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Synthesis of Novel Discotic Mesogen Containing Electron-Transportable Oxadiazole Moiety

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We synthesized and characterized a novel discotic liquid crystalline material (**THOB**) composed of 1,3,5-tri-substituted benzene core and 2-(4-hexyloxyphenyl)-oxadiazol-5-yl arms. Chemical structure of **THOB** was characterized using ¹H-NMR and mass spectroscopy and its thermal behavior was determined using DSC and polarized optical microscopy. **THOB** showed narrow mesophase region at around 128 °C and exhibited nematic-like texture.

Keywords Discotic liquid crystal; Oxadiazole; Star molecule.

INTRODUCTION

Discotic liquid crystals (LCs) are well known materials in the supramolecular chemistry due to their self-assembly characteristics such as columnar architectures. Since these unique structures normally enhance carrier mobility along column axis, discotic LCs have been applied to organic-conductor,^[1] photo-conductor^[2] and organic light emitting diode.^[3,4] There are two different classes of interactions acting as a driving force for forming a columnar structure in discotic LCs. One is a core-to-core interaction of molecules with bulky aromatic core, as exemplified by triphenylene- and phthalocyanine-cored discogens.^[5,6] The other is an arm-to-arm interaction between molecules that have small core and polar arms such as tri- or hexa-substituted benzene derivatives.^[7,8] In the latter case, if the polarity of arm is not enough, such as multiyne, the mesogens form a discotic nematic LC rather than a columnar architecture.^[9] That is, the polarity of arm is essential in the small-core mesogens for the formation of columnar phase. Ester or amide group has usually been adopted for this purpose.^[7,8] However, these polar groups (esters, amides, *etc.*) inevitably break the conjugation of arm and result in partially non-conjugated

molecules. In this work, we aimed at the synthesis of fully conjugated discotic LC that might combine the photo-functionality and columnar architecture. From the semi-empirical molecular orbital calculation, it was found that the transverse dipole moment of oxadiazole moiety (3.60 D) is higher than ester (2.85 D) or amide (3.35 D). Thus, we designed and synthesized a novel discotic LC composed of small benzene core and three identical conjugated arms containing oxadiazole moiety. which could provide a transverse polarity as well as electron transportability.

EXPERIMENTAL SECTION

The chemical structure and synthetic routes of the novel discotic LC, 1,3,5-tris[2-(4-hexyloxyphenyl)-oxadiazol-5-yl]benzene (**THOB**, **3**), is depicted in FIGURE 1. All the reagents were used as received from Aldrich Chemical Co. Structures of **1**, **2**, and **3** were identified with 300 MHz ¹H-NMR (JeoJ JNM-LA300) spectra using CDCl₃ solution. The molar mass of **THOB** was measured with GC/MS (JMS AX505WA) in FAB mode



FIGURE 1 Synthetic scheme of oxadiazole-containing discotic LC.

4-Hexyloxy ethylbenzoate (1).

33.24 g (0.2 mol) of 4-hydroxy ethylbenzoate was dissolved in 100 mL ethanol and 11.22 g (0.2 mol) of KOH and catalytic amount of KI were added to the solution. The solution was heated to 60 °C with magnetic stirring and 27.48 mL (0.2 mol) of 1-chlorohexane was then added dropwise. The reaction was conducted under reflux

until completion in about 6 h. The reaction mixture was then poured into cold water and extracted with ethylacetate. After removal of solvent, the crude product was reprecipitated into *n*-hexane (Yield 82%). ¹H-NMR; 7.99 (d, 2H), 6.89 (d, 2H), 4.31 (q, 2H), 4.00 (t, 2H).

4-Hexyloxy-benzoic acid hydrazide (2).

25.0 g (0.1 mol) of 1 was suspended in 150 mL of ethanol/H₂O (7/3 volume ratio) solution and two equivalent of KOH was added. This mixture was refluxed for 3 h and poured into excess cold water. Solution was neutralized and the precipitate was collected by filtration. The thoroughly dried white solid was suspended in dichloromethane (10 mL) solution containing 7.3 mL of thionyl chloride. After adding catalytic amounts of N,N-dimethyl formamide (DMF), the solution was heated to 70 °C with magnetic stirring for 2 h. The reaction mixture was cooled to 0 °C and diluted with 15 mL of Na-dried tetrahydrofuran (THF). And then, this solution was added dropwise to a vigorously stirred mixture composed of 24 mL (0.5mol) of hydrazine monohydrate and 20 mL of triethylamine (TEA). The reaction mixture was stirred for 20 min and then diluted with excess THF. The yellowish salt was eliminated by filtration and solvent was removed with rotary vacuum evaporator. After impurities were eliminated through flash column of silica gel (Merck 60, 70-230 mesh) using ethyl acetate, white solid was obtained by elution with THF (Yield 70 %). ¹H-NMR; 7.72 (d, 2H), 6.90 (d, 2H), 5.99 (t, 2H).

1,3,5-Tris[2-(4-hexyloxyphenyl)-oxadiazol-5-yl]benzene [THOB] (3).

2.6 g (0.01 mol) of 1,3,5-benzene tricarboxylic acid chloride was prepared from tricarboxylic acid and 5mL of thionyl chloride and subsequently reacted with THF solution containing 9.5 g (0.04 mol) of **2** and 20 mL of TEA to give acid hydrazide. After stirring for 20 min, the reaction mixture was diluted with excess THF and yellowish salt was eliminated by filtration. Obtained yellow solid was dissolved and refluxed in 20 mL of POCl₃ for 2 h to effect ring closure. The solution was then poured into cold water and neutralized. After extraction with dichloromethane, the crude product was carefully purified by column chromatography on silica gel using dichloromethane:ethyl acetate:*n*-hexane (1:1:1) as elucnt (Yield 45%). ¹H-NMR; 9.02 (t, 3H), 8.15 (d, 6H), 7.08 (d, 6H), 4.07 (t, 6H); m/z; 811 (calcd. 810).

RESULTS AND DISCUSSION

Novel discotic mesogen, **THOB** was synthesized in good yield and its structure was successfully identified. Phase transition temperatures and enthalpy changes of **THOB** were investigated using Perkin-Elmer 7 differential scanning calorimeter (DSC) and are listed in TABLE 1. It was observed in heating trace that **THOB**

showed crystal to liquid crystal transition at 123.4 °C with enthalpy change of 22.31 Jg^{-1} and liquid crystal to isotropic transition at 128.2 °C with very small enthalpy change (0.21 Jg^{-1}). In the subsequent cooling cycle, only isotropic to crystal transition was detected by DSC. However, we could detect very narrow mesophase range (*ca.* 1-2 °C) even in the cooling process by polarized optical microscopy (POM). Mesophase texture of **THOB** was not common, and we could not clarify the lattice structure of **THOB** by small angle X-ray diffraction, owing to the experimental difficulty related to the extremely narrow mesophase range. It is speculated that the larger polarity and shorter hexyloxy tail increased crystallinity of **THOB**, which resulted in a reduced tendency of mesophase formation. Further structural modifications including the change of the tail group are currently underway in our laboratory to obtain wider mesophase range.

compound	Т/°С (ДН/Јд ⁻¹)	
	Heating	Cooling
[THOB]	K 123.4 (22.31) D 128.2 (0.21) I	I 101.6 D 100 K ^a

TABLE 1 Phase behavior of **THOB**. Transition temperatures and enthalpy changes were determined by DSC (scan rate 10 °C min⁻¹). ^aTransition was observed only in polarizing microscopy and enthalpy change could not be detected in cooling trace.

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