by H-bonding. Upon complexation of these salicylideneimines with metals, interesting LC behaviour could be achieved [32]. The molecular structural aspect and thermal behaviour of higher oligomers between monomers and polymers have been reviewed in detail with the purpose of indicating their similarity with those of LC dimers [29,30]. These unconventional structures form a most exciting class of anisotropic materials from a fundamental and practical aspect: the structural properties of such compounds should progress to important

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core knowledge for a better comprehending of the molecular structure-mesomorphic properties relationship for LC macromolecules.

Latest improvement in LC research has been stimulated by the new insight in designing nonconventional molecules such as banana-shaped molecules [33], bowl-like or hollow cone shaped molecules [34], and badminton shuttlecock-shaped molecules [35]. Hence, we tried to design a novel LC trimer different from traditional linear LC trimers and thought that a new molecular skeleton for LC formation can be display interesting behaviour. Herein, we report the synthesis, structural and mesomorphical characterization of novel LC trimers derived from TREN core and cyanobiphenyl arms (Fig. 1). Such compounds can be readily obtained in good quantities through simple, high yielding synthetic steps.

2. Experimental

2.1. Materials and methods

Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at room temperature on a Varian 400 MHz spectrometer in CDCl_3 or $\text{DMSO}-d_6$. Chemical shifts are expressed in δ units and ^1H - ^1H coupling constants in Hz. FT-IR spectra were obtained on a Perkin Elmer Spectrum 100 FTIR spectrometer. Elemental analyses were determined on a Leco CHNS 932 instrument. Analytical TLC was performed using Merck prepared plates (silica gel60 F₂₅₄ on aluminium). TGA of the samples (5–10 mg) was performed with Seteram thermal gravimetric analyzer at temperature range of 20–700 °C with 10 °C/min heating ramp under argon atmosphere. DSC measurements were performed using Seteram DSC 131 under nitrogen against an indium standard at a heating/cooling rate 10 °C/min. Transition temperatures were determined as the onset of the maximum in the endotherm or exotherm. The textures of the liquid-crystalline phase were observed with a Polarized Optical Microscopy, Leica DMLM microscope equipped with Linkam LTS420 hot stage and T95 LinkPad temperature controller, LNP95 liquid nitrogen cooling system, and a digital camera. All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck, and Aldrich and used without further purification.

2.2. Synthesis

2.2.1. *N,N',N''*-Tris[4-hydroxybenzylideneaminoethyl]amine (3)

The compound was synthesized according to the previously published procedure [36]. Yield: 1.02 g (% 85). ^1H NMR (400 MHz,

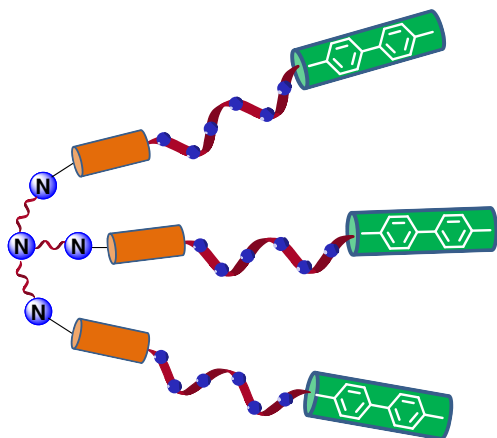


Fig. 1. Schematic representation of LC trimer.

$\text{DMSO}-d_6$) δ : 8.02 (s, 3H, $-\text{CH} = \text{N}-$), 7.41 (d, $J = 8.63$ Hz, 6H, Ar-H), 6.75 (d, $J = 8.63$ Hz, 6H), 3.51 (t, 6H, $-\text{CH}_2-\text{N} =$), 2.75 (t, 6H, $\text{N}-\text{CH}_2-$). IR (ν_{max} , cm^{-1}): 2835 (C-H stretching), 1639 (CH = N stretching), 1579, 1500 (C = C, arom.), 1449 (C-H bending), 1223, 1154 (C-O stretching).

2.2.2. *4'-[(6-Bromohexyl)oxy]-1,1'-biphenyl-4-carbonitrile (6a)*

The compound was synthesized according to the previously published procedure [37]. Yield: 2.83 g (% 79). ^1H NMR (400MHz, CDCl_3) δ : 7.66 (dd, $J = 8.29$ Hz, 4H, $\text{H}_{2,3,5,6}$), 7.53 (d, $J = 8.70$ Hz, 2H, $\text{H}_{2,6'}$), 6.99 (d, $J = 8.70$ Hz, 2H, $\text{H}_{3,5'}$), 4.01 (t, 2H, $-\text{O}-\text{CH}_2-$), 3.43 (t, 2H, Br- CH_2-), 1.98–1.75 (m, 4H, $-\text{CH}_2-$), 1.52 (m, 4H, $-\text{CH}_2-$). IR (ν_{max} , cm^{-1}): 3048, 2922, 2857 (C-H stretching), 2226 (Ar-CN), 1599, 1578, 1492 (C = C, arom.), 1466, 1432 (C-H bending), 1241, 1180 (C-O stretching).

2.2.3. *4'-[(8-Bromooctyl)oxy]-1,1'-biphenyl-4-carbonitrile (6b)*

The compound was synthesized according to the previously published procedure [37]. Yield: 2.93 g (% 76). M.p. 117–119 °C. ^1H NMR (400 MHz, CDCl_3) δ : 7.66 (dd, $J = 8.28$ Hz, 4H, $\text{H}_{2,3,5,6}$), 7.53 (d, $J = 8.66$ Hz, 2H, $\text{H}_{2,6'}$), 6.99 (d, $J = 8.66$ Hz, 2H, $\text{H}_{3,5'}$), 4.00 (t, 2H, $-\text{O}-\text{CH}_2-$), 3.42 (t, 2H, Br- CH_2-), 1.95–1.71 (m, 4H, $-\text{CH}_2-$), 1.52–1.32 (m, 8H, $-\text{CH}_2-$). IR (ν_{max} , cm^{-1}): 3044, 2931, 2856 (C-H stretching), 2222 ($-\text{C} \equiv \text{N}$), 1601, 1523 (C = C, arom.), 1494, 1472 (C-H bending), 1248, 1179 (C-O stretching).

2.2.4. The preparation of LC trimers. General procedure

A mixture of *N,N',N''*-tris[4-hydroxybenzylideneaminoethyl]amine (3) (50 mg, 0.109 mmol, 1.0 eq), corresponding bromides (6a or 6b) (0.327 mmol, 3.0 eq), K_2CO_3 (90.4 mg, 0.654 mmol, 6.0 eq) and KI (5.5 mg, 0.033 mmol, 0.3 eq) in DMF (3 mL) was stirred at 100 °C. The progress of the reaction is monitored by TLC. After completion of the reaction, the mixture was allowed to cool to rt, water (30 mL) added, and the mixture was stirred for 30 min. Then the precipitate was filtered, washed with water, methanol and acetonitrile. The product was recrystallized from a mixture of dichloromethane/methanol.

2.2.4.1. *N,N',N''*-Tris(((4-((6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl)oxy)benzylidene)amino)ethyl)amine (T6). The compound was prepared according to the general procedure above. Yield: 0.112 g (78%) of a pale yellow powder. Elemental analysis for $\text{C}_{84}\text{H}_{87}\text{N}_7\text{O}_6$, found (calculated): C 78.02 (78.17), H 6.75 (6.79), N 7.69 (7.60). ^1H NMR (400 MHz, CDCl_3) δ : 8.07 (s, 3H, $-\text{CH} = \text{N}-$), 7.65 (d, $J = 8.48$ Hz, 12H, Ar-H), 7.51 (m, 12H, Ar-H), 6.92 (d, $J = 8.75$ Hz, 6H, Ar-H), 6.87 (d, $J = 8.73$ Hz, 6H, Ar-H), 4.19–3.80 (m, 12H, $-\text{OCH}_2-$), 3.65 (t, 6H, $-\text{CH} = \text{N}-\text{CH}_2-$), 2.91 (t, 6H, $-\text{N}-\text{CH}_2-$), 1.90–1.76 (m, 12H, $-\text{CH}_2-$), 1.62–1.50 (m, 12H, $-\text{CH}_2-$). ^{13}C NMR (400 MHz, CDCl_3) δ : 161.3, 160.9, 159.7, 145.2, 132.6, 131.3, 129.6, 129.1, 128.3, 127.1, 127.0, 119.1, 115.0, 114.4, 110.0, 67.9, 67.8, 60.0, 55.8, 29.2, 25.9. IR (ν_{max} , cm^{-1}): 3038, 2939, 2865 (C-H stretching), 2225 ($-\text{C} \equiv \text{N}$), 1642 (CH = N stretching), 1603, 1578, 1510, 1494 (C = C, arom.), 1472, 1433 (C-H bending), 1249, 1179 (C-O stretching).

2.2.4.2. *N,N',N''*-Tris(((4-((8-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)octyl)oxy)benzylidene)amino)ethyl)amine (T8). The compound was prepared according to the general procedure above. Yield: 0.104 g (74%) of a pale yellow powder. Elemental analysis for $\text{C}_{90}\text{H}_{99}\text{N}_7\text{O}_6$, found (calculated): C 78.57 (78.63), H 7.20 (7.26), N 7.21 (7.13). ^1H NMR (400 MHz, CDCl_3) δ : 8.06 (s, 3H, $-\text{CH} = \text{N}-$), 7.66 (d, $J = 8.23$ Hz, 12H, Ar-H), 7.61 (m, 12H, Ar-H), 6.99 (d, $J = 8.66$ Hz, 6H, Ar-H), 6.87 (d, $J = 8.53$ Hz, 6H, Ar-H), 4.03–3.95 (m, 12H, $-\text{OCH}_2-$), 3.65 (t, 6H, $-\text{CH} = \text{N}-\text{CH}_2-$), 2.91 (t, 6H, $-\text{N}-\text{CH}_2-$), 1.85–1.76 (m, 12H, $-\text{CH}_2-$), 1.54–1.38 (m, 24H, $-\text{CH}_2-$). ^{13}C NMR (400 MHz, CDCl_3) δ : 161.2, 161.0, 159.7, 145.2, 132.6, 131.2, 129.6, 129.1, 128.3, 127.0, 119.1, 115.0, 114.7, 114.4, 109.9, 68.3, 68.1, 67.9, 60.0, 55.8, 29.3, 29.2, 25.9. IR (ν_{max} , cm^{-1}): 3040, 2935, 2856 (C-H stretching), 2225 ($-\text{C} \equiv \text{N}$), 1642 (CH = N stretching),

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