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Organometallic chiral liquid crystals: bis{4-[ω-(cholest-5-en-3-yloxycarbonyl)alkoxy]phenylethynyl}mercury complexes

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We report the synthesis and thermal behaviour of the first chiral organometallic trimesogens having bis[(4-phenyl)ethynyl]mercury as the central core connected on either side to cholesteryl ester moieties through either even–even (C_4) or odd–odd (C_3, C_5 and C_7) central alkylene spacers. All the organomercury trimesogens exhibit a chiral nematic phase. These mercury complexes are extremely sensitive to heat, in a manner reminiscent of other reports.

1. Introduction

Thermotropic metal-containing mesogens, either organometallic systems (with metal–carbon or metal-π bonds) or coordination complexes (with metal–heteroatom bonds) commonly termed metallomesogens attract much attention in their own right [1]. After the first report [2] of mesomorphic behaviour in metal-containing liquid crystals, several guidelines have been suggested for mesophase formation in monomeric metallomesogens and subsequently extended to polymers [3]. Till now many metallomesogens have been reported incorporating mostly 3d (V, Mn, Fe, Co, Ni, and Cu) and some 4d- and 5d(Mo, Rh, Pd, Ag, Ir, Pt and Au)-block metals. Several p-block metals (Zn, Cd, Hg, Pb, Tl) have also been employed to realize mesogenic complexes. Metallomesogens are known to exhibit a variety of interesting phenomena, e.g. paramagnetism [4], ferroelectric properties, one-dimensional electrical conductivity [5], optical effects [6] like dichroism and non-linear optical behaviour, and electro-optical [7] properties. These observations have inspired many researchers to design and synthesize new mesogens with variation in the molecular structure of the ligands to incorporate different metal atoms.

In comparison with the exhaustive studies on mesogenic coordination compounds, organometallics have been investigated to a lesser extent owing to their sensitivity to heat. The organometallic complexes reported so far involve only the metals mercury, palladium or platinum [1], the mercury-based compounds being least studied. In fact the diaryl mercury Schiff's base derivatives exhibiting smectic phases reported by Vorländer in 1923 are early examples of organometallic mesogens [1(*a*), 8]. This was followed, fifty years later, by reports on the mercury-bridged twins, the bis(*p*-*n*-hexyloxyphenyl) [9] and bis(4′-*n*-alkylbiphenyl-4-yl)mercury [10] complexes. Dimers, namely bis[(4-alkoxyphenyl)ethynyl]-mercury complexes, show smectic A (SmA) and/or nematic (N) phases [11]. Phenylacetylene dimers having a benzene nucleus substituted with either a monoalkyl [11], or mono-/di-/tri-alkoxy tails have been recently reported from this laboratory [12]. The mercury bridged penta-alkoxytriphenylene dimers have also been reported from this laboratory [13]. To the best of our knowledge only one report is available on chiral liquid crystals containing a mercury atom [14]. Interestingly, these chiral azomercury complexes show a room temperature chiral smectic C (SmC*) phase.

Non-metallic dimers consisting of two identical (symmetrical) or non-identical (unsymmetrical) mesogenic segments joined together through a polymethylene spacer are known to exhibit mesomorphic behaviour [15]. Unsymmetrical dimers, especially the cholesterol-based chiral compounds, show a remarkable polymorphic sequence [16] and wide temperature range chiral smectic A (SmA*) or chiral nematic (N*) phases [17]. Adding one more mesogenic unit at one of the ends of the dimer through an alkylene spacer furnishes a linear trimer (also referred to as a trimesogen or a triplet) [18]. Such trimesogens can be grouped into three categories: (i) symmetrical (the three mesogenic

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units are identical), (ii) semi-symmetrical (two of the mesogenic segments are identical) and (iii) unsymmetrical (all the mesogenic cores are different). All these trimers have been realized and reported to show some interesting thermal behaviour, their mesomorphic properties being critically dependent on the length and parity of the two connecting alkylene spacers [18(*b*)]. In this paper we restrict ourselves to the trimesogens of type (ii).

However, to get a better understanding of structure–mesomorphic relations, many variations in the molecular structure of the mesogenic cores, as well as alkylene spacers, need to be attempted. Recently we reported the molecular design, synthesis and characterization of trimesogens of type (ii) consisting of benzalazine as a central core connected linearly at both termini to cholesteryl ester moieties either through even–even or odd–odd alkylene spacers. One of these trimesogens stabilizes the twist grain boundary phase with smectic C* blocks (TGBC* phase) [18(*b*)]. In continuation of our work on similar compounds, here we report the first trimesogenic metallomesogens (**1a–d**) consisting of bis[(4-phenyl)-ethynyl]mercury as the central core connected axially at both termini to cholesteryl ester moieties through either even–even or odd–odd alkylene spacers.

2. Experimental

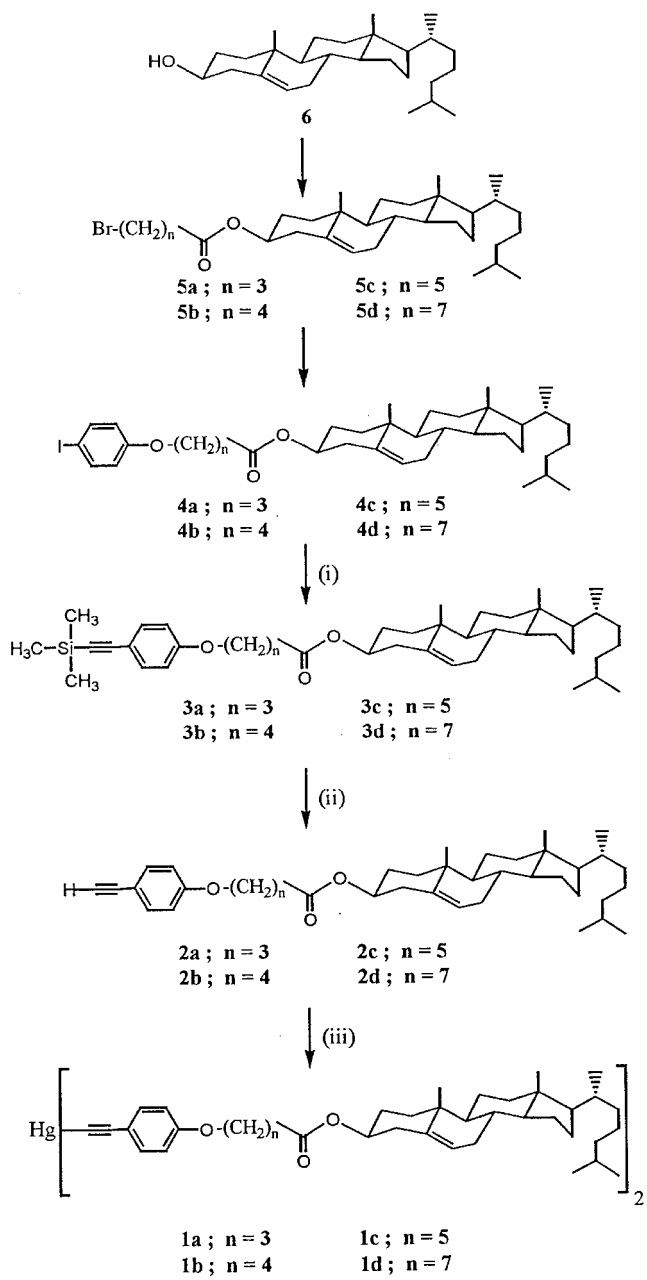
2.1. *General*

Cholesterol, trimethylsilylacetylene, 8-bromo-octanoic acid, 6-bromohexanoic acid, 5-bromovaleric acid and 4-bromobutyric acid were obtained from Aldrich. Solvents and other common chemicals were obtained from local sources. Solvents were purified and dried following standard procedures. The compounds synthesized, except the metallomesogens, were purified by coloumn chromatographic techniques using neutral aluminium oxide as stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge10, F254). IR spectra were recorded using a Perkin Elmer Spectrum 1000 FTIR spectrometer. NMR spectra were recorded using a Bruker AMX-400 spectrometer (400 MHz). For ^{1}H NMR spectra, the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as internal standard. Mass spectra were recorded using a Jeol JMS-600H spectrometer in the FAB$^+$ mode, using 3-nitrobenzyl alcohol as a liquid matrix. Elemental analysis was performed using a Perkin-Elmer instrument. The materials were investigated for their liquid crystalline behaviour using a polarizing optical microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90) and by differential scanning calorimetry (Perkin Elmer DSC7). Optical observations were made using either clean untreated glass slides or slides treated for homogeneous or for homeotropic alignment of the molecules.

2.2. *General procedure for the preparation of cholesteryl ω-[(4-trimethylsilylethynyl)phenoxy]alkanoates (**3a–d**)*

(see the scheme)

A mixture of cholesteryl ω-(4-iodophenoxy) alkanoate (**4a–d**) (1.42 mmol, 1 equiv), trimethylsilylacetylene (0.28 ml, 2 mmol, 1.4 equiv), bis(triphenylphosphine)-palladium(II) chloride (20 mg, 0.02 mmol), triphenylphosphine (100 mg, 0.38 mmol), and copper(I) iodide



Scheme. Synthetic route employed for the mercury complexes. Reagents and conditions; (i) trimethylsilylacetylene, $[(C_6H_5)_3P]_2PdCl_2$, Ph_3P, CuI, Et_3N, rt, 24 h; (ii) $Bu_4N^+F^-$, THF, rt, 3 h; (iii) alkaline aq. solution of mercuric iodide, 0–5°C, 10 min.

(100 mg, 0.52 mmol) in dry triethylamine (10 ml) was stirred at room temperature under an argon atmosphere for 24 h. The reaction mixture was filtered through a celite bed and the filtrate evaporated *in vacuo* yielding a dark brown solid that was purified by coloumn chromatography using neutral aluminium oxide. Elution with a mixture of 5% EtOAc–hexanes furnished a white crystalline compound that was further purified by repeated recrystallizations from CH_2Cl_2–EtOH.

2.2.1. *Cholesteryl 4-(4-trimethylsilylethynylphenoxy)-butanoate (**3a**)*

Yield = 750 mg (78%); R_f = 0.12 (10% EtOAc–hexanes). IR (KBr Pellet) ν_{max}: 2951, 2850, 2158, 1729, 1605 and 1507 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.38 (d, J = 8.7 Hz, 2H, Ar), 6.79 (d, J = 8.7 Hz, 2H, Ar), 5.36 (brd, J = 3.96 Hz, 1H, olefinic), 4.61 (m, 1H, CHOCO), 3.99 (t, J = 6.1 Hz, 2H, 1 × OCH_2), 2.6–2.2 (m, 4H, 2 × allylic methylene), 2.2–1.04 (m, 28 H, 11 × CH_2, 6 × CH), 1.01 (s, 3H, × CH_3), 0.91 (d, J = 6.48 Hz, 3H, 1 × CH_3), 0.87 (d, J = 1.68 Hz, 3H, 1 × CH_3), 0.85 (d, J = 1.64 Hz, 3H, 1 × CH_3), 0.67 (s, 3H, 1 × CH_3) and 0.23 (s, 9H, 3 × CH_3, Me_3Si). ^{13}C NMR (100 MHz, $CDCl_3$): 173.19, 159.53, 140.05, 133.85, 123.07, 115.58, 114.72, 105.65, 92.75, 74.33, 67.82, 57.1, 56.55, 50.44, 42.72, 40.14, 39.93, 38.56, 37.39, 37.0, 36.59, 36.2, 32.31, 32.27, 28.97, 28.63, 28.42, 28.22, 24.69, 24.24, 23.22, 22.96, 22.07, 21.44, 19.72, 19.12, 12.5 and 0.5. FAB Mass: 644.9 $[M]^+$. Elemental analysis calc. for $C_{42}H_{64}O_3Si$: C 78.25, H 10.00; found: C 78.54, H 10.24%.

2.2.2. *Cholesteryl 5-(4-trimethylsilylethynylphenoxy)-pentanoate (**3b**)*

Yield = 780 mg (82%); R_f = 0.17 (10% EtOAc–hexanes). IR (KBr Pellet) ν_{max}: 2951, 2850, 2152, 1738 and 1506 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.38 (d, J = 8.88 Hz, 2H, Ar), 6.79 (d, J = 8.88 Hz, 2H, Ar), 5.36 (brd, J = 3.76 Hz, 1H, olefinic), 4.60 (m, 1H, CHOCO), 3.96 (t, J = 5.54 Hz, 2H, 1 × OCH_2), 2.37–2.29 (m, 4H, 2 × allylic methylene), 2.01–1.03 (m, 30 H, 12 × CH_2, 6 × CH), 1.01 (s, 3H, × CH_3), 0.91 (d, J = 6.52 Hz, 3H, 1 × CH_3), 0.86 (d, J = 1.8 Hz, 3H, 1 × CH_3), 0.85 (d, J = 1.8 Hz, 3H, 1 × CH_3), 0.67 (s, 3H, 1 × CH_3) and 0.23 (s, 9H, 3 × CH_3, Me_3Si). ^{13}C NMR (100 MHz, $CDCl_3$): 172.8, 159.1, 139.62, 133.44, 122.65, 115.13, 114.29, 105.22, 92.34, 73.91, 67.39, 56.67, 56.11, 50.0, 42.29, 39.70, 39.5, 38.13, 36.96, 36.57, 36.16, 35.77, 34.24, 31.98, 31.90, 28.54, 28.21, 27.99, 27.79, 24.26, 23.80, 22.80, 22.54, 21.65, 21.0, 19.3, 18.69, 11.83 and 0.5. FAB Mass: 658.9 $[M]^+$. Elemental analysis calc. for $C_{43}H_{66}O_3Si$: C 78.37, H 10.09; found: C 78.84, H 10.34%.

2.2.3. *Cholesteryl 6-(4-trimethylsilylethynylphenoxy)-hexanoate (**3c**)*

Yield = 730 mg (76%); R_f = 0.21 (10% EtOAc–hexanes). IR (KBr Pellet) ν_{max}: 2943, 2850, 2158, 1734 and 1508 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.38 (d, J = 8.9 Hz, 2H, Ar), 6.79 (d, J = 8.8 Hz, 2H, Ar), 5.36 (brd, J = 4.04 Hz, 1H, olefinic), 4.62 (m, 1H, CHOCO), 3.94 (t, J = 6.4 Hz, 2H, 1 × OCH_2), 2.31 (t, J = 7.2 Hz, 4H, 2 × allylic methylene), 2.01–1.03 (m, 32 H, 13 × CH_2, 6 × CH), 1.01 (s, 3H, 1 × CH_3), 0.91 (d, J = 6.5 Hz, 3H, 1 × CH_3), 0.86 (d, J = 1.8 Hz, 3H, 1 × CH_3), 0.85 (d, J = 1.8 Hz, 3H, 1 × CH_3), 0.67 (s, 3H, 1 × CH_3) and 0.22 (s, 9H, 3 × CH_3, Me_3Si). FAB Mass: 672.2 $[M]^+$. Elemental analysis calc. for $C_{44}H_{68}O_3Si$: C 78.52, H 10.18; found: C 78.68, H 10.43%.

2.2.4. *Cholesteryl 8-(4-trimethylsilylethynylphenoxy)-octanoate (**3d**)*

Yield = 800 mg (83%); R_f = 0.23 (10% EtOAc–hexanes). IR (KBr Pellet) ν_{max}: 2945, 2920, 2851, 2156, 1733, and 1507 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.38 (d, J = 8.9 Hz, 2H, Ar), 6.79 (d, J = 8.9 Hz, 2H, Ar), 5.36 (brd, J = 4.04 Hz, 1H, olefinic), 4.60 (m, 1H, CHOCO), 3.92 (t, J = 6.5 Hz, 2H, 1 × OCH_2), 2.31–2.2 (m, 4H, 2 × allylic methylene), 2.01–1.03 (m, 36 H, 15 × CH_2, 6 × CH), 1.01 (s, 3H, 1 × CH_3), 0.91 (d, J = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, J = 1.8 Hz, 3H, 1 × CH_3), 0.85 (d, J = 1.8 Hz, 3H, 1 × CH_3), 0.67 (s, 3H, 1 × CH_3) and 0.23 (s, 9H, 3 × CH_3, Me_3Si). Elemental analysis calc. for $C_{46}H_{72}O_3Si$: C 78.80, H 10.35; found: C 79.05, H 10.45%.

2.3. *General procedure for the preparation of cholesteryl (4-ethynylphenoxy)alkanoates (**2a**–**d**)*

To a solution of the protected alkyne (**3a**–**d**) (0.74 mmol) in dry THF was added a solution of $Bu_4N^+F^-$ in THF (2 ml) dropwise under an argon atmosphere. The resultant dark violet coloured solution was allowed to stir for 3 h at room temperature. The reaction mixture was then treated with a saturated aqueous solution of $NaHCO_3$ and shaken with ether (3 × 10 ml). The combined organic extracts were repeatedly washed with water and brine and then dried over anhydrous sodium sulphate. Evaporation of the solvent furnished an off-white solid, which was purified by coloumn chromatography on neutral aluminium oxide. Elution with a mixture of 10% EtOAC–hexanes afforded a white solid.

2.3.1. *Cholesteryl 4-(4-ethynylphenoxy)butanoate (**2a**)*

Yield = 410 mg (quantitative); R_f = 0.39 (10% EtOAc–hexanes). IR (KBr Pellet) ν_{max}: 2948, 2850, 2145, 1731, and 1508 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.41 (d, J = 8.8 Hz, 2H, Ar), 6.82 (d, J = 8.8 Hz, 2H, Ar), 5.36 (brd, J = 4.1 Hz, 1H, olefinic), 4.61 (m, 1H, CHOCO), 4.00

(t, $J = 6.12$ Hz, 2H, $1 \times OCH_2$), 2.99 (s, 1H, ethynyl H), 2.5–2.2 (m, 4H, $2 \times$ allylic methylene), 2.13–1.03 (m, 28 H, $11 \times CH_2$, $6 \times CH$), 1.00 (s, 3H, $1 \times CH_3$), 0.91 (d, $J = 6.52$ Hz, 3H, $1 \times CH_3$), 0.86 (d, $J = 1.8$ Hz, 3H, $1 \times CH_3$), 0.85 (d, $J = 1.76$ Hz, 3H, $1 \times CH_3$) and 0.67 (s, 3H, $1 \times CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 172.9, 159.64, 140.01, 133.99, 123.1, 114.87, 114.6, 84.07, 76.16, 74.53, 67.25, 57.1, 56.55, 50.44, 42.72, 40.14, 39.93, 38.55, 37.34, 37.0, 36.59, 36.2, 32.31, 32.27, 31.47, 28.63, 28.42, 28.21, 25.01, 24.69, 24.24, 23.22, 22.97, 21.44, 19.71, 19.12 and 12.26. FAB Mass: 572.0 $[M]^+$. Elemental analysis calc. for $C_{39}H_{56}O_3$: C 81.77, H 9.85; found: C 81.49, H 9.88%.

2.3.2. *Cholesteryl 5-(4-ethynylphenoxy)pentanoate (**2b**)*

Yield = 420 mg (quantative); $R_f = 0.4$ (10% EtOAc–hexanes). IR (KBr Pellet) ν_{max}: 2945, 2840, 2101, 1744, and 1508 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.41 (d, $J = 8.8$ Hz, 2H, Ar), 6.82 (d, $J = 8.8$ Hz, 2H, Ar), 5.36 (brd, $J = 4.76$ Hz, 1H, olefinic), 4.60 (m, 1H, CHOCO), 3.97 (t, $J = 5.64$ Hz, 2H, $1 \times OCH_2$), 2.98 (s, 1H, ethynyl H), 2.37–2.29 (m, 4H, $2 \times$ allylic methylene), 2.02–1.03 (m, 30 H, $12 \times CH_2$, $6 \times CH$), 1.01 (s, 3H, $1 \times CH_3$), 0.91 (d, $J = 6.52$ Hz, 3H, $1 \times CH_3$), 0.87 (d, $J = 1.8$ Hz, 3H, $1 \times CH_3$), 0.85 (d, $J = 1.76$ Hz, 3H, $1 \times CH_3$) and 0.67 (s, 3H, $1 \times CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 172.79, 159.31, 139.61, 133.56, 122.66, 114.41, 114.03, 83.69, 75.69, 73.92, 67.43, 56.67, 56.11, 49.99, 42.29, 39.70, 39.5, 38.13, 36.96, 36.57, 36.16, 35.77, 34.22, 31.84, 28.53, 28.21, 27.99, 27.79, 24.26, 23.80, 22.80, 22.55, 21.65, 21.0, 19.3, 18.69 and 11.84. FAB Mass: 586.0 $[M]^+$.

2.3.3. *Cholesteryl 6-(4-ethynylphenoxy)hexanoate (**2c**)*

Yield = 425 mg (quantitative); $R_f = 0.41$ (10% EtOAc–hexanes). IR (KBr Pellet) ν_{max}: 2947, 2920, 2851, 2160, 1707 and 1508 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.41 (d, $J = 8.76$ Hz, 2H, Ar), 6.82 (d, $J = 8.8$ Hz, 2H, Ar), 5.36 (brd, $J = 3.96$ Hz, 1H, olefinic), 4.65 (m, 1H, CHOCO), 4.00 (t, $J = 6.14$ Hz, 2H, $1 \times OCH_2$), 2.99 (s, 1H, ethynyl H), 2.5–2.2 (m, 4H, $2 \times$ allylic methylene), 2.2–1.0 (m, 32 H, $13 \times CH_2$, $6 \times CH$), 1.01 (s, 3H, $1 \times CH_3$), 0.91 (d, $J = 6.48$ Hz, 3H, $1 \times CH_3$), 0.87 (d, $J = 1.76$ Hz, 3H, $1 \times CH_3$), 0.85 (d, $J = 1.72$ Hz, 3H, $1 \times CH_3$) and 0.67 (s, 3H, $1 \times CH_3$). FAB Mass: 600.9 $[M]^+$. Elemental analysis calc. for $C_{41}H_{60}O_3$: C 81.95, H 10.06; found: C 82.08, H 10.17%.

2.3.4. *Cholesteryl 8-(4-ethynylphenoxy)octanoate (**2d**)*

Yield = 430 mg (quantitative); $R_f = 0.45$ (10% EtOAc–hexanes). IR (KBr Pellet) ν_{max}: 2947, 2851, 2149, 1702 and 1504 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.41 (d, $J = 8.8$ Hz, 2H, Ar), 6.82 (d, $J = 8.8$ Hz, 2H, Ar), 5.37 (brd, $J = 3.9$ Hz, 1H, olefinic), 4.62 (m, 1H, CHOCO), 3.94 (t, $J = 6.5$ Hz, 2H, $1 \times OCH_2$),2.98 (s, 1H, ethynyl H), 2.3–2.2 (m, 4H, $2 \times$ allylic methylene), 2.0–1.03 (m, 36 H, $15 \times CH_2$, $6 \times CH$), 1.01 (s, 3H, $1 \times CH_3$), 0.91 (d, $J = 6.56$ Hz, 3H, $1 \times CH_3$), 0.87 (d, $J = 1.8$ Hz, 3H, $1 \times CH_3$), 0.85 (d, $J = 1.64$ Hz, 3H, $1 \times CH_3$) and 0.67 (s, 3H, $1 \times CH_3$). FAB Mass: 628.2 $[M]^+$. Elemental analysis calc. for $C_{43}H_{64}O_3$: C 82.11, H 10.25; found: C 82.51, H 10.37%.

2.4. *General procedure for the preparation of bis{4-[ω-(cholest-5-en-3-yloxycarbonyl)alkoxy]-phenylethynyl}mercury (**1a**–**d**)*

Into a well stirred and cooled (0–5°C) freshly prepared alkaline solution of mercuric iodide [19] (3 ml) a solution of cholesteryl ω-(4-ethynylphenoxy) alkanoate (**2a**–**d**) (0.13 mmol) in a mixture of EtOH and diethyl ether was added dropwise over a period of 10 min. An off-white solid separated and was collected by filtration. This was washed thoroughly with water and cold EtOH. The crude compound was then recrystallized repeatedly from a mixture of CH_2Cl_2–hexanes (1:10).

2.4.1. *Bis{4-[ω-(cholest-5-en-3-yloxycarbonyl)-propyloxy]phenylethynyl}mercury (**1a**)*

Yield = 86 mg (65%). IR (KBr Pellet) ν_{max}: 2948, 2851, 2156, 1748 and 1508 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.40 (d, $J = 8.7$ Hz, 4H, Ar), 6.82 (d, $J = 8.7$ Hz, 4H, Ar), 5.37 (brd, $J = 4$ Hz, 2H, olefinic), 4.61 (m, 2H, $2 \times$ CHOCO), 4.0 (t, $J = 6$ Hz, 4H, $2 \times OCH_2$), 2.5–2.2 (m, 8H, $4 \times$ allylic methylene), 2.2–1.05 (m, 56 H, $22 \times CH_2$, $12 \times CH$), 1.01 (s, 6H, $2 \times CH_3$), 0.91 (d, $J = 6.5$ Hz, 6H, $2 \times CH_3$), 0.87 (d, $J = 1.6$ Hz, 6H, $2 \times CH_3$), 0.86 (d, $J = 1.6$ Hz, 6H, $2 \times CH_3$) and 0.67 (s, 6H, $2 \times CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 172.90, 159.57, 140.02, 134.24, 123.11, 119.65, 114.89, 114.78, 106.32, 74.53 67.26, 57.1, 56.55, 50.44, 42.73, 40.14, 39.93, 38.55, 37.39, 37.0, 36.59, 36.2, 32.31, 32.27, 31.47, 28.42, 28.63, 28.21, 25.01, 24.69, 24.24, 23.22, 22.97, 21.44, 19.72, 19.12 and 12.5. FAB Mass: 1343.3 $[M]^+$. Elemental analysis calc. for $C_{78}H_{110}O_6Hg$: C 69.69, H 8.25; found: C 69.38, H 8.13%.

2.4.2. *Bis{4-[ω-(cholest-5-en-3-yloxycarbonyl)-butyloxy]phenylethynyl}mercury (**1b**)*

Yield = 95 mg (72.5%). IR (KBr Pellet) ν_{max}: 2950, 2845, 2156, 1748 and 1508 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.40 (d, $J = 8.8$ Hz, 4H, Ar), 6.82 (d, $J = 8.8$ Hz, 4H, Ar), 5.37 (brd, $J = 4.48$ Hz, 2H, olefinic), 4.60 (m, 2H, $2 \times$CHOCO), 3.97 (t, $J = 5.36$ Hz, 4H, $2 \times OCH_2$), 2.37–2.29 (m, 8H, $4 \times$ allylic methylene), 2.02–1.04 (m, 60 H, $24 \times CH_2$, $12 \times CH$), 1.01 (s, 6H, $2 \times CH_3$), 0.91 (d, $J = 6.52$ Hz, 6H, $2 \times CH_3$), 0.87 (d, $J = 1.84$ Hz, 6H, $2 \times CH_3$), 0.85 (d, $J = 1.8$ Hz, 6H, $2 \times CH_3$) and 0.67 (s, 6H, $2 \times CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 172.79, 159.24, 139.61, 133.81, 122.66, 119.18, 114.44, 114.22,

105.94, 73.92 67.43, 56.66, 56.11, 49.99, 42.29, 39.70, 39.49, 38.13, 36.96, 36.57, 36.16, 35.77, 34.23, 31.84, 31.78, 28.52, 28.21, 27.99, 27.79, 24.27, 23.80, 22.80, 22.65, 21.65, 21.0, 19.3, 18.69 and 11.84. FAB Mass: 1371.5 $[M]^+$. Elemental analysis calc. for $C_{80}H_{114}O_6Hg$: C 70.01, H 8.37; found: C 69.50, H 8.28%.

2.4.3. *Bis{4-[ω-(cholest-5-en-3-yloxycarbonyl)-pentyloxy]phenylethynyl}mercury (**1c**)*

Yield = 90 mg (67%). IR (KBr Pellet) ν_{max}: 2949, 2920, 2851, 2150, 1747 and 1508 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.40 (d, J = 8.64 Hz, 4H, Ar), 6.81 (d, J = 8.68 Hz, 4H, Ar), 5.37 (brd, J = 3.8 Hz, 2H, olefinic), 4.62 (m, 2H, 2 × CHOCO), 4.00 (t, J = 6.02 Hz, 4H, 2 × OCH_2), 2.5–2.2 (m, 8H, 4 × allylic methylene), 2.2–1.05 (m, 64 H, 26 × CH_2, 12 × CH), 1.01 (s, 6H, 2 × CH_3), 0.91 (d, J = 6.44 Hz, 6H, 2 × CH_3), 0.86 (d, J = 1.36 Hz, 6H, 2 × CH_3), 0.85 (d, J = 1.37 Hz, 6H, 2 × CH_3) and 0.67 (s, 6H, 2 × CH_3). FAB Mass: 1399.2 $[M]^+$. Elemental analysis calc. for $C_{82}H_{118}O_6Hg$: C 70.33, H 8.49; found: C 69.93, H 8.29%.

2.4.4. *Bis{4-[ω-(cholest-5-en-3-yloxycarbonyl)-heptyloxy]phenylethynyl}mercury (**1d**)*

Yield = 95 mg (95%). IR (KBr Pellet) ν_{max}: 2941, 2920, 2145, 1735 and 1506. ^1H NMR (400 MHz, $CDCl_3$): 7.40 (d, J = 8.72 Hz, 4H, Ar), 6.82 (d, J = 8.76 Hz, 4H, Ar), 5.37 (brd, 2H, olefinic), 4.60 (m, 2H, 2 × CHOCO), 3.94 (t, J = 6.44 Hz, 4H, 2 × OCH2), 2.31–2.25 (m, 8H, 4 × allylic methylene), 2.02–1.03 (m, 72 H, 30 × 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 = 1.72 Hz, 6H, 2 × CH_3), 0.85 (d, J = 1.72 Hz, 6H, 2 × CH_3) and 0.67 (s, 6H, 2 × CH_3). FAB Mass: 1456.0 $[M]^+$. Elemental analysis calc. for $C_{86}H_{126}O_6Hg$: C 70.92, H 8.71; found: C 70.5, H 8.95%.

3. Results and discussion

3.1. *Synthesis*

The trimesogenic mercury complexes (**1a–d**) and their intermediates (**2a–d**, **3a–d**, **4a–d** and **5a–d**) were synthesized as outlined in the scheme. The cholesteryl ω-bromoalkanoates (**5a–d**) were synthesized by treating commercial, optically pure cholesterol with the ω-bromoalkanoyl chlorides [16, 17]. The cholesteryl ω-(4-iodophenoxy) alkanoates (**4a–d**) were prepared by reacting 4-iodophenol with the bromo compounds **5a–d** as reported in the literature [17]. Upon coupling these iodo-compounds **4a–d** with trimethylsilylacetylene under palladium(0)–copper(I) catalyzed reaction conditions, the protected cholesteryl phenylacetylenes **3a–d** were obtained in 70–80% yield. These acetylenes were treated with *tetra-n*-butylammonium fluoride to give the cholesteryl phenylacetylenes **2a–d** in quantitative yields. The trimesogenic mercury complexes **1a–d** were obtained when a freshly prepared aqueous alkaline solution of mercuric iodide [19] was treated with the cholesteryl phenylacetylenes. The molecular structures of these mercury complexes and the intermediates were confirmed by spectroscopic analysis (see § 2 for details).

3.2. *Thermal behaviour*

All the intermediates and the target molecules were investigated for their thermal behaviour by polarizing optical microscopy and differential scanning calorimetry. The results are summarized in the table. It is surprising to note that the intermediate cholesteryl ω-[(4-trimethylsilylethynyl)phenoxy] alkanoates (**3a–d**) are non-mesomorphic, though they contain cholesterol as a chiral moiety which is itself a pro-mesogenic structure. This behaviour could be attributed to the presence of the bulky terminal trimethylsilyl group in the molecule. The corresponding free phenyl acetylenes, namely the cholesteryl ω-(4-ethynylphenoxy) alkanoates (**2a**, **2c**, **2d**) show an enantiotropic N* mesophase; although compound **2b** does not. The significant differences in clearing temperature can be explained as follows. In these compounds (**2a–d**), the cholesterol moiety and the phenylacetylene core are linked to the alkylene spacer via a carbonyl group and an ether linkage respectively. In these and similar types of compound (dimers) the conventional way of counting for the parity of the spacer is to consider only the number of carbon atoms in the methylene units (as in our presentation). For example, compound **2a** is considered to be an odd-member of the series because three methylene units separate the two rigid cores, whereas if the carbon atom of carbonyl group is also taken as a part of the central spacer then

Table. Transition temperatures[a] (°C) and associated enthalpies (J gm^{-1}) in parentheses of the intermediates and metallomesogens: Cr = crystal; N* = chiral nematic; I = isotropic phase; d = decomposes.

Compounds	Phase transition sequence
1a	Cr_1 150.0 (19.5) Cr_2 199.6 (10.2) N* 240[b] d
1b	Cr_1 124.2 (13.6) Cr_2 186.5 (19.4) N* 215 [b] d
1c	Cr_1 155.3 (31.2) Cr_2 211.8 (19.2) N* 240 [b] d
1d	Cr 165.5 (42.9) N* 205 d
2a	Cr 104.7 (52.8) N* 144.3 (2.15) I
2b	Cr 108.5 (66.9) I
2c	Cr_1 73.7 (24.5) Cr_2 94.6 (42) N* 132.2 (2.7) I
2d	Cr 74.5 (56.5) N* 119.9 (3.1) I
3a	Cr 104.5 (64.6) I
3b	Cr 101.3 (51.5) I
3c	Cr 115.2 (51.8) I
3d	Cr 131.9 (67.7) I

[a] Peak temperatures in the DSC thermograms obtained during heating cycles at 5°C min^{-1}.

[b] At this temperature the complex decomposes.

it would be an even-member. However, for the sake of uniformity with the conventions followed in the literature and our earlier publications [15–18] we count only the number of methylene units in considering the parity of the spacer unit. Thus compounds **2a**, **2c** and **2d** (in which the total number of carbons in the spacer is 4, 6 and 8, respectively) exhibit higher clearing temperatures than **2b** (in which the spacer is C_5). We have verified this point by molecular modelling (CS Chem3D software). This showed that the length of the molecule **2a** in its most extended *all-trans*-conformation is about 29 Å while for **2b** it is about 24 Å. The reduced length due to a larger bending angle in the case of **2b** explains the decrease in the clearing temperature and the non-mesomorphic behaviour.

On the other hand, the thermal behaviour of the organomercury trimesogens (**1a–d**) has been rather disappointing. All these complexes (**1a–c**) with the exception of **1d** exhibit transitions corresponding to the change from one crystalline state to another. The mercury complex **1a** having a C_3-paraffinic spacer melts to a mesophase at 200°C, exhibiting a non-specific texture. On shearing, a focal-conic pattern (figure 1) appears and in some regions of the slide a finger print pattern was also noticed (figure 2). These textures are characteristic of the N* phase and indicate that the pitch of the helix is quite large. On further heating, some dark regions begin to appear in the field of view that could be attributed to slow thermal decomposition of the compound. At about 240°C the complex decomposes completely. Compound **1b** consisting of a C_4-spacer melts to a mesophase at 186°C exhibiting an oily streak texture which on slight shearing changes to a planar texture (figure 3) indicating the presence of the N* phase. On further heating, large dark regions appear and finally decomposition is complete at about 215°C. The organomercury complex **1c** on heating melts to an N* phase showing a focal-conic textural pattern, as seen for compound **1a**,

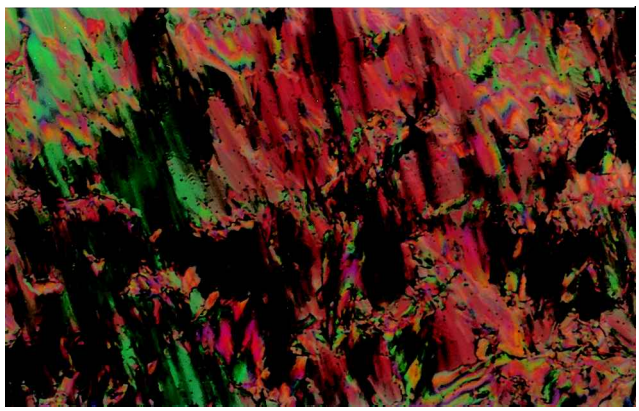


Figure 1. Photomicrograph of the broken focal-conic texture observed for complex **1a** in the N* phase at 228°C.

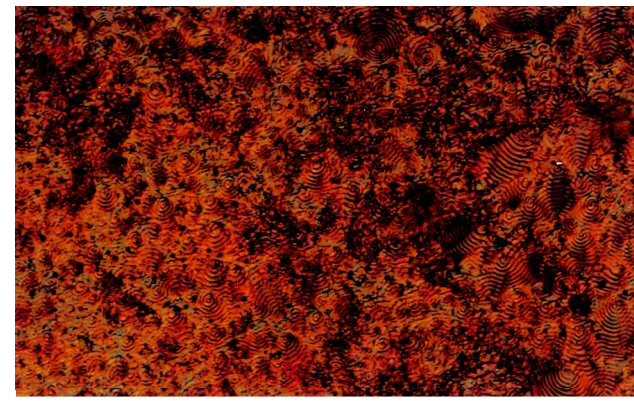


Figure 2. Photomicrograph of the finger-print pattern observed for complex **1a** in the N* phase at 228°C in another region of the slide.

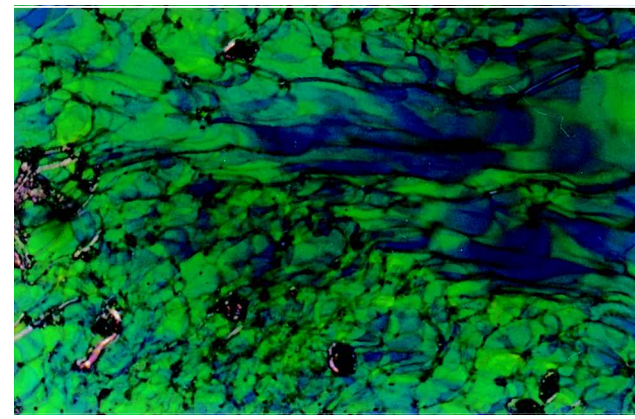


Figure 3. Photomicrograph of the planar texture of the N* phase observed for complex **1b** at 192°C.

that remains uniform over the entire region. This was true whether the substrate was just clean glass or a glass plate treated with either a polyimide solution for planar orientation or a silane solution for homeotropic alignment. Needless to say, this trimer also shows sensitivity to heat. The complex **1d** upon heating melts to an N* phase exhibiting an oily streak texture and on further heating it decomposes at about 205°C. Overall it appears that these complexes are highly sensitive to heat.

4. Summary

In conclusion, we have reported the synthesis and thermal behaviour of cholesteryl phenylacetylenes and their corresponding mercury complexes. These serve as the first examples of organomercury trimesogenic compounds. These organomercury trimesogens, having bis[(4-phenyl)ethynyl]mercury as the central core connected on each side to cholesteryl ester moieties through either an even–even (C_4) or odd–odd (C_3, C_5 and C_7) central alkylene spacer, show the chiral nematic phase.

These mercury complexes are extremely sensitive to heat as has been evident from other reports on such complexes.

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