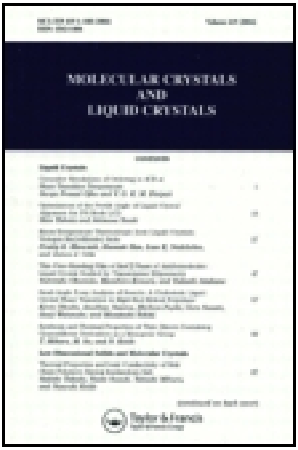

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Room-Temperature Discotic Nematic Liquid Crystals

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ROOM-TEMPERATURE DISCOTIC NEMATIC LIQUID CRYSTALS

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The use of discotic nematic liquid crystals instead of calamitic nematic liquid crystals to improve the viewing angle of a liquid crystal display device has recently been reported. Compared to the large number of calamitic molecules showing nematic phase at room temperature, the number of disk-shaped molecules showing subambient discotic nematic phase N_D *are rare. In this paper we present the design, synthesis, mesomorphic behaviour and structure-property relationship of discotic nematic liquid crystals based on benzene multiyne core.*

Keywords: discotic nematic liquid crystals; hexaalkynylbenzene; pentaalkynylbenzene; multi-ynes; liquid crystal display

INTRODUCTION

Twenty five years ago, in November 1977 a paper appeared in "*Pramana*", in which Chandrasekhar and his colleagues reported that not only rod-like molecules, but also compounds with disc-like molecular shape are able to form mesophases [1]. This discovery has opened up a whole new field of liquid crystal research. Mesophases formed by disc-shaped molecules, now commonly referred to as discotic liquid crystals, are primarily of two types – nematic and columnar [2–7]. A few discotic molecules are also reported to form discotic lamellar mesophases [8–12]. Recently, these materials are attracting much attention due to their remarkable electro-optical properties. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction [13–16]. Thus the columns may be described as

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molecular wires. Discotic liquid crystals based on various aromatic cores such as triphenylene, phthalocyanine, tricycloquinazoline, etc., have recently been emerged as a new class of fast photoconducting materials. Photoinduced charge carrier mobility (hole mobility) in the range of $10^{-3}\,\mathrm{cm^2v^{-1}s^{-1}}$to $0.38\,\mathrm{cm^2V^{-1}s^{-1}}$ has been reported in various columnar mesophases [17–20]. Electroluminescence and photovoltaic devices based on discotic liquid crystals have been prepared recently [21–26]. Mechanism of charge transport and one-dimensional energy migration has also been studied extensively in these materials [27–33].

In addition to the above mentioned non-display applications, discotic nematic liquid crystals have recently been reported to be useful for display applications also. We know that most of the liquid crystal displays (LCDs) are twisted nematic (TN) and supertwisted nematic (STN) type. The liquid crystal materials used in these devices are exclusively the calamitic liquid crystals (composed of rod-shaped molecules). In order to operate the device at ambient temperature, a number of calamitic nematic liquid crystals having room temperature mesophases have been synthesised. Although twisted nematic display devices are working well, the viewing angle is a critical problem for these displays. Several methods have been developed to widen the viewing angle of TN and STN devices [34–37] but some additional complex processes are required.

Unlike calamitic nematic liquid crystals, discotic nematic liquid crystals exhibit negative birefringence ($\Delta n < 0$). The negative birefringence film formed by polymerised nematic discotic LCs can be used as compensation foils to enlarge the viewing angle of twisted nematic LCDs [38,39]. In fact, this represents the first commercial application of discotic liquid crystals.

Chandrasekhar and his co-workers recently disclosed a novel approach to improve the viewing angle of a display device by utilising discotic nematic liquid crystals instead of calamitic nematic liquid crystals [40]. The device prepared using hexaalkynylbenzene based discotic nematic liquid crystal, exhibit wide and symmetrical viewing angle. However, the material used in the device has high temperature discotic nematic mesophase and, therefore, the device could not be tested at room temperature.

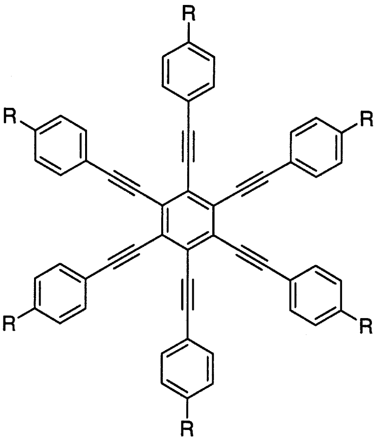
Compared to the large number of calamitic molecules showing nematic phase, the number of disk-shaped molecule showing discotic nematic phase N_D are rare and to our knowledge, only one compound having the discotic nematic phase at room-temperature is known [41]. In this hexaalkynylbenzene derivative a branched alkyl chain was directly connected to the phenyl ring to reduce melting and clearing temperatures. Here we present the synthesis, characterisation, thermal behaviour and structure-property relationship of several new hexa- and pentaalkynylbenzene based molecules.

DESIGN AND SYNTHESIS

In order to understand the structure-property relationship and to prepare room-temperature discotic nematic liquid crystals, we chose to work on discotic multiynes primarily because a number of compounds of this class are already known to show stable discotic nematic phases [42] and, therefore, some minor structural modifications may lead to materials having room-temperature discotic nematic phases. Studying the thermal behaviour of known compounds carefully, it can be deduced that increasing the size of peripheral alkyl chains in hexaalkynylbenzene derivatives gradually decreases the melting and clearing temperatures (Fig. 1) [42]. Hexaalkynylbenzene derivatives having only up to nine carbon atoms in the peripheral chains are known in the literature. Therefore, it would be interesting to know the thermal behaviour of higher homologues such as compound number **12a** and **12b** (Scheme 1).

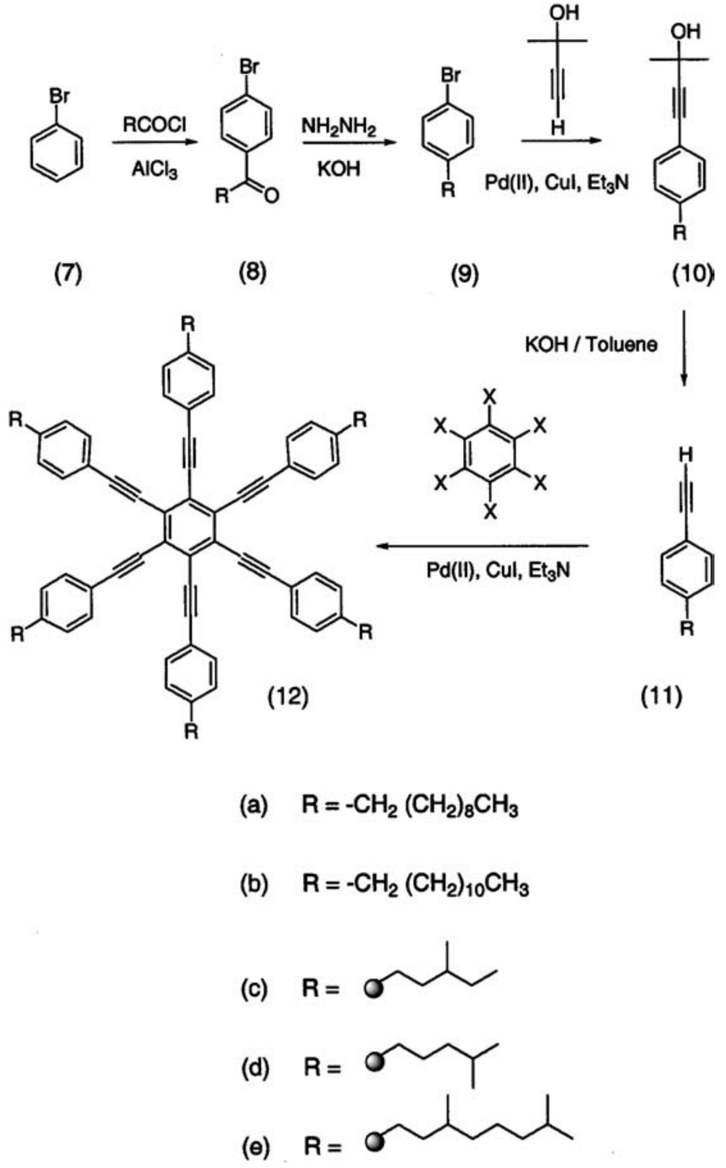
The use of branched chains in liquid crystals often reduces melting and isotropic temperatures. The decrease in the transition temperature could be due to the disorder caused by branched chains and stereoheterogeneity. This methodology has been successfully applied in the case of several discotic liquid crystals forming columnar mesophases [43–48]. To check whether this technique is also effective in the case of alkoxymultiyns based discotic nematic liquid crystals, we designed compound **17a** and **17b** (Scheme 2).

In the case of triphenylene based discotic nematic liquid crystals, it has been observed that a lateral methyl group substitution reduces the transition



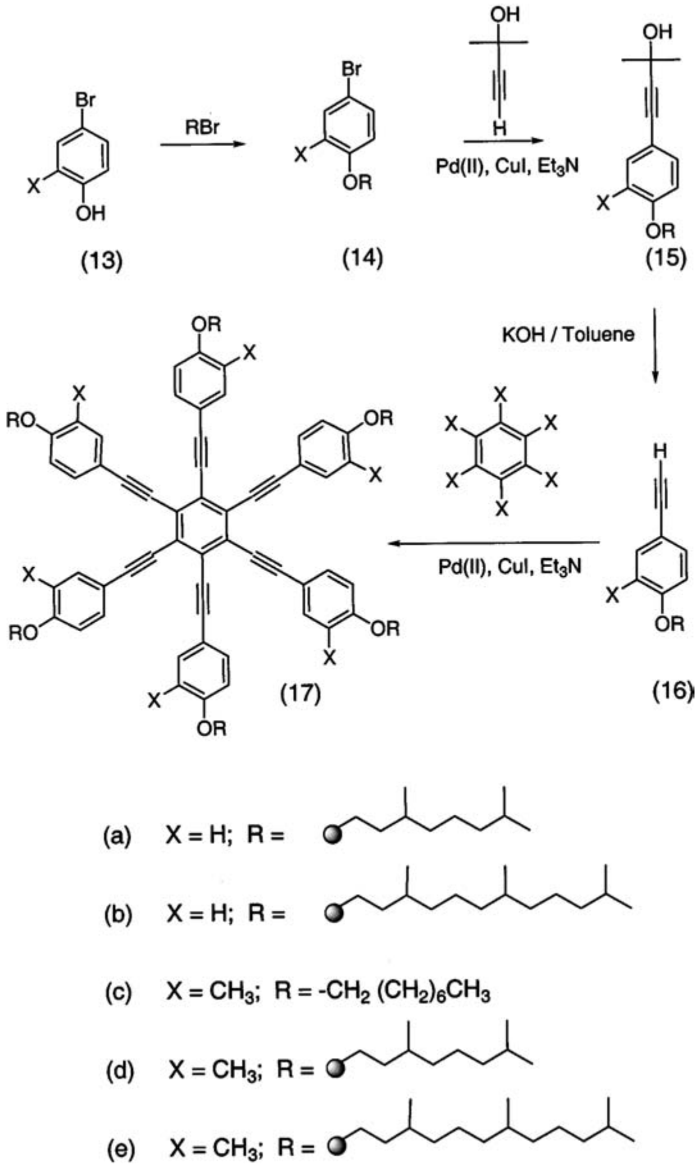
1. R = OC_7H_{15}	Cr 109 N_D 193 I
2. R = C_5H_{11}	Cr 170 N_D 185 I(dec)
3. R = C_6H_{13}	Cr 124 N_D 142 I
4. R = C_7H_{15}	Cr 98 N_D 131 I
5. R = C_8H_{17}	Cr 80 N_D 96 I
6. R = C_9H_{19}	Cr 67 N_D 83 I

FIGURE 1 Thermal behavior of some of the hexaalkynyl benzene.



SCHEME 1

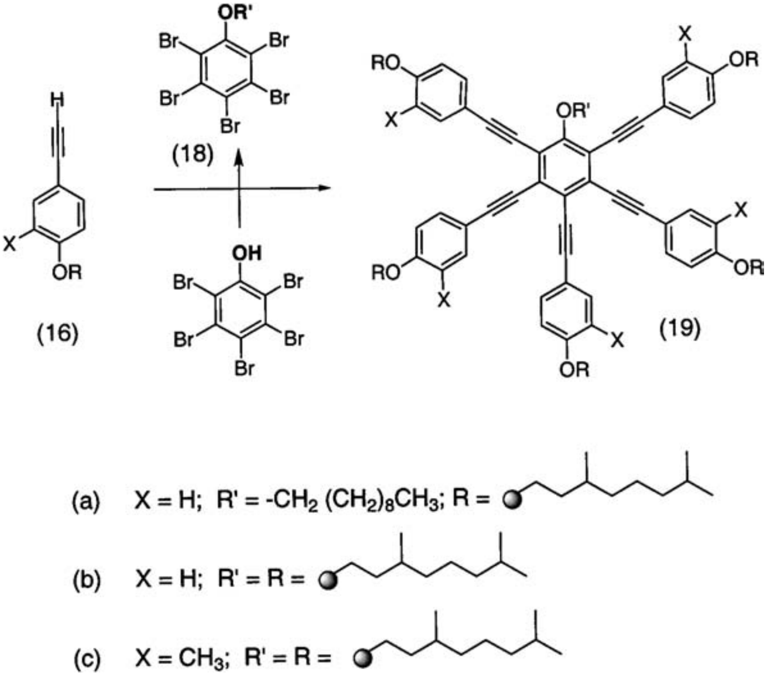
temperatures significantly [49,50]. Compound **17c**, **17d** and **17e**were designed to find the effects of lateral methyl group substitution in alkoxy-multiyns (Scheme 2).



SCHEME 2

From the thermal data of compound **1** and **5** (Fig. 1) [42], it is clear that when the peripheral alkyl chains are attached to the phenyl ring in the hexaalkynylbenzene *via* oxygen atom, the melting and clearing temperatures are higher compared to when the alkyl chains are directly attached to the ring. Again, as mentioned above, it is also known that when the peripheral aliphatic side chains of various cores are branched, the mesophase is widened but the type of the mesophase formed is not affected by the introduction of branching in many cases [46]. Therefore, this may be anticipated that by replacing the normal alkyl chains by branched alkyl chains connected directly to the phenyl ring, the melting points of alkynylbenzene derivatives may reduce and thus, stabilize the mesophase. We have utilised this technology to prepare the first room-temperature discotic nematic liquid crystal [41]. Now we designed several more derivatives in which branched chains of various carbon atoms are attached directly to the core (compound **12c**, **12d** and **12e**, Scheme 1).

Finally, pentaalkynylbenzene derivatives (compound **19a**, **19b** and **19c**, Scheme 3) having a combination of branched and normal alkoxy chains were also designed to achieve room-temperature discotic nematic liquid crystals.



SCHEME 3

SYNTHESIS OF ALKYL-SUBSTITUTED HEXAYNES

All the hexaalkynylbenzene derivatives were prepared following the literature methods [41,42] as shown in Scheme 1. Commercially available acids were converted to acid chlorides using oxalyl chloride at room temperature. Friedel-Crafts acylation of the bromobenzene with the above acid chlorides gives the 1-Bromo-4-alkanoylbenzene **8**. Wolff-Kishner reduction of these ketones furnished 1-Bromo-4-alkylbenzene **9**. Pd-catalysed alkynylation of different alkyl-substituted bromobenzenes **9**. with 2-methyl-3-butyn-2-ol afforded the protected phenylacetylenes **10**. which were deprotected using KOH in refluxing toluene to yield the phenylacetylenes **11**. A palladium-catalysed coupling of these alkyl-chain substituted phenylacetylenes **11** with hexabromobenzene yielded the desired alkyl-substituted hexaynes **12**. All the final compounds were purified by repeated column chromatography. They were homogenous on TLC plate and their spectral data were in accordance with the structure.

SYNTHESIS OF ALKOXY-SUBSTITUTED HEXAYNES

Alkoxy-substituted hexaynes can be prepared easily as shown in Scheme 2 [42]. Alkylation of *p*-bromophenol **13** under classical reaction conditions furnished 4-alkoxybromobenzenes **14**. These bromobenzenes can be converted to free accetylenes **16** as described above (Scheme 2). Final multiynes can be prepared by a palladium-catalysed coupling of these alkoxy chain substituted phenylacetylenes **16** with hexabromobenzene. Similarly, lateral methyl-substituted multiynes can also be prepared starting from 4-bromo-*o*-cresol.

SYNTHESIS OF ALKOXY-SUBSTITUTED PENTAYNES

Commercially available pentabromophenol can be alkylated to get mono-alkoxy-pentabromobenzene **18** (Scheme 3). Condensation of acetylenes **16** with **18** as described above yielded desired pentaynes **19**.

THERMAL BEHAVIOUR

The thermal behavior of all the compounds was investigated by optical polarising microscopy. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarising microscope.

The crystalline compound **12a** melts at 71°C to an isotropic liquid. On cooling from the isotropic phase, the schlieren texture of nematic phase appeared at 54°C and crystallises at 34°C. The thermal behaviour is reproducible and, therefore, the N_D phase of **12a** is monotropic in nature. The higher homologue **12b** is non-liquid crystalline. It melts at 57°C and crystals appear from the isotropic melt at about 40°C on cooling. Branched-chain derivatives **12c** and **12d** were also found to be non-liquid crystalline. The 3-methylpentane derivative **12c** melts at about 250°C with decomposition and the 4-methylpentane derivative **12d** melts at 195°C with partial decomposition. Compound **12e** was not pure enough to be analysed.

In the alkoxy series (Scheme 2) compound **17a** with 3,7-dimethyloctane periphery melts at 80°C to a nematic mesophase which clears at 124°C. On cooling the nematic phase appears at 123°C and crystallises at 64°C. The higher homologue **17b** having 3,7,11-trimethyldodecane periphery was in liquid state (non-liquid crystalline) at room temperature. Compound **17c** having a lateral methyl group substitution and normal octyloxy chains shows discotic nematic phase at 95°C. It changes to isotropic liquid at 176°C on heating with partial decomposition. Peripheral branched alkoxy and lateral methyl group substituted compound **17d** also gives N_D phase at 71°C on heating. Its colour changes from light yellow to brownish on heating to isotropic temperature (broad 147–160°C) indicating partial decomposition of the material at higher temperature. Like **17b**, the higher homologue **17e** having 3,7,11-trimethyldodecane periphery and a lateral methyl group was also in liquid state at room temperature.

In the pentayne series, compound **19b** was non-liquid crystalline but other two derivatives **19a** and **19c** were found to be liquid crystalline at room temperature. While the discotic nematic mesophase of compound **19a** clears at 40°C, it changes to isotropic liquid at 73°C in the case of **19c**. On cooling, the N_D phase appears with very limited supercooling and remains stable down to room temperature. Both the compounds show a glass transition at about −35°C in DSC heating and cooling cycles. It is interesting to note that in the case of triphenylene based nematics, a lateral methyl group substitution usually decreases the isotropic temperature [49,50] but in the case of benzene multiynes the effect is reverse. All the benzene multiynes having lateral methyl group substitution show higher clearing temperature compared to materials without lateral methyl substitution.

CONCLUSION

Several new benzene hexa- and pentaalkynes were prepared and characterised. Two of them show very broad discotic nematic mesophase stable well below and above the room temperature. These materials may be useful for wide viewing LCD devices.

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