SHORT PAPER

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Cholesterol-based linear trimesogens: synthesis and evaluation of mesomorphic behaviour

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Several trimesogens consisting of benzalazine as a central mesogenic segment, connected linearly on both the terminals with the cholesteryl ester moieties through either even–even or odd–odd alkylene spacers, have been synthesised and investigated for their liquid crystalline properties

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The conventional thermotropic liquid crystal consists of anisometric molecules (mesogens) that are either rod-shaped (calamitic) or disc-shaped (discotic). However, it is now well documented that compounds with non-classical molecular structures such as oligomers, also show liquid crystalline properties.[1] Among these, linear oligomeric liquid crystals (LOLCs), that are formed by joining 2 to 8 mesogenic (anisometric) cores in an end–end (axial) fashion by means of alkylene spacers, are attracting special attention, not only because they are considered as model compounds for polymeric liquid crystals but also due to their interesting thermal behaviour.[2-4] The first member of the LOLCs, namely the dimesogen (also called dimer) composed of either identical (symmetrical) or non-identical (non-symmetrical) mesogenic molecules connected by a central spacer, has been extensively studied.[2]

The linear addition of one more mesogenic moiety to a dimesogen via a flexible spacer results in the next higher oligomesogen, namely the trimesogen (also called trimers or triplets).[3] These trimesogens are of interest as they exhibit liquid crystalline properties. Further, it has been demonstrated recently that a flexible backbone based, virtual trimer model successfully accounts for the transitional properties of side chain liquid crystalline polymers.[3b] Based on the molecular structure of individual anisometric entities there can be three possible combinations for these trimers: (i) all of them are structurally identical; (ii) two of them are identical while the third entity is different; and (iii) all the three are different.

In the present investigation, we focus our attention on the trimesogens of the type (ii). Only a few such trimesogens have been reported, which exhibit remarkable mesomorphic behavior that seems to be dependant on (a) the molecular structures of two identical terminal and a central mesogenic cores and (b) the combination of two central alkylene spacers (either even-odd or even–even or odd–odd).[3d-h] However, in order to establish a clear structure-property relation in such systems different mesogenic as well as spacer combinations have to be explored. Working in this direction we report here synthesis and characterisation of some new trimesogens of the type (ii).

The aromatic diazines, namely the α,α′-dimethylbenzalazines and their variants have shown to exhibit an interesting mesomorphic behaviour.[5] Despite this, only slight attention has been given to such type of liquid crystals. On the other hand, cholesterol is a well-known natural product and frequently appears (in the form of its ester derivative) as an important building block in many liquid crystalline molecular assemblies. In the proposed trimesogens of the type (ii), we intended to employ α,α′-dimethylbenzalazine as a central core and the cholesteryl ester as the terminal cores, joined together through either even–even or odd–odd alkylene spacers. The trimesogens, consisting of three mesogenic segments separated by either even–even (**1b**) or odd–odd (**1a**, **c**, **d**) spacerely were realised by the O-alkylation of the 4,4′-dihydroxy-α,α′-dimethylbenzalazine (**3**) with cholesteryl bromoalkanotes[2d] **2a–d** (which were synthesised by treating commercial optically pure cholesterol with bromoalkanoyl chlorides[2e]) under mild basic reaction conditions as shown in Scheme 1.

The molecular structures of the trimesogens (**1a–d**) were confirmed with help of spectroscopic analysis. The IR, ^{1}H and ^{13}C NMR spectrum of all the trimesogens look alike. The IR spectrum show absorption bands in the region of ν_{max}/cm^{-1} 2935–2952, 1728–1737 and 1593–1604 due to C–H (paraffinic), C=O and C=N stretching vibrations respectively. In the ^{1}H NMR spectrum, eight aromatic protons appear as two doublets (d) at δ 7.8 and 6.9 respectively, while the olefinic, methine (of ester) and oxymethylene (of paraffinic chain) protons resonate at δ 5.3, 4.6 and 4.0 as broad d, multiplet (m) and triplet (t) respectively. It is well known that benzalzines and their derivatives can exist in three types of configurational isomers (*E–E*, *E–Z* and *Z–Z*). However, it has been observed that the usual synthetic methods, such as has been employed to prepare 4,4′-dihydroxy-α,α′-dimethylbenzalazine in the present investigation, furnish mostly the *E–E* isomer. This is supported by the observation that the methyl groups of benzylidene core resonate as a singlet (s) at δ 2.3.[5] In ^{13}C NMR spectra at the higher frequency (downfield) region, trimesogens show eight peaks, each resonating in the region of 172.5–173.2 (C=O), 160.1–160.5 (C=N), 157–157.8 (Ar), 139.6–139.9 (olefinic), 131.1–131.5 (Ar), 128.0–128.3 (Ar), 122.5–122.9 (olefinic) and 114.1–114.4 (Ar) as expected, which unambiguously establish their molecular structures.

The mesomorphic properties of the trimesogens **1a–d** were examined by optical polarising light microscopy and differential scanning calorimetric studies. The results are summarised in Table 1. All the members exhibited an enantiotropic chiral nematic (N*) mesophase with a characteristic oily streak texture when the sample was placed on an untreated glass plate. The trimesogen **1b** shows, while cooling from the N* phase, a monotropic mesophase below 139.4° C with a shearable non-specific texture, which we refer to as the X phase. The trimesogen **1c** placed in a cell treated for planar orientation, shows another mesophase below the N* mesophase that exists till crystallisation at about 120° C. In a wedge type cell with a similar surface treatment the N* phase exhibits, as expected, Grandjean Cano lines since in this geometry there is a helical twist normal to the plates in the phase. On crossing to the

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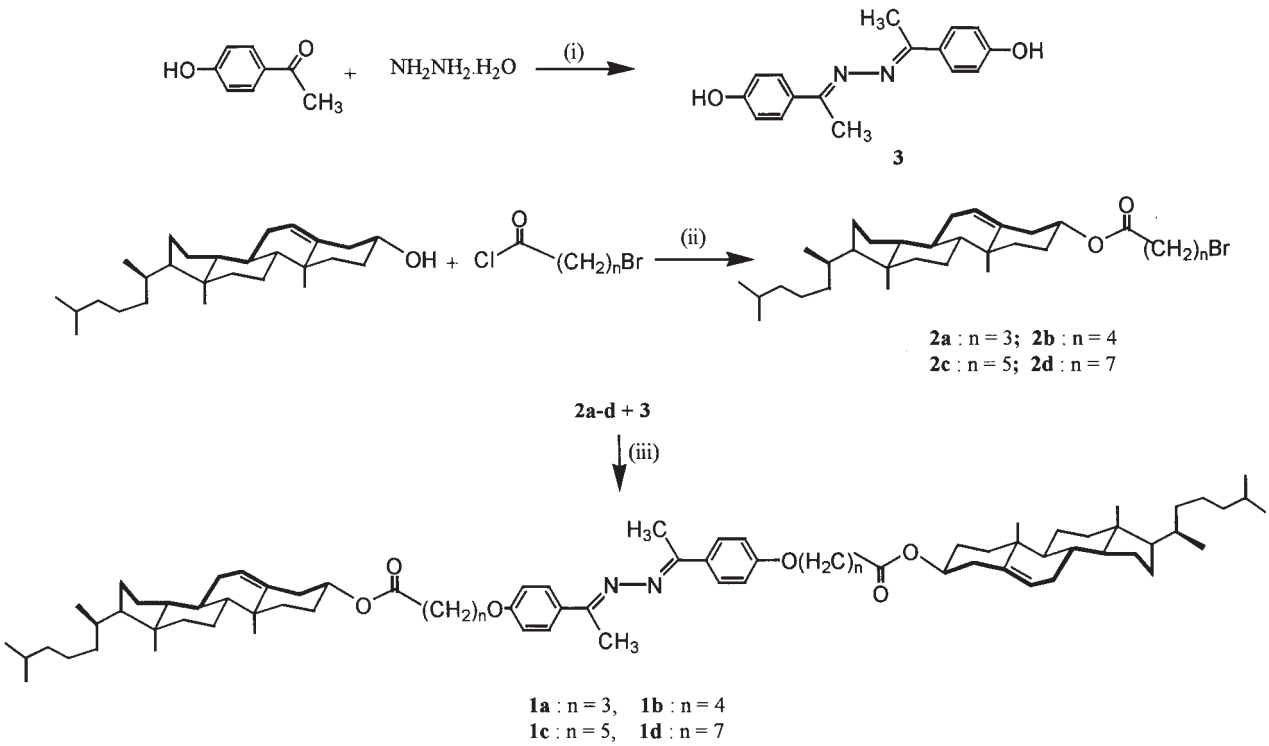

Scheme 1 Reagents and conditions: (i) abs. EtOH, reflux, 120h, 35%; (ii) Pyridine-THF, rt, 12h; and (iii) Acetone, K_2CO_3, reflux, 60h, quantitative.

second mesophase, a square grid pattern appears superimposed on the Grandjean Cano lines. These characteristic optical features, especially the square grid pattern, has been reported for the twist grain boundary with smectic C* blocks (TGB_{C*}).[6] Thus the trimesogenic compound **1c**, exhibits TGB_{C*} phase over an approximately 20° C temperature range. This observation is significant given the fact, that, to the best of our knowledge the TGB_{C*} phase has been seen only in very few single component systems. It is worth mentioning here that these trimesogens show a shift in the transition temperatures with the repeated heating\cooling cycles, indicating that these molecules are sensitive to heat.

In conclusion, we have synthesised some new trimesogens of the type (ii) comprised of a benzalazine as a central mesogenic segment connected linearly on both the terminals with the cholesteryl ester moieties through either even–even (**1b**) or odd–odd (**1a**, **c**, **d**) alkylene spacers. All the trimesogens exhibit an enantiotropic N* phase. Interestingly, among the trimesogen consisting of odd-odd alkylene spacers, the trimesogen **1c** having C_5- parity exhibits a TGB_{C*} phase, indicating that the length of the two central paraffinic spacers are critical in order to stabilise the TGB_{C*} phase.

Table 1 Transition temperatures[a] (°C) and enthalpies (J/g) of trimesogens. The enthalpy values are enclosed in brackets.

Trimesogen	Mode	Phase transition sequence
1a	Heating	Cr 216.2 (55.9) N* 265 (8.9) I
	Cooling	I 259.4 (8.6) N* 175.9 (48.9) Cr
1b	Heating	Cr 167.4 (65.9) N* 200.4 (3.5) I
	Cooling	I 199.4 (3.5) N* 148.5 (2.9) X 139.4 (53.5) Cr
1c	Heating	Cr 154 (40.5) TGBC* 176.4b N* 237 (8.1) I
	Cooling	I 232.4 (7.1) N* 174.4b TGBC* 119.9 (25) Cr
1d	Heating	Cr 165 (33.6) N* 213.5 (8.3) I
	Cooling	I 211.7 (7.6) N* 137.6 (26) Cr

[a]Peak temperatures in the DSC thermograms obtained during heating cycle at 5°/min.
[b]Phase transition was observed under polarising microscope but too weak to get be detected in DSC
I = isotropic liquid state; N* = chiral nematic phase; TGB_{C*} = twist grain boundary with smectic C* blocks phase; X = unknown phase; Cr = Crystal

Experimental

General information: 4-Hydroxyacetophenone, ethanol, acetone, (HPLC grade) and potassium carbonate were obtained from local sources. Acetone was used as received, whereas ethanol and potassium carbonate were dried following standard procedure. Cholesterol and 1-bromoalkanes were obtained from Aldrich. IR spectra were recorded using a Perkin Elmer Spectrum 1000 FT-IR spectrometer. ^{1}H NMR spectra were recorded using a Bruker AMX-400 (400 MHz) spectrometer and the chemical shifts are reported relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a Jeol JMS-600H spectrometer in the FAB^+ mode using 3-nitrobenzylalcohol as a liquid matrix. The identification of the mesophases and the transition temperatures of the trimesogens were determined using a polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90). Optical observations were made with either ordinary glass slides or slides treated for homogeneous alignment or for homeotropic alignment of the molecules. The enthalpy of the phase transition were measured using a differential scanning calorimeter (Perkin Elmer DSC7). The melting transitions of non-mesogenic compounds were recorded using the same microscope hot-stage.

4,4′-dihydroxy-α,α′-dimethylbenzalazine (**3**): A flask equipped with a magnetic stirr bar, reflux condenser and argon inlet was charged with absolute ethanol (50ml), 4-hydroxyacetophenone (10 g, 73 mmol) and hydrazine hydrate (1.2 g, 24 mmol). The reaction mixture was heated to reflux for 120 h and the yellow solid which sepa-

rated after cooling was collected by filtration. The crude material was poured into hot water (60–70ºC), stirred for 20 min then collected by filtration. It was purified by repeated recrystallisations (to constant m.p.) from a mixture of water–ethanol as an intense yellow solid; m.p.223–224.5ºC (lit[5]. m.p. 223); yield: 4.1 g (35 %); IR (KBr pellet): ν_{max} 3479, 1591, 1171 and 838 cm[1]; [1]H NMR (DMSO-d_6, 400 MHz): δ 9.8 (s, 2H, 2×-OH), 7.76 (d, *J* = 7.64 Hz, 4H, Ar), 6.82 (d, *J* = 7.68 Hz, 4H, Ar) and 2.24 (s, 6H, 2× -CH_3); FAB Mass: 268.7 [M^+] (Calculated for $C_{16}H_{16}N_2O_2$).

N,N′-Bis{α-methyl-4-[1-(cholest-5-en-3-yloxycarbonyl)alkoxy]benzylidine}hydrazines (**1a–d**): These trimesogens were synthesised following a typical synthetic procedure as given below: Into a 100 ml two-necked round-bottomed flask equipped with a water condenser and a nitrogen inlet were placed acetone (HPLC grade, 50 ml), anhyd. potassium carbonate [8 g, 58 mmol, (31 equiv.)], cholesteryl 4/5/6/8-bromoalkanoates (**2a–d**) [3.9 mmol (2.1 equiv.)] and 4,4′-dihydroxy-α,α′-dimethylbenzalazine (**3**) [0.5g, 1.86 mmol, (1 equiv.)] were added sequentially through the other neck of the flask and the flask was flushed with nitrogen gas for some time. After closing the neck with a septa, the reaction mixture was heated to reflux for 60 h with vigorous stirring and was filtered through a Celite bed when hot. The solid which separated from the filtrate was collected by filtration, dissolved in CH_2Cl_2 (40ml) and the resultant solution was washed with a 10 % solution of $NaOH_{(aq)}$ (20ml×2), 0.1M $HCl_{(aq)}$(20ml×2), 5% solution of $NaOH_{(aq)}$ (10ml ×2), water (10ml ×2), brine and then was dried over anhyd. Na_2SO_4. Evaporation of solvent furnished a yellow solid that was purified by repeated recrystallisations (4 times) from a mixture of CH_2Cl_2 –ether (9:1) to give a yellow crystalline compound which was collected by filtration and washed with ether then dried in air; yield: quantitative

N,N′-Bis{4-α-methyl-4-[(cholest-5-en-3-yloxycarbonyl)propyl-3-oxy]benzylidine}hydrazine (**1a**): IR (KBr pellet): ν_{max} 2952, 1737, 1604, 1250 and 832 cm[-1]; [1]HNMR ($CDCl_3$, 400MHz): δ 7.85 (d, *J* = 8.8 Hz, 4H, Ar), 6.91 (d, *J* = 8.9 Hz, 4H, Ar), 5.37 (brd, *J* = 4.24 Hz, 2H, olefinic), 4.61 (m, 2H, 2×-CH-O-CO-), 4.05 (t, *J*=6.08 Hz, 4H, 2×-OCH_2-), 2.50–2.32 (m, 8H, 4 × allylic methylene), 2.31 (s, 6H, 2×-CH_3), 2.20–0.94 (m, 56H, 22×-CH_2-, 12×-CH-), 1.01 (s, 6H, 2×-CH_3), 0.91 (d, *J* = 6.52 Hz, 6H, 2×-CH_3), 0.87 (d, *J* = 1.76 Hz, 6H, 2×-CH_3), 0.85 (d, *J* = 1.76 Hz, 6H, 2×-CH_3) and 0.67 (s, 6H, 2×-CH_3); [13]C NMR ($CDCl_3$, 100MHz) : δ 172.52, 160.13, 157.78, 139.66, 131.43, 128.07, 122.67, 114.21, 74.11, 66.89, 56.72, 56.18, 50.07, 42.39, 39.76, 39.53, 38.16, 37.0, 36.61, 36.19, 35.79, 31.90, 31.13, 28.22, 28.0, 27.83, 24.71, 24.28, 23.84, 22.79, 22.55, 21.05, 19.31, 18.72, 14.75 and 11.86; FAB Mass: 1176.8 [M^+] (Calculated for $C_{78}H_{116}N_2O_6$).

N,N′-Bis{4-α-methyl-4-[(cholest-5-en-3-yloxycarbonyl)butyl-4-oxy]benzylidine}hydrazine (**1b**): IR (KBr pellet): ν_{max} 2948, 1732, 1593, 1257 and 832 cm[-1]; [1]HNMR ($CDCl_3$, 400MHz): δ 7.85 (d, *J* = 8.8 Hz, 4H, Ar), 6.91 (d, *J* = 8.8 Hz, 4H, Ar), 5.37 (brd, *J* = 3.92 Hz, 2H, Olefinic), 4.61 (m, 2H, 2×-CH-O-CO-), 4.01 (t, *J*=6.08 Hz, 4H, 2×-OCH_2-), 2.39–2.30 (m, 8H, 4 × allylic methylene), 2.31 (s, 6H, 2×-CH_3), 2.02-0.98 (m, 60H, 24×-CH_2-, 12×-CH-), 1.01 (s, 6H, 2×-CH_3), 0.91 (d, *J* = 6.48 Hz, 6H, 2×-CH_3), 0.87 (d, *J* = 1.68 Hz, 6H, 2×-CH_3), 0.85 (d, *J* = 1.68 Hz, 6H, 2×-CH_3) and 0.67 (s, 6H, 2×-CH_3); [13]C NMR ($CDCl_3$, 100MHz) : δ 172.77, 160.23, 157.81, 139.68, 131.33, 128.08, 122.64, 114.21, 73.93, 67.50, 56.72, 56.18, 50.07, 42.34, 39.76, 39.53, 38.18, 37.02, 36.61, 36.21, 35.79, 34.23, 31.90, 28.64, 28.22, 27.90, 27.84, 24.28, 23.84, 22.79, 22.55, 21.72, 21.05, 19.31, 18.72, 14.73 and 11.85; FAB Mass: 1204.6 [M^+] (Calculated for $C_{80}H_{120}N_2O_6$).

N,N′-Bis{4-α-methyl-4-[(cholest-5-en-3-yloxycarbonyl)pentyl-4-oxy]benzylidine}hydrazine (**1c**): IR (KBr pellet): ν_{max} 2941, 1728, 1604, 1252 and 833 cm[-1]; [1]HNMR ($CDCl_3$, 400MHz): δ 7.85 (d, *J* = 8.8 Hz, 4H, Ar), 6.91 (d, *J* = 8.9 Hz, 4H, Ar), 5.37 (brd, *J* = 3.92 Hz, 2H, olefinic), 4.61 (m, 2H, 2×-CH-O-CO-), 4.0 (t, *J*=6.38 Hz, 4H, 2×-OCH_2-), 2.35–2.27 (m, 8H, 4 × allylic methylene), 2.31 (s, 6H, 2×-CH_3), 2.0-0.98 (m, 64H, 26×-CH_2-, 12×-CH-), 1.01 (s, 6H, 2×-CH_3), 0.90 (d, *J* = 6.48 Hz, 6H, 2×-CH_3), 0.87 (d, *J* = 1.72 Hz, 6H, 2×-CH_3), 0.85 (d, *J* = 1.72 Hz, 6H, 2×-CH_3) and 0.66 (s, 6H, 2×-CH_3); [13]C NMR ($CDCl_3$, 100MHz) : δ 173.01, 160.28, 157.82, 139.66, 131.18, 128.02, 122.62, 114.14, 73.81, 67.70, 56.67, 56.12, 50.01, 42.30, 39.72, 39.50, 38.14, 36.98, 36.58, 36.16, 35.77, 34.56, 31.88, 29.0, 28.21, 28.0, 27.81, 25.59, 24.77, 24.27, 23.81, 22.80, 22.55, 21.01, 19.31, 18.70, 14.75 and 11.84; FAB Mass: 1232.9 [M^+] (Calculated for $C_{82}H_{124}N_2O_6$).

N,N′-Bis{4-α-methyl-4-[(cholest-5-en-3-yloxycarbonyl)heptyl-7-oxy]benzylidine}hydrazine (**1d**)- IR (KBr pellet): ν_{max} 2935, 1731, 1597, 1254 and 836 cm[-1]; [1]HNMR ($CDCl_3$, 400MHz): δ 7.85 (d, *J* = 8.8 Hz, 4H, Ar), 6.91 (d, *J* = 8.8 Hz, 4H, Ar), 5.37 (brd, *J* = 4.2 Hz, 2H, Olefinic), 4.61 (m, 2H, 2×-CH-O-CO-), 4.0 (t, *J*=6.5 Hz, 4H, 2×-OCH_2-), 2.30–2.26 (m, 8H, 4 × allylic methylene), 2.31 (s, 6H, 2×-CH_3), 2.02–0.98 (m, 72H, 30×-CH_2-, 12×-CH-), 1.01 (s, 6H, 2×-CH_3), 0.91 (d, *J* = 6.52 Hz, 6H, 2×-CH_3), 0.87 (d, *J* = 1.72 Hz, 6H, 2×-CH_3), 0.85 (d, *J* = 1.72 Hz, 6H, 2×-CH_3) and 0.67 (s, 6H, 2×-CH_3); [13]C NMR ($CDCl_3$, 100MHz) : δ 173.20, 160.38, 157.83, 139.70, 131.15, 128.01, 122.59, 114.16, 73.72, 67.96, 56.68, 56.13, 50.03, 42.30, 39.73, 39.51, 38.16, 36.99, 36.59, 36.17,35.78, 34.64, 31.86, 29.14, 28.99, 28.21, 27.99, 27.82, 25.85, 24.95, 24.27, 23.82, 22.80, 22.54, 21.02, 19.30, 18.70, 14.74 and 11.84; FAB Mass: 1288.5 [M^+] (Calculated for $C_{86}H_{132}N_2O_6$).

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