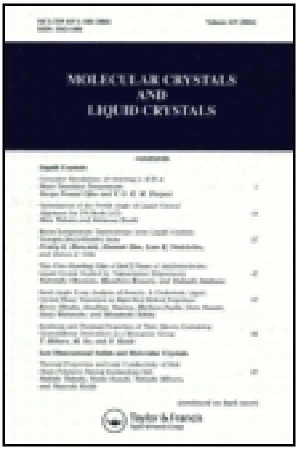

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New Chiral Discotic Liquid Crystals

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New Chiral Discotic Liquid Crystals

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Some new triphenylene based chiral discotic liquid crystals have been prepared from readily available, naturally occurring amino acids and terpene. Triphenylene derivatives bearing one (**3a-b, 4a**), three (**2a**) and six (**1a-c**) chiral chains have been synthesised and studied for their mesomorphic properties. Such materials may serve as excellent dopants to induce chiral phases. Induction of cholesteric phase in a nematic-discotic phase by doping with these chiral discotic LCs has been studied.

Keywords: Chiral discotic liquid crystals; triphenylene; leucine; isoleucine; citronellol

INTRODUCTION

The history of liquid crystals (LCs) started with chiral molecules, the esters of cholesterol, and since then several new chiral molecules were extensively explored for their use in twisted nematic, thermochromic, ferroelectric, *etc.*, devices. Though chiral calamitic LCs have been become on of the most important topics in the field of LCs and several compounds showing chiral nematic (N^*) and chiral smectic (Sc^*) mesophases are known, only a few chiral discotic (disc-like) LCs are known in the literature.

After the discovery of discotic liquid crystals in 1977 [1], efforts were made to prepare optically active discotic LCs to observe the effects of molecular chirality on mesophase formation and their physical properties. Destrade *et al.*, reported the synthesis of chiral esters of benzene, triphenylene and truxene showing a cholesteric phase 1980 [2]. Macroscopic evidence of molecular chirality in the columnar mesophase formed by two enantiomers

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of hexaesters of triphenylene with (R)-(+)- and (S)-(−)-3-methylnonanoic acid has been reported [3]. Observation of cholesteric phase and evidence of a chiral superstructure in phthalocyanine based discotic LCs have also been reported recently [4]. Ferroelectric switching in chiral discotic LCs was though to be a rare possibility till 1992 when Bock and Helfrich reported for the first time that the tilted phase of chiral discotic dibenzopyrene derivatives is ferroelectric [5]. A significant amount of work has been done by Bock and co-workers on the electrooptical and ferroelectrical switching of various chiral discotic LCs [5]. As the interest in chiral discotic liquid crystals is growing, several chiral multiyne derivatives were prepared and their helical twisting power was studied [6]. The phenomenon of selective reflection, helix inversion and induction of blue phases was also observed by doping a nematic–discotic phase with chiral dopants [6, 7]. However, in our own experience as well as that of others [8] many of these alkynes are not very thermally stable. Induction of cholesteric phases by charge transfer complexation of discotic molecules was also reported recently [9]. In most of the chiral discotic LCs, the chiral centre was placed in all the peripheral chains. Spiess and co-worker felt that such a high chiral perturbation may not generate a spiral column with a pitch extending over several discs within the column. They replaced only one of the six peripheral alkoxy chains of a hexaalkoxy triphenylene by a chiral ester chain [10]. The nature of the glass transition in a columnar phase formed by this material was extensively studied by X-ray scattering, 2D NMR and dielectric spectroscopy [10].

Clearly, significant research activities are going-on in the field of chiral discotic LCs and new materials are required to see the influence of chirality on the physical properties of the mesophases formed by disk-shape molecules. We have recently reported the synthesis of a variety of triphenylene derivatives [11] and in this communication we wish to report the synthesis and characterisation of some new triphenylene based chiral discotic LCs synthesised from readily available, naturally occurring amino acids and terpene.

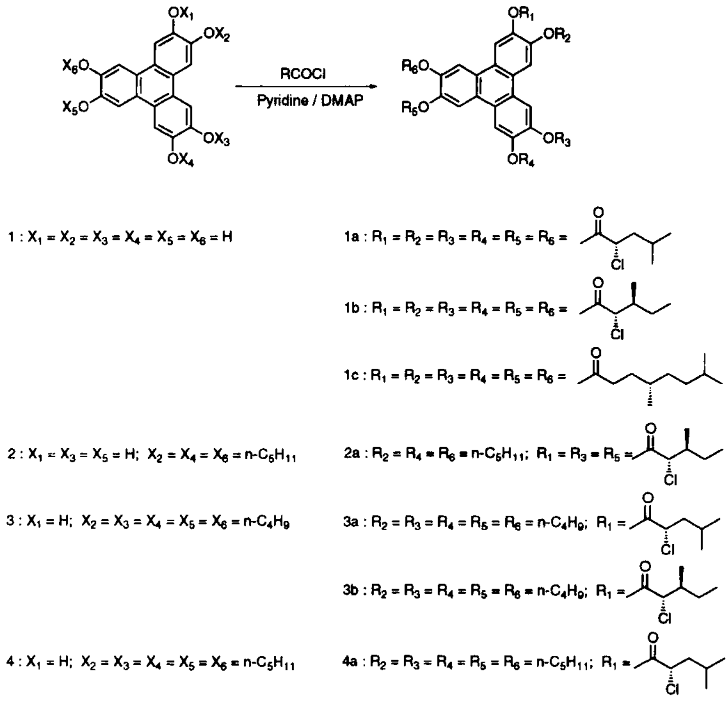
EXPERIMENTAL

General Information

Chemicals and solvents (AR quality) were obtained locally and used as such without any purification. Column chromatographic separations were performed on silica gel (70–230 and 200–400 mesh). Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). ^{1}H and ^{13}C NMR spectra were recorded on a 200 MHz Bruker Aveance Series DPX-200 NMR spectrometer. All chemical shifts are reported in δ(ppm) units downfield from Me_4Si, and J values are given in Hz. Optical rotations were measured on a JASCO polarimeter in chloroform ($c = 1$). IR spectra were recorded on a Schimadzu IR-435 spectrometer as solids over KBr pellets. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMFRT polarizing microscope as well as by differential scanning calorimetry (DSC7 Perkin–Elmer). The heating and cooling rate was 5°C/min. Synthesis of different triphenylene derivatives is outlined in Scheme 1.

Synthesis of 1a, 1b and 1c

Typical procedure for the synthesis: **1a**: To magnetically stirred solution of 2,3,6,7,10,11-hexahydroxytriphenylene trihydrate **1** [12] (0.216 g, 0.69 mmol)



SCHEME 1 Synthesis of new chiral triphenylene derivatives.

and 4-*N*,*N*-dimethylaminopyridine (DMAP) (15 mol%) in dry pyridine (2 ml, deoxygenated) was added (S)-2-chloro-4-methylpentanoic acid chloride (1.4 g, 8.2 mmol) over a period of 15 min. at 0°C under argon. The resultant suspensions was allowed to warm to room temperature and stirred for 24 hrs. The reaction mixture was poured into ice-cold aqueous. 0.01 N HCl (10 ml) and extracted with ether (3 × 10 ml). The combined ether extracts were washed with water, brine and dried over anhydrous sodium sulphate. Solvent was removed under vacuum and the resultant dark brown viscous oil was purified by column chromatography over silica gel. Elution with $CHCl_3$ afforded a off-white solid that was recrystallized from absolute alcohol to yield 0.063 g (10%) of **1a**. R_f 0.71 ($CHCl_3$); $[\alpha]_D = -8°$; IR: ν_{max} 3005, 2955 and 1767 cm^{-1}; ^1H NMR ($CDCl_3$): 8.03 (*s*, 6H, Ar), 4.72 (*t*, *J* = 12, 6H, 6XCHCl), 2.09 (*m*, 18H, $6XCH_2$, 6XCH), 1.09 (*d*, *J* = 5.8, 18H, $6XCH_3$) and 1.03 (*d*, *J* = 6, 18H, $6XCH_3$).

1b: White solid; yield: 35%; R_f 0.74 ($CHCl_3$); IR: ν_{max} 3010, 2980 and 1780 cm^{-1}; $[\alpha]_D = -34°$; ^1H NMR ($CDCl_3$): 8.07 (*m*, 6H, Ar), 4.58 (*m*, 6H, 6XCHCl), 2.24 (*m*, 6H, 6XCH), 1.55 (*m*, 12H, $6XCH_2$), 1.18 (*d*, *J* = 3.6, 18H, $6XCH_3$) and 1.04 (*t*, *J* = 5, 18H, $6XCH_3$).

1c: Off white solid yield: 72%; R_f 0.72 ($CHCl_3$); $[\alpha]_D = +6°$; IR: ν_{max} 3010, 2970 and 1768 cm^{-1}; ^1H NMR ($CDCl_3$): 8.23 (*s*, 6H, Ar), 2.65 (*dd*, *J* = 15.4, 5.7, 6H, 6XCHCO), 2.42 (*dd*, *J* = 15.8, 8.3, 6H, 6XCHCO), 2.17 (*m*, 6H, 6XCH), 1.44 (*m*, 36H, $18XCH_2$), 1.09 (*d*, *J* = 6.6, 18H, $6XCH_3$) and 0.89 (*d*, *J* = 6.5, 36H, $12XCH_3$); ^{13}C NMR: 170.5, 142.1, 127.5, 118.1, 41.6, 39.1, 37.1, 30.3, 27.9, 24.7, 22.7, 22.6 and 19.9.

Synthesis of 2a

A similar procedure was followed as above using 2,6,10-trihydroxy-3,7,11-tripentyloxytriphenylene **2** [11h] (0.102 g, 0.2 mmol), 4-*N*,*N*-dimethylaminopyridine (10 mol%) and (2S, 3S)-2-chloro-3-methylpentanoic acid chloride (0.182 g, 1.08 mmol). The pale yellow solid obtained was recrystallized from a mixture of ether and methanol (1:3) which furnished a white solid 100 mg (57%) of **2a**. R_f 0.62 ($CHCl_3$); $[\alpha]_D = +207°$; IR: ν_{max} 3000, 2950 and 1765 cm^{-1}; ^1H NMR ($CDCl_3$): 7.79 (*s*, 3H, Ar), 7.41 (*s*, 3H, Ar), 4.92 (*brd*, *J* = 3.9, 3H, 3XCHCl), 4.08 (*m*, 6H, $3XOCH_3$), 2.31 (*m*, 3H, 3XCH), 1.82 (*m*, 6H, $3XCH_2$), 1.61 (*m*, 6H, $3XCH_2$), 1.43 (*m*, 6H, $3XCH_2$), 1.26 (*d*, *J* = 6.6, 9H, $3XCH_3$) and 0.96 (*m*, 18H, $6XCH_3$).

Synthesis of 3a, 3b and 4a

A similar procedure was followed as above using 2-hydroxy-3,6,7,10,11-pentabutyloxytriphenylene **3** [11f] (0.069 mmol), DMAP (5 mol%) and (2S)-2-chloro-4-methylpentanoic acid chloride (0.017 g, 0.1 mmol in 1 ml of THF). The off white solid was recrystallized from a mixture of ether and methanol (1 : 3) which gave a white solid 40 mg (79%) of **3a**. R_f 0.72 (Ethyl acetate-hexane: 1 : 3); $[\alpha]_D = +6°$; IR: ν_{max} 3005, 2950 and 1765 cm^{-1}, ^{1}H NMR ($CDCl_3$): 8.09 (*s*, 1H, Ar), 7.85 (*s*, 2H, Ar), 7.82 (*s*, 2H, Ar), 7.77 (*s*, 1H, Ar), 4.67 (*t*, *J* = 6.3, 1H, 1XCHCl), 4.24 (*m*, 10H, 5XOCH$_2$), 1.98 (*m*, 13H, 6XCH$_2$, 1XCH), 1.61 (*m*, 14H, 7XCH$_2$) and 0.92 (*m*, 21H, 7XCH$_3$).

3b: White solid; yield: 77%; R_f 0.65 (Ethyl acetate-hexane: 1 : 3); $[\alpha]_D = +21°$; IR: ν_{max} 3000, 2950 and 1768 cm^{-1}; ^{1}H NMR ($CDCl_3$): 8.06 (*s*, 1H, Ar), 7.86 (*s*, 2H, Ar), 7.82 (*s*, 2H, Ar), 7.77 (*s*, 1H, Ar), 4.72 (*d*, *J* = 4.7, 1H, CHCl), 4.32 (*m*, 10H, 5XOCH$_2$), 2.24 (*m*, 1H, CH), 1.91 (*m*, 10H, 5XCH$_2$), 1.58 (*m*, 12H, 6XCH$_2$), 1.24 (*d*, *J* = 6.7, 3H, 1XCH$_3$) and 1.08 (*m*, 18H, 6XCH$_3$)

4a: Off-white solid; yield: 73%; R_f 0.71(Ethyl acetate-hexane: 1 : 3); $[\alpha]_D = -3°$ IR: ν_{max} 2970, 2800 and 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$): 8.09 (*s*, 1H, Ar), 7.85 (*s*, 2H, Ar), 7.82 (*s*, 2H, Ar), 7.77 (*s*, 1H, Ar), 4.67 (*t*, *J* = 6.2, 1H, 1XCHCl), 4.24 (*m*, 10H, 5XOCH$_2$), 1.99 (*m*, 13H, 6XCH$_2$, 1XCH), 1.47 (*m*, 20H, 10XCH$_2$) and 1.02 (*m*, 21H, 7XCH$_3$).

THERMAL BEHAVIOUR

The thermal behaviour of all the new compounds (**1a–c, 2a, 3a–b** and **4a**) are represented in Table I.

As may be seen from the data, all the new compounds, except **2a** are mesogenic and they exhibit classical textures of columnar mesophases upon cooling from the isotropic liquid. These textures are very similar to known textures for Col$_h$ phases (D_h phases according to previously followed notation). While in **1c** this phase stays till room temperature without showing any sign of crystallisation or any other transitions, compounds **1a** and **1b** show three unidentified broad transitions. The mesophases formed by compounds **1a** and **1b** are monotropic in nature. It was also observed that on keeping for some time above isotropic temperature, both compounds start decomposing. In the case of monoesters **3a**, **3b** and **4a**, a single mesophase transition was observed upon cooling and this is similar to

TABLE I Phase transition temperatures and enthalpies of new chiral triphenylene derivatives. Cr = crystal, M = mesophase, I = isotropic

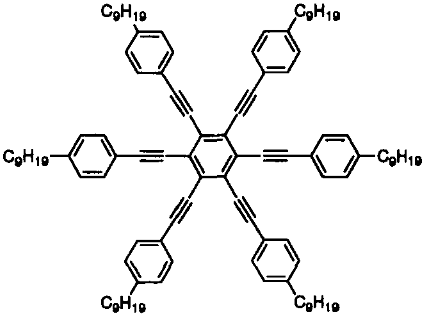
Compound	*Condition*	*Transition*	*T(°C)*	*ΔH(kJ/mol)*
1a	Ist heating	Cr-I	268.0	12.2
	Ist cooling	I-M	266.8	2.5
1b	Ist heating	Cr-I	264.1	32.6
	Ist cooling	I-M	243.7	23.2
1c	Ist heating	M-I	112.1	4.8
	Ist cooling	I-M	107.0	4.8
2a	Ist heating	Cr-I	200.9	7.8
3a	Ist heating	M-I	200.7	21.8
	Ist cooling	I-M	198.7	20.1
3b	Ist heating	M-I	192.7	21.8
	Ist cooling	I-M	188.9	20.4
4a	Ist heating	M-I	191.1	20.2
	Ist cooling	I-M	189.2	19.1

the behaviour of known (2S, 3S)-2-chloro-3-methyl-pentanoyloxy-pentakis(pentyloxy)-triphenylene which forms a highly ordered columnar liquid crystalline mesophase with a helical superstructure [10]. Mesophase stabilisation in these type of molecules due to steric hindrance of ester group has been discussed by Spiess and co-workers [10]. The above mentioned known compound shows a glass transition at about − 50°C [10] but the compound **3b**, the lower homologue of the above compound (pentabutyloxy chains and same chiral monoester) did not freeze to glass till − 60°C. Surprisingly, the crystal to melting transition has not been seen in any of these compounds but this type of abnormal behaviour has also been reported for other discotic LCs [13]. The melting transition for a very similar compound (2S, 3S)-2-chloro-3-methylpentanoyloxy-pentakis(pentyloxy)-triphenylene has also not been reported [10].

RESULTS AND DISCUSSION

The main aim of the present work was the development of highly chiral discotic LC dopants which can give helical twist in the nematic-discotic phases. To have a high twisting power of a chiral dopant, it is good to have polar group placed close to or better directly attached to the chiral centre. Also attachment of the chiral centre close to the core is important to increase the macroscopic chirality of the system. We chose two amino acids, leucine, isoleucine and a terpene, β-citronellol which are readily available in 100% optical purity to attach to the triphenylene core to achieve the requirement. The amino group of the two amino acids were replaced by the chloro group in S_{Ni} fashion using the Sandmeyer reaction conditions. These chloro acids were converted to acid chlorides with oxalyl chloride and the resultant acid chlorides were used to esterify the hexahyroxy-triphenylene [12], trialkoxy-trihydroxy-triphenylene [11h] and monohydroxy-pentaalkoxy-triphenylene [11f] under classical esterification conditions. The other chiral acid was prepared by first reducing the β-citronellol with Pd/C and H_2 at room temperature and 1 atmospheric pressure. The primary alcohol was oxidised to carboxylic acid using Jones oxidative reaction conditions and it was then converted to acid chloride and attached to triphenylene core.

Compared to the large number of calamitic molecules showing nematic phase, the number of disk-shaped molecule showing nematic phase N_D are rare. Various discotic multiynes having N_D phases, recently reported [14], are very suitable for studies as their clearing temperatures are not very high and they are known to show chiral nematic–discotic phase on doping with suitable chiral molecules [7, 9]. We chose the hexakis[(4-nonylphenyl)ethinyl)]-benzene **5** as host discotic molecule. It was prepared as reported [6–9, 14] and its phase behaviour, Cr 67°C N_D 83°C I, was found to be in agreement with the reported data [7]. All the new compounds were characterised by spectral analysis.

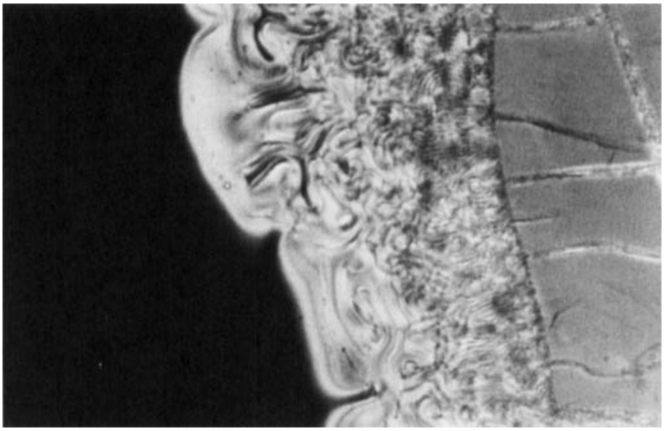


5

COMPOUND 5 Structure of hexakis[(4-nonylphenyl)ethinyl)]-benzene, Cr 67°C N_D 83°C I [7].

The induction of chiral phase in nematic–discotic phase of **5** was qualitatively checked by contact preparation. When the N_D phase of **5** was allowed to mix with the chiral triphenylene **1b**, induction of chiral nematic–discotic phase N_D^* was clearly seen at the interface as shown in Photograph 1.

As the clearing temperatures of these chiral triphenylene hexaesters were very high, we reduced the number of ester chains in the periphery and prepared triphenylene derivatives having one chiral ester-five ether chains



PHOTOGRAPH 1 Contact preparation of nematic-discotic compound **5** (left hand side) and chiral triphenylene derivative **1b** showing cholesteric phase at the contact region at 50°C (crossed polarizers, magnification X 320). (See Color Plate II).

(**3a**-**b**, **4a**) and three chiral ester-three ether chains (**2a**). These compounds were easily prepared by esterification of mono and trifunctionalized triphenylenes recently reported by us [11]. Contact preparation of all these materials, however, does not show any chiral induction in the host nematic-discotic phase.

Nevertheless, all the new triphenylene discotic LCs show highly ordered columnar phases which may be very useful for the study of conductivity, photoconductivity, one-dimensional charge migration, *etc*.

CONCLUSIONS

We have reported the synthesis of some new chiral triphenylene derivatives having six (**1a**-**c**), three (**2a**) and one (**3a**-**b**, **4a**) chiral chain/s in the periphery to evaluate their helical twisting power in nematic-discotic (N_D) phases. A qualitative contact mixture of **1b** and the nematic-discotic phase of the Compound **5** shows the induction of N_D^* phase. The potential uses of chiral discotic liquid crystals in ferroelectrical switching and other electro-optic applications need the development of new chiral discotic liquid crystals. Chiral discotic liquid crystals prepared from easily accessible triphenylene core and cheaply available chiral chains may serve this purpose. New chiral dopants may be very useful for various academic studies. It may also be possible to obtain tilted chiral columnar phases in pure chiral discotic LCs as well as in their mixtures. Preparation of other triphenylene based new chiral discotic LCs, quantitative evolution of their helical twisting power, characterisation of ordered columnar phases by X-ray and their various uses are currently under investigation in our laboratories.

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