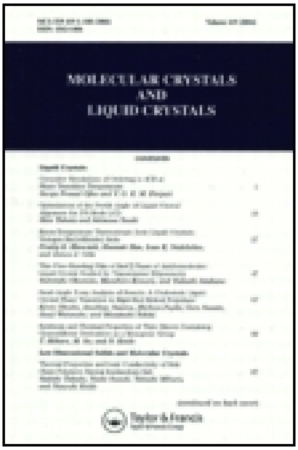

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# A Novel Dimesogen with a Cholesteric Phase of Wide Temperature Range: Synthesis and Characterisation

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# A Novel Dimesogen with a Cholesteric Phase of Wide Temperature Range: Synthesis and Characterisation

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Dimesogenic compounds consisting of two non-identical mesogenic units connected through a polymethylene spacer are now of interest in the area of liquid crystal research. Previous studies have shown that dimesogens made up of a cholesteryl ester unit and a Schiff's base unit connected through a central alkyl spacer give rich mesomorphism. We have taken up investigations to study the effects of replacing the Schiff's base moiety with a tolan unit. As an example, the dimesogen; cholesteryl 6-[4-(4-*n*-butyloxyphenylethynyl)phenoxy]hexanoate was synthesized and studied for its liquid crystalline properties. Although this compound shows only one mesophase, *viz*., the cholesteric phase, the temperature range of the mesophase is very wide, perhaps one of the largest ranges reported to date.

*Keywords:* Wide range cholesteric phase; dimesogen; tolan; Schiff's base

## INTRODUCTION

The synthesis of compounds consisting of two mesogenic units connected by a flexible spacer has attracted attention [1] because firstly, these dimesogens (which can be called dimers if the two mesogenic units are identical) help in understanding the behaviour of semi-rigid main chain polymeric systems which they resemble [2] and secondly they could exhibit quite different properties from those of the individual mesogenic units. For example, Jung-Il, Jin [3a] and Hardouin *et al.* [3b] reported a dimesogen made up of a

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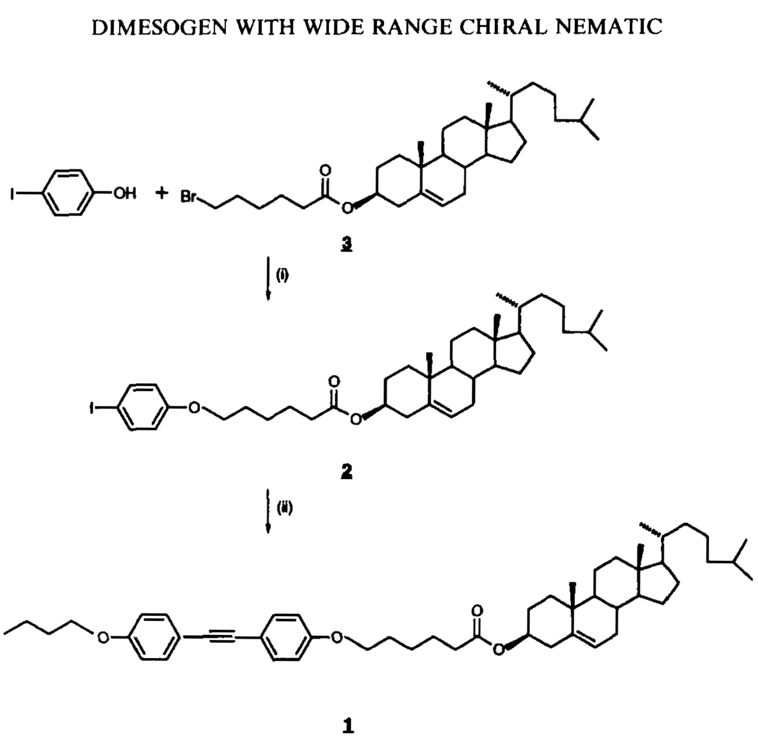
cholesteryl ester unit and a classical Schiff's base moiety connected through a central polymethylene spacer which exhibits reentrant sequences involving chiral smectic C phases and incommensurate smectic phases, none of which are observed in the individual mesogens themselves. As these authors have remarked in a later paper [3c] these materials are moisture sensitive, and in our own experience such type of compounds [4] seems to be thermally not very stable. A possible replacement for Schiff's base unit is the diphenylacetylene or what is generally termed as tolan. These tolanes are known to exhibit smectic and nematic phases [5].

In this paper we report the synthesis of one such dimesogen namely cholesteryl 6-[4-(4-*n*-butyloxyphenyl ethynyl)phenoxyl]hexanoate, hereafter referred to as 1, and its mesophase behaviour.

## RESULTS AND DISCUSSION

The synthetic sequence starting from cholesteryl 6-bromohexanoate (3) is shown in Scheme I. The starting material 3 was obtained by the esterification of the commercially available, optically pure cholesterol with 6-bromohexanoic acid chloride [3]. It was then treated with iodophenol to achieve etherification which furnished the key intermidiate compound 2 in 87% yield. The $Pd^{\circ}$ catalysed cross-coupling reaction [6] between 4-(*n*-butyloxy)phenylacetylene [7] and the iodo compound 3 provided the final compound 1 (Yield: 52%). The molecular structure of this dimesogen has been confirmed by IR, $^{1}H$ and $^{13}C$ NMR spectral analyses. Details of spectral analyses are as follows: IR (thin film): $\gamma_{max}$ 2940, 2890, 1720 and 1605 $cm^{-1}$, $^{1}$HNMR (500 MHz, $CDCl_3$): $\delta$ 7.43 (d, $J=8.2$ Hz, 4H, Ar), 6.86 (d, $J=6.05$ Hz, 2H, Ar), 6.84 (d, $J=6$ Hz, 2H, Ar), 5.38 (brd, $J=4.2$ Hz, 1H, Olefinic), 4.62 (m, 1H, -CHOCO- ), 3.98(t, $J=6.5$ Hz, 4H, $2\times OCH_2$), 2.25–0.95 (m, 40H, $17\times CH_2$, $6\times CH$), 1.02 (s, 3H, $CH_3$), 0.96 (t, $J=7.45$ Hz, 3H, $CH_3$), 0.92 (d, $J=6.45$ Hz, 3H, $CH_3$), 0.87 (d, $J=2.1$ Hz, 3H, $CH_3$), 0.86 (d, $J = 2.1$ Hz, 3H, $CH_3$) and 0.68 (*s*, 3H, $CH_3$); $^{13}$CNMR (50 MHz, $CDCl_3$): 172.9, 158.9, 158.8, 139.7, 132.8, 122.6, 115.6, 115.5, 114.5, 87.92, 73.8, 67.7, 56.7, 56.2, 50.1 42.3, 39.7, 39.5, 38.1, 37, 36.6, 36.2, 35.8, 34.5, 31.9, 31.2, 28.8, 28.2, 28, 25.6, 24.7, 24.3, 23.8, 22.8, 22.5, 21, 19.3, 19.2, 18.7, 13.8 and 11.8.

This compound was characterized using optical microscopy (Leitz DMRXP) and differential scanning calorimetry (Perkin Elmer DSC7). Figure 1 shows the DSC scans taken in both the heating and cooling modes at a rate of 5°C/min. In the heating mode three strong peaks are observed. Optical microscopic observations indicate that the peak at 107.7°C



SCHEME I Synthetic sequence for the dimesogen 1. **Reagents and conditions:** (i) anhyd. $K_2CO_3$, Cat.KI, 2-butanone, 70°C, 24 hrs; (ii) 4-(butyloxy)phenylacetylene, $[(C_6H_5)_3P]_2PdCl_2$, CuI, $Ph_3P$, $Et_3N$, 75°C, 16 hrs.

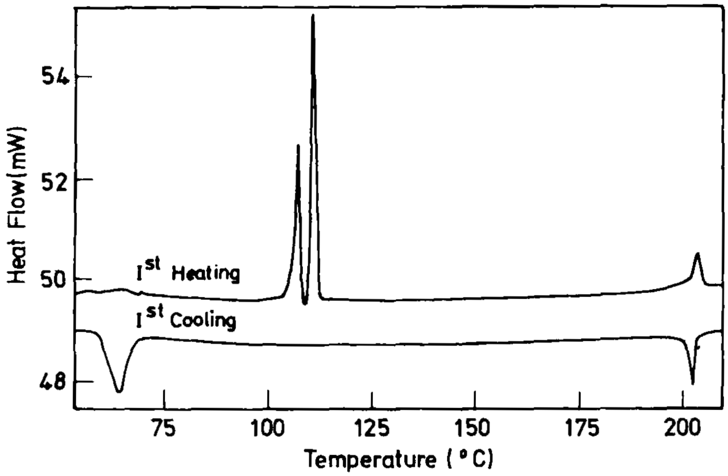


FIGURE 1 Differential scanning thermograms as a function of temperature for the heating and cooling cycles for dimesogen 1.

($\Delta H = 16.7$ kJ/mol) corresponds to a transition between two crystalline forms. The compound melts to cholesteric phase at 111.5°C and transforms to the isotropic phase at 203.3°C. The transition enthalpies for these two transitions are 24.0 and 3.8 kJ/mol respectively. When the sample is taken between a glass slide and a cover slip the cholesteric phase shows the oily streak texture (Fig. 2) which on slight shear changes to a planar texture. The colour of the planar texture was observed to gradually change with temperature. These features are characteristic features of a cholesteric phase. No other change was observed till the sample crystallised at ~64°C, thus establishing a wide temperature range (~130°C in the cooling mode) for the cholesteric phase.

To check on the thermal stability of the compound, DSC scans were repeated four times. The phase transition temperatures of all the heating and cooling cycles are in good agreement with each other (except for a slight variation in the crystallization temperature). A further check was performed by doing $^1$HNMR spectral analysis of the sample used for DSC runs, which conformed to the scans taken earlier.

In summary the dimesogen 1 having a diphenylacetylene moiety and a cholesteric unit connected by polymethylene spacer ($C_5$) has been synthesized. This compound exhibits a cholesteric phase with a wide temperature range (~130°C), perhaps one of the largest ranges reported till

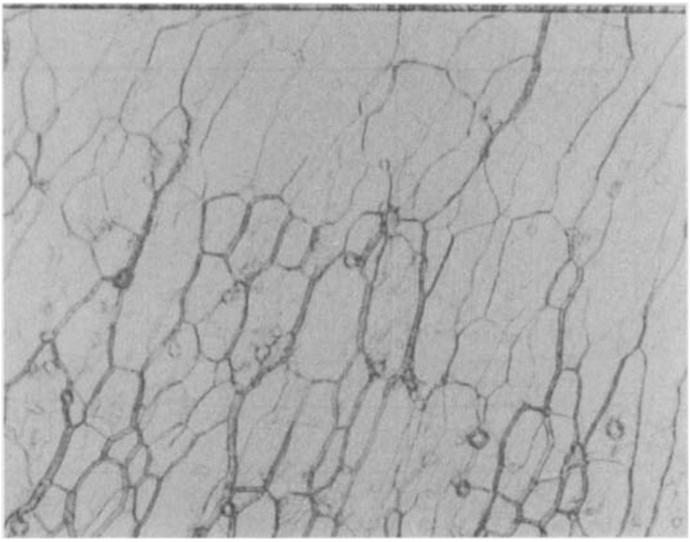


FIGURE 2 Optical texture observed on cooling from isotropic phase at 99.8°C for the dimesogen 1 between crossed polarizers (× 320). (See Color Plate X).

now. Other significant features of this compound are its good thermal stability and the isotropic phase transition temperature comparable to other cholesteryl monomeric derivatives [8]. We are continuing our synthetic work on such type of compounds to explore the possibility of further widening the cholesteric mesophase range and perhaps extending it to room temperature.

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