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Synthesis, mesomorphic properties and structural studies on 1,3,5-trisubstituted benzene-based star-shaped derivatives containing Schiff base ester as the peripheral arm

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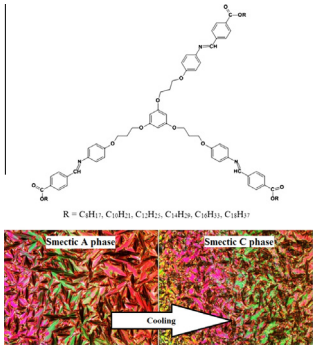
GRAPHICAL ABSTRACT



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ABSTRACT

Six new symmetrical three-armed star-shaped liquid crystals comprising phloroglucinol (1,3,5-trihydroxybenzene) as a core center and three Schiff base ester as the mesogenic arms have been synthesized. Their molecular structures were supported by spectroscopic techniques (FT-IR, ^{1}H NMR, ^{13}C NMR and two dimensional COSY, HMQC and HMBC). Each of the member differs in the length of the terminal alkyl chain (R—COO— where R = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$). All the star-shaped mesogens are found to be monotropic smectogens with the short chain derivative (R = C_8H_{17}) exhibits only smectic A phase. While both the smectic A and smectic C phases are common for the derivatives with $C_{10}H_{21}$—$C_{16}H_{33}$ alkyl chain, the member with $C_{18}H_{37}$ shows only smectic C phase. Further investigation by X-ray diffraction confirms the smectic phase of the materials whereby two sharp reflections at 28.8 Å and 57.3 Å recorded via small angle in a ratio of 1:2 indicate unambiguously the presence of layered structure and a diffused scattering via the wide angle (4.5 Å) indicates a liquid-like order within the smectic layer. Increasing the length of terminal flexible chain has influenced remarkably the thermal and phase stability of the titled compounds. Besides, the liquid crystalline properties of all intermediary ω-brominated Schiff base ester prior joining to the benzene core were also evaluated.

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1. Introduction

The investigation on non-conventional liquid crystals (LCs) has become an interesting research area within the last two decades [1,2]. This class of liquid crystals is a type of molecule with an anisotropic shape that deviates from the classical rod- and disc-shaped molecules [3]. One of the requirements in the design of novel non-conventional mesogens is that it must allow for the possibility of segregating the incompatible molecular segments. The core group of the mesogen utilized can be any shape as long as it is sufficiently flexible to provide nano-segregation as it plays a vital

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role in the self-assembly or self-organization of liquid crystal structure [4]. Non-conventional star-shaped LCs, is considered as one of the simplest multi-arm mesogens consisting of a disc-like core as a central unit (mesogenic or non-mesogenic) with at least three mesogenic peripheral arms. This type of mesogen has attracted increasing interest owing to their symmetrical structures and interesting properties. Various mesophases can be exhibited by the star-shaped mesogens, including the discotic columnar phase as well as the nematic, smectic and cholesteric phase [5–10]. This is because this class of liquid crystals has both disc-like units with high substitution symmetry which is favourable for the formation of discotic mesophase and structural elements (rod-like mesogenic units) that promote calamitic mesomorphism [11]. They are also termed as *Hekates* in order to easily differentiate them from other mesogenic trimer such as linear trimers or irregular tripodes [12]. The numerous applications of star-shaped LCs include non-linear optical filters, flat panel displays and fast switching materials [13–16]. In addition, some of the star-shaped LCs tend to exhibit glassy properties [17,18] upon cooling from isotropic state and this phenomenon is imperative to show uncommon optical, mechanical and thermal stable properties [19–22] and preferred to be utilized as soft functional materials like anisotropic electron/hole-, ion-, proton conducting and electro-optical application [23].

A great number of star-shaped mesogens comprising of a benzene unit as a core group have been synthesized and their properties investigated [17,24–27]. Liquid crystalline behaviour of a star-shaped mesogen is presumably dependent on its molecular architecture in which the molecular geometry of the peripheral unit may bring about substantial changes in its mesomorphic properties. From the literature studies, star-shaped mesogens can exhibit both nematic and smectic phase characteristic of calamitic LCs and also columnar phase, which is commonly found in discotic LCs. For instance, Kumar and Manickam had prepared two series of star-shaped trimers whereby three triphenylene-based or nitro-functionalized triphenylene-based units were synthesized as the peripheral mesogenic unit and linked to the 1-,3-,5-position of the benzene central core via an alkyl spacer and ester linkage [28]. From their findings, the nitro-functionalized compound exhibited a monotropic columnar phase at 158.7 °C on cooling while the unfunctionalized compound was found to be non-mesogenic, which crystallized at 166 °C on cooling. Yao and co-workers had also synthesized a series of cholesteric star-shaped mesogens based on phloroglucinol with three ω-cholesteric alkyl diacid monoester fragments as the peripheral units. Cholesteric focal-conic texture was detected in their liquid crystalline state. In addition, as the diacid alkyl spacer lengthened, the melting temperature descended but the mesomorphic temperature range increased [7]. Therefore, it has been demonstrated that benzene ring can be utilized as a suitable structural component in synthesizing the star-shaped LCs.

Due to the growing scientific interest in the synthesis of star-shaped LCs, this has prompted us to further investigate the anisotropic properties of phloroglucinol-based star-shaped LCs. Recently, the mesomorphic behaviour of phloroglucinol-based symmetrical star-shaped mesogens containing three Schiff base ether peripheral units has been documented [29]. From our study, all the analogues exhibited predominately SmC phase except for the member possessing the shortest terminal alkyl chain. The formation of smectic phase by the star-shaped mesogen was found to be generated by the side-by-side organization of the peripheral arms which lie parallel to each other. Thus, the mesophase formation of the star-shaped mesogens is mainly attributed to the rod-like calamitic Schiff base units whereas the benzene core acts only as a linking group interconnecting the rods. To the best of our knowledge, there were relatively few studies on the star-shaped LCs incorporating a core unit of phloroglucinol (1,3,5-trihydroxybenzene) with Schiff base ester derivatives as the peripheral units. Moreover, morphologies of star-shaped mesogens can be further regulated by carefully adjusting the molecular topology. As the continuation of our effort to understand the structure–property in such star-shaped system, this paper describes the synthesis and mesomorphic properties of a homologue series of trimeric star-shaped LCs, 1,3,5-tris[{alkyl-(4-phenylimino)methyl}benzoate-4′-oxy]propyloxy benzene. It is a star-shaped system functionalized with a disc-shaped benzene ring as a core unit and three linearly extended rod-like Schiff base ester fragments in its periphery (Fig. 1). Each of the members differs in the even-parity terminal alkyl chain length ($R = C_nH_{2n+1}$) of which the n ranges from 8 to 18. Besides, the influence of the terminal alkyl chain length on the phase behaviour of the star-shaped compounds is discussed in the following discussion.

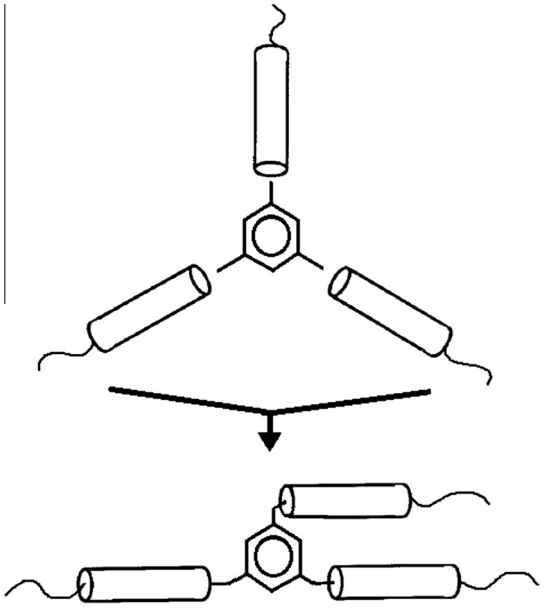

Fig. 1. A schematic illustration of the structure of *Hekates* in which three rod-shaped molecular subunits attached to a benzene central linking unit via a flexible spacer to give the three-armed star-shaped compound.

2. Experimental

2.1. Reagents and chemicals

The starting materials such as phloroglucinol anhydrous, 4-carboxybenzaldehyde, 4-aminophenol were obtained from Acros Organics (Geel, Belgium). 1-Bromooctance, 1-bromodecane, 1-bromododecane, 1-bromotetradecane, 1-bromohexadecane, 1-bromoactadecane and 1,3-dibromopropane, TLC Silica gel 60 F_{254} aluminium sheets and silica gel 60 (0.040–0.063 mm) for column chromatography were purchased from Merck (Darmstadt, Germany). Potassium carbonate anhydrous was purchased from QREc (Auckland, New Zealand) while potassium iodide was purchased from Fisher Scientific (Waltham, MA, USA). All the chemicals and solvents were used directly without further purification.

2.2. Characterization

2.2.1. Physical measurements

The CHN analytical data were acquired on Perkin Elmer 2400 LS series CHNS/O analyzer. Melting point of the compounds were measured using Gallenkamp melting point apparatus.

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