A novel calamitic liquid crystalline oligomer composed of three non-identical mesogenic entities: synthesis and characterization

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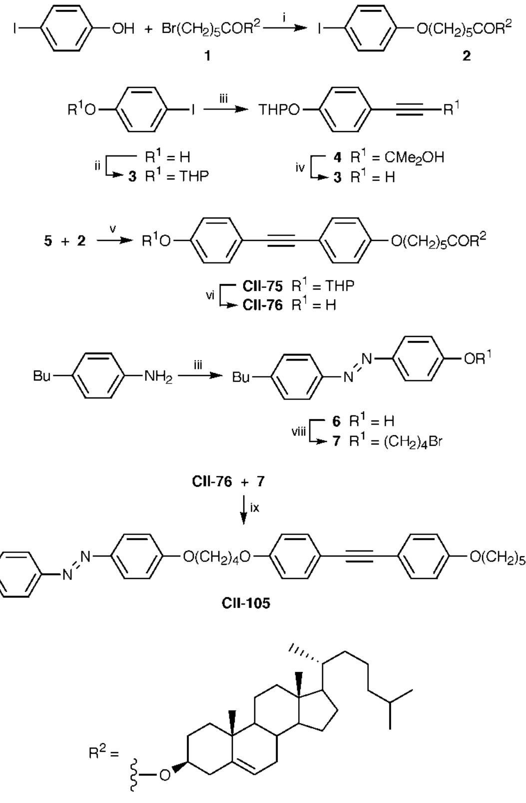
The synthesis and evaluation of the mesomorphic properties of the first trimesogen consisting of three non-identical calamitic mesogenic entities have been described.

Liquid crystalline dimers[1] (dimesogens) consisting of two identical (symmetrical) or non-identical (non-symmetrical) mesogenic units have gained attention as these are regarded as model compounds for main chain[2] and side chain liquid crystalline polymers.[3] The non-symmetrical dimers are markedly different from those of symmetrical ones as they exhibit interesting polymorphic sequence[4] and stabilize wide range chiral nematic (N*)[5a] and smectic A (SmA) mesophases.[5b] The addition of one more mesogenic moiety to a dimer *via* a flexible spacer results in the next higher oligomer, which has been called a trimesogen, trimer or triplet liquid crystal.[6] We shall adopt the term ‘trimesogen’ in this article. Based on the molecular structure of the individual calamitic entities there can be three possible combinations: (i) all of them are structurally identical, (ii) two of them are identical while the third entity is different, and (iii) all three are different. These trimesogens are of interest because of the recent demonstration that a flexible backbone based virtual trimer model successfully accounts for the transitional properties of side chain liquid crystalline polymers.[3b] Trimesogens of type (i) and (ii) were reported for the first time in 1986[7] and since then a few other examples of these types have been reported.[6] To the best of our knowledge trimesogens of type (iii) have not been reported to date. In continuation of our work on oligomeric liquid crystals, here we present the synthesis of the first type (iii) trimesogen composed of three different calamitic mesogenic entities, namely, cholesteryl ester, diphenylacetylene (tolan) and azobezene moieties.

In our recent investigations we had demonstrated that the combination of a cholesteryl ester unit and a tolan unit through an *n*-pentyl (odd) spacer stabilizes a wide-range N* phase.[5a] Owing to a change in the helical pitch the N* phase shows a temperature dependent wavelength of selective reflectivity (thermochromism). Another field of materials research that has been of considerable current interest is the phenomenon of photochromism, which holds lot of promise for applications such as optical information storage technology.[8] Therefore we aimed to synthesize a trimesogen which is multifunctional, satisfying two criteria: (i) it exhibits thermochromism over a wide range of temperature, and (ii) it is photochromic at the same time. A major advantage of single component multifunctional liquid crystal is that the problem of phase separation, which occurs in mixtures of mesogenic monomers and functional monomers, is avoided.[9] Here we report the synthesis of such a multifunctional liquid crystal and a preliminary investigation of the mesomorphic properties of this novel trimesogen.

The synthetic approach employed for the trimesogen, cholesteryl 6-{4-[4-[(4-butylphenylazophenoxy)butoxy]phenylethynyl]phenoxy}hexanoate (**CII-105**), is shown in Scheme 1. It was conceived that **CII-105** could be prepared by combining two key fragments, the non-symmetrical dimeric phenol **CII-76** and butylbromo azobenzene **7**. Accordingly, both the fragments were synthesized and coupled under mild basic conditions to give **CII-105** as a yellow crystalline compound.†

The liquid crystalline properties of **CII-105** were studied using an optical polarizing microscope (Leitz DMRXP) and a differential scanning calorimeter (Perkin Elmer DSC7). For polarizing microscopic observations, glass plates coated with a polyimide solution and unidirectionally rubbed were used. On cooling from the isotropic phase (I) at 247.7 °C the N* phase with a characteristic planar texture is seen in which the nematic director lies in the plane of the substrates. This ensures that the helical axis is perpendicular to the glass plates, *i.e.* along the viewing direction. At a second transition below 215 °C, the texture changes to a square grid pattern, which persists down to 119 °C, when it transforms into a third mesophase. If the sample is observed in a wedge type cell with similar surface treatment to the parallel cell, Grandjean Cano dislocation lines are observed in both the cholesteric and second mesophases demonstrating that there is a helical twist normal to the plates in both cases. Thus the low temperature phase shows the Cano lines superposed on the square grid pattern (see Fig. 1). If the plates are treated to give a homeotropic alignment, a filament texture is observed with an undulatory structure whose



Scheme 1 *Reagents and conditions*: i, anhydrous K_2CO_3, cat. KI, butan-2-one, 70 °C, 24 h, 84%; ii, dihydropyran, PPTS, CH_2Cl_2, room temp., 12 h, quant.; iii, 2-methylbut-3-yn-2-ol, $(PPh_3)_2PdCl_2$, CuI, PPh_3, Et_3N, 65 °C, 16 h, 80%; iv, KOH, toluene, 110 °C, 2 h, 64%; v, $(PPh_3)_2PdCl_2$, CuI, PPh_3, Et_3N, 75 °C, 16 h, 75%; vi, TsOH, MeOH–THF, room temp., 30 min, 68%; vii, $NaNO_2$, HCl, phenol, 0–5 °C, 2 h, 78%; viii, 1,4-dibromobutane, anhydrous K_2CO_3, acetone, 60 °C, 90%; ix, anhydrous K_2CO_3, DMF, 80 °C, 24 h, 52%.

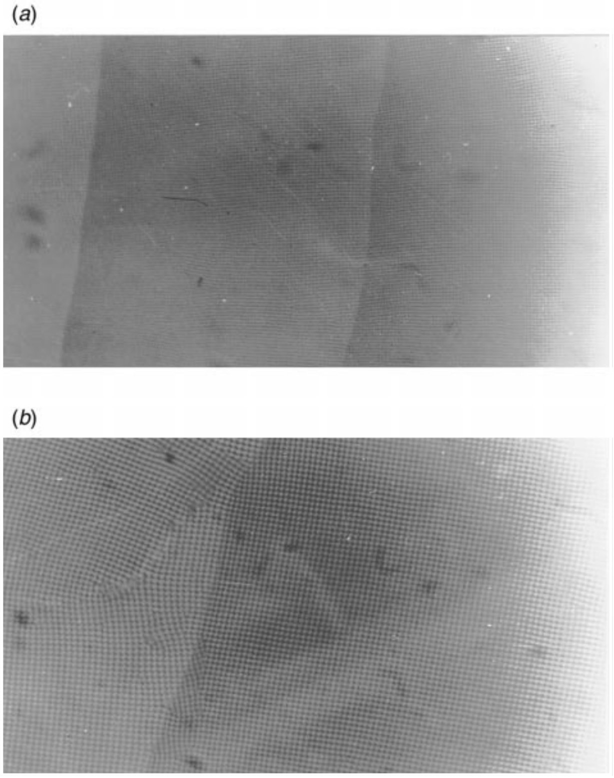


Fig. 1 Optical microscopic texture observed (magnification 400×) for the $UTGB_{C*}$ phase at 212.3 °C while cooling from the N* phase. (*a*) The Grandjean Cano lines (the two striations running from the top to the bottom of the picture) indicate the presence of a helix whose axis is normal to the photograph.The square grid patterns [shown on an enlarged scale in (*b*)] arise from a two-dimensional modulation perpendicular to the helix. The simultaneous existence of both these features is supposed to be proof of the existence of the $UTGC_{C*}$ phase.

periodicity is approximately the same as that of the spacing in the square grid pattern mentioned above. Again, the filament texture remains unchanged down to 119 °C. The features described here for the low temperature mesophase are identical to the textural observations for the very recently reported[10] undulated twist grain boundary ($UTGB_{C*}$) phase in a binary system as well as in a single compound. While in the binary mixture the $UTGB_{C*}$ phase is reported to occur over a narrow range of temperature (~ 4 °C),[10a] the range is not mentioned in the case of the single compound.[10c] In view of these observations it is remarkable that the second mesophase in **CII-105**, which shows the essential features of the $UTGB_{C*}$ phase, *viz.* simultaneous existence of a square grid texture and a helical structure perpendicular to it, exists over a large temperature range of 90 °C. According to the proposed model,[10a] the $UTGB_{C*}$ phase is a highly frustrated phase characterized by modulations in all the three dimensions, with the two-dimensional undulation of the smectic C*-like blocks being orthogonal to the helix of the TGB structure. Hence, it is all the more interesting to see that a phase with such a highly-frustrated structure exists over a wide temperature range. The mesophase below 119 °C seems to be a highly ordered one, and its detailed characterisation is underway.

The transition temperatures obtained from the cooling mode DSC scan along with the enthalpies are given in Scheme 2 (the transition from the cholesteric to the second mesophase was too weak for any reliable calculation of the enthalpy). It is worth mentioning here that the trimesogen **CII-105** is thermally stable during repeated heating and cooling cycles through the mesophases–isotropic transition, as confirmed by a ^1H NMR scan of the same sample which had been subjected to the DSC experiments. The profile obtained was identical, within experimental error, to that for the pristine sample.

$$\mathrm{I} \xrightarrow[(12.06\ \mathrm{J\ g^{-1}})]{247.7\ ^\circ\mathrm{C}} \mathrm{N^*} \xrightarrow{215\ ^\circ\mathrm{C}} \mathrm{UTGB_{C^*}} \xrightarrow[(1.72\ \mathrm{J\ g^{-1}})]{119.15\ ^\circ\mathrm{C}} \mathrm{X} \xrightarrow[(7.04\ \mathrm{J\ g^{-1}})]{93.2\ ^\circ\mathrm{C}} \mathrm{K}$$

Scheme 2 The number in parenthesis indicates the transition enthalpy; X is a highly ordered mesophase and yet to be fully characterized; K = crystal.

In conclusion we have achieved the synthesis of the first trimesogen containing three non-identical calamitic mesogenic entities connected by flexible spacers. The compound is multifunctional, containing themochromic and photochromic mesogenic units. Such substances have potential as materials for information storage technology and replace mixtures of mesogenic compound in different applications, thereby solving phase separation problems associated with such mixtures. These may perhaps also serve as model compounds (which are yet to be realized) for co-polymeric liquid crystals. Interestingly, this oligomer stabilizes a recently discovered $UTGC_{C*}$ phase—supposed to be a highly frustrated phase—over a wide temperature range of 90 °C and thus invites systematic investigations so as to understand this behavior.

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Notes and references

† The trimesogen **CII-105** and other intermediates exhibited spectral data consistent with their molecular structure. *Selected data* for **CII-105**: ν_{max}(KBr)/cm^{-1} 2950, 2863, 1729, 1607 and 1578; δ_H(500 MHz, $CDCl_3$) 7.89 (d, *J* 8.9, 2H, Ar), 7.8 (d, *J* 8.15, 2H, Ar), 7.44 (d, *J* 5.9, 2H, Ar), 7.42 (d, *J* 5.8, 2H, Ar), 7.3 (d, *J* 8.15, 2H, Ar), 7.0 (d, *J* 8.95, 2H, Ar), 6.87 (d, *J* 8.75, 2H, Ar), 6.84 (d, *J* 8.85, 2H, Ar), 5.36 (br d, *J* 4.85, 1H, olefinic), 4.6 (m, 1H, C*H*OCO), 4.12 (br t, 2H, OCH_2), 4.06 (br t, 2H, OCH_2), 3.96 (t, *J* 6.4, 2H, OCH_2), 2.68 (t, *J* 7.65, 2H, ArCH_2), 2.31 (m, 4H, 2 × C=CH_2), 2.01–0.9 (m, 40H, 17 × CH_2, 6 × C*H*), 1.02 (s, 3H, CH_3), 0.94 (t, *J* 7.25, 3H, CH_3), 0.91 (d, *J* 6.5, 3H, CH_3), 0.87 (d, *J* 2.1, 3H, CH_3), 0.86 (d, *J* 2.1, 3H, CH_3) and 0.67 (s, 3H, CH_3); δ_C(100 MHz, $CDCl_3$) 172.93, 161.22, 158.87, 158.75, 151.05, 147.1, 145.73, 139.67, 132.83, 128.99, 124.54, 122.59, 122.51, 115.8, 115.61, 114.67, 114.5, 88.04, 87.91, 73.82, 67.77, 67.69, 67.48, 56.69, 56.16. 50.05, 42.31, 39.74, 39.51, 38.16, 36.99, 36.59, 36.19, 35.77, 35.52, 34.54, 33.41, 31.88, 28.87, 28.2, 27.82, 25.95, 25.57, 24.76, 24.26, 23.83, 22.77, 22.53, 22.3, 21.03, 19.28, 18.71, 13.88 and 11.835; *m/z* (FAB) 1001 $[MH]^+$ (calc. for $C_{67}H_{88}N_2O_5$).

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