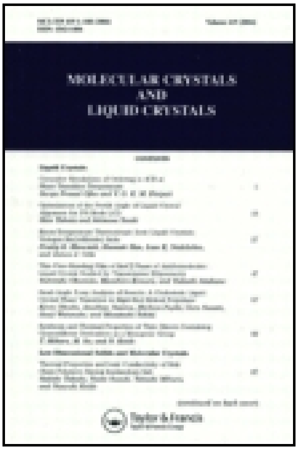

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Discotic Mesogens of 1,3,5-Tris(4-(3,4,5-Trialkyloxy-Benzoyloxy)Benzoyloxy)Benzene Homologues

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DISCOTIC MESOGENS OF 1,3,5-TRIS(4-(3,4,5-TRIALKYLOXY-BENZOYLOXY)BENZOYLOXY)BENZENE HOMOLOGUES

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Discotic mesogens were synthesized by esterification of 1,3,5-tris(4-hydroxybenzoyloxy)benzene with 3,4,5-trialkyloxybenzoic acids in DCC/DMAP/THF. These derivatives were studied by optical microscopy, differential scanning calorimetry and powder X-ray diffractometry. Optically uniaxially negative columnar phases were observed for derivatives having dodecyloxy and hexadecyloxy chains. Hexagonal packing of columns was observed from the results of X-ray diffraction. However, the diameter of the column is less than the molecular dimension indicating the interdigitations of peripheral chains of the neighboring columns.

INTRODUCTION

Since the reports of columnar phases formed by low molar mass disk-like molecules [1–3], there has been a large number of thermotropic mesogens of this type designed and synthesized [4]. Columnar phases are constructed with columns arranged in regular arrays and each column is a stack of disk-like molecules in order or disorder periodicity. The disk-like molecule consists of a central core connected by peripheral flexible chains such that core–core interactions cause the molecules to pile up and the flexible chains constitute the outer shell of each column. Therefore, in order to keep the molecules ordered in the liquid state, it is preferred to have larger cores (fused rings or pi-conjugated system) for providing better core–core interactions. In the mean time, in order to have enough fluidity, and also to fill the space around the core sufficiently, the number of peripheral flexible

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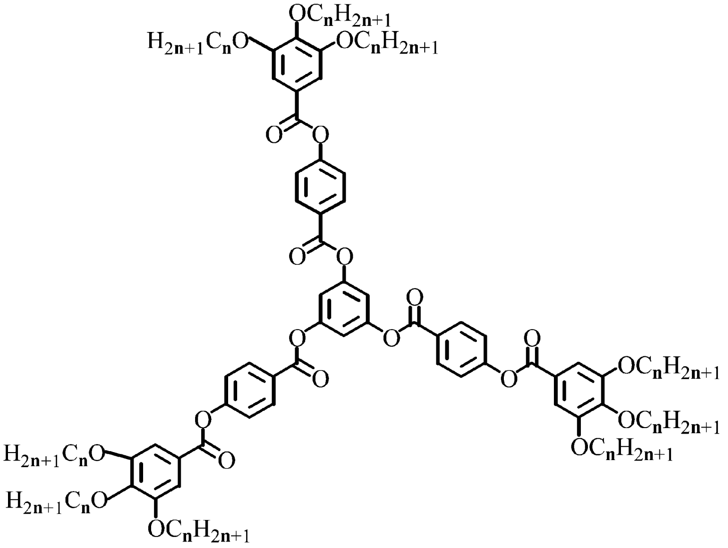
chains is high, usually more than four [4]. With this consideration, the reports for observation of columnar phases for derivatives consisted of the simplest core, 1,3,5-trisubstituted benzene, are rather limited. While there are reports for observing mesophases for derivatives of 1,3,5-benzenetricarboxylic acid, no mesophases are observed for derivatives of 1,3,5- trihydroxybenzene [5–9]. The present study shows that columnar phases indeed exist for compounds (**An**) obtained by esterification of 1,3,5-trihydroxybenzene, provided that each arm consists of two 4-hydroxybenzoic acids in series and with the hydrocarbon chains longer than 12 carbon units.

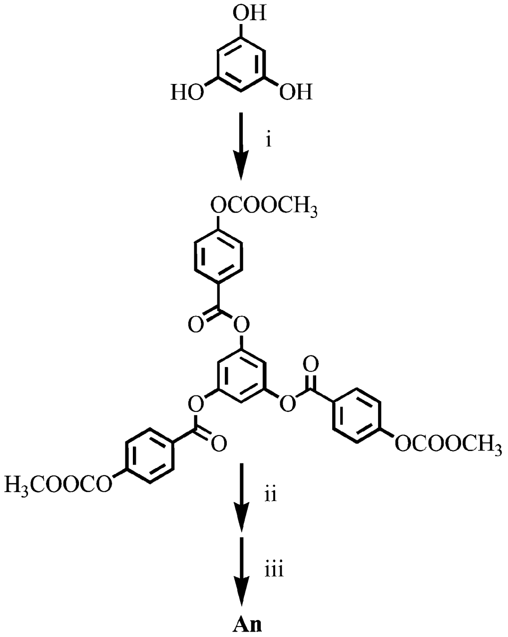


An

n = 12, 16

EXPERIMENTAL

The synthetic procedures are shown in Scheme 1. The 1,3,5-trihydroxybenzene is esterified with a protected benzoyl chloride in pyridine/THF at room temperature. After deprotection, the esterification with the 3,4,5-trialkyloxybenzoic acids via DCC/DMAP in THF results in the desired products (**An**, where n is the number of carbon atoms in the hydrocarbon chain). The final products are purified by column chromatography with silica gel as the stationary phase and with suitable eluents. All the results of elemental analysis and proton NMR spectra are consistent with the



i) 4-$CH_3OCOOC_6H_4COCl$ / pyridine / THF
ii) a. NH_3 / H_2O / EtOH ; b. H^+
iii) $3C_nH_{2n+1}OC_6H_2COOH$ / DCC / DMAP / THF
n = 12, 16

SCHEME 1

desired structures. The mesophases are characterized by optical polarzing microscopy (Nikon, OPTIPHOT) in conjunction with a heating stage (Mettler, FP800, FP82HT), and the results are listed in Table I along with the enthalpy changes of the corresponding phase transitions obtained by differential scanning calorimetry (Perkin-Elmer, DSC 2). The powder

TABLE I The Phase Behaviors for Compounds **A12** and **A16**. Temperature in °C, and Enthalpy Change (in parenthesis) in kJ/mol

Compound	Phase behavior
A12	Col_h 48.3 (7.9) I
A16	Cr 43.2 (82.7) Col_h 53.0 (10.9) I

X-ray diffraction study is carried out at the National Synchrotron Radiation Research Center (Hsinchu, Taiwan) with sample packed in capillary.

RESULTS AND DISCUSSION

The compound **A12** is a paste at room temperature, and exhibits birefringence when placed in between the microscope slide and cover slip. Textures resemble those of typical columnar hexagonal textures can be developed upon cooling from the isotropic state, as shown in Figure 1. There are dark areas, which exhibit uniaxially negative sign under the conoscopic configuration. The DSC thermogram displays an enthalpy change of 7.9 kJ/mol for the isotropic–mesophase transition. This value suggests the existence of columnar phases.

The X-ray diffraction pattern displays a very strong peak and two tiny peaks at the small angle region (Fig. 2a). The spacing of the small angle peaks are 37.62:21.72:18.64 Å = 1: 0.577:0.5. This result indicates that the columns are hexagonally packed in the mesophase. A broad band without sharp peak is observed at the large angle region indicates that the molecules are disorder within the column. For the compound **A16**, similar results, optical microscopic observations, DSC and X-ray diffraction

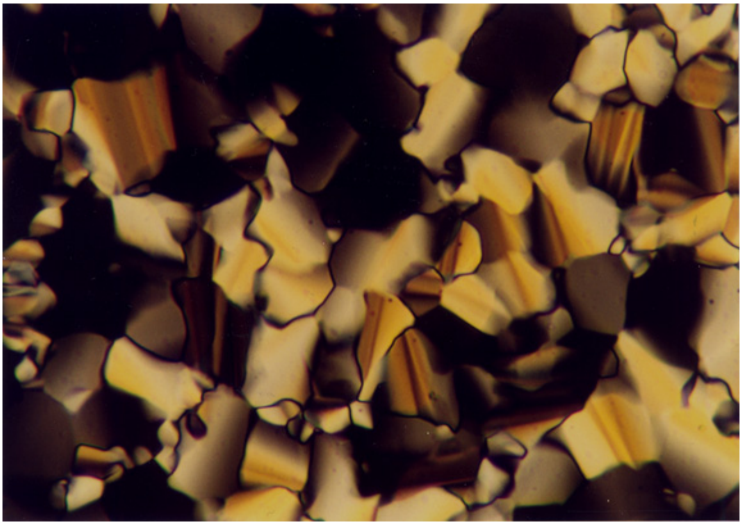


FIGURE 1 The textures observed for compound **A12** on cooling from the isotropic state to 46.2°C. The vertical edge is 0.25 mm. (See COLOR PLATE VII)

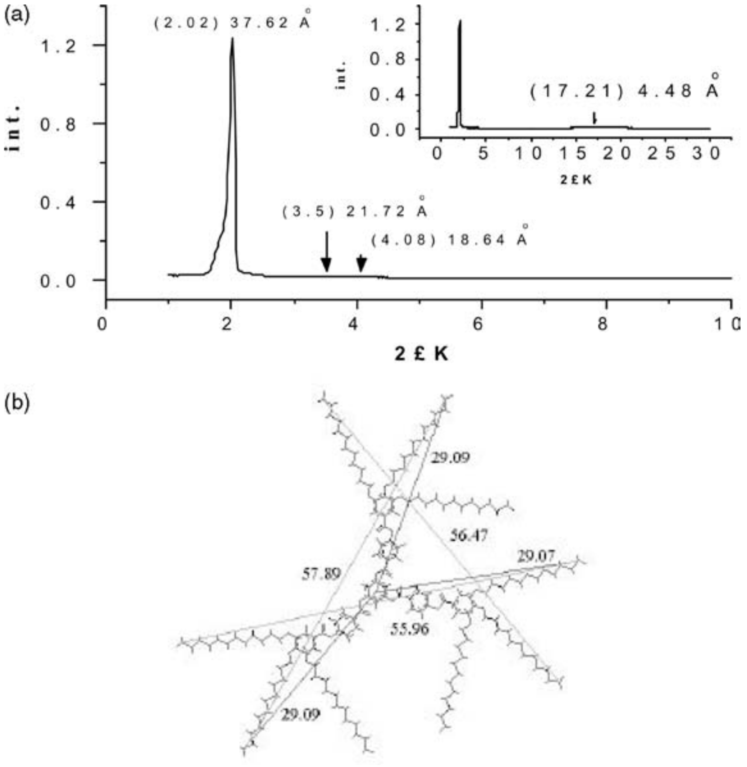


FIGURE 2 (a)The X-ray diffraction pattern for compound **A12** at 39°. (b) The molecular dimension of compound **A12** calculated with HyperChem 5.0 AM1.

pattern, are observed. The mesophase temperature of **A16** is slightly above room temperature.

The distance between the centers of neighboring columns (hexagonally packed) is 43.44 Å as evaluated form the results of X-ray diffraction. The molecular diameter for compound **A12**, assuming a flat disk geometry and all-trans conformation for the hydrocarbon chains, is 56–58 Å as calculated with the Hyper Chem 5.0 AM1 (Fig. 2b). This discrepancy could be accounted for the liquid-like behaviors and large conformational variations (away from the all-trans) of the hydrocarbon chains, and also the possible interdigitations of the peripheral chains of the neighboring columns.

A homologue with shorter hydrocarbon chains (octyloxy) is also prepared, and only an isotropic liquid state is observed at room temperature. As compared to the results reported in the literature [5–9], the formation of columnar phases for the present series is attributed to the large core–core interaction, which is caused by the presence of two benzoate units in series in the arms of the 1,3,5-trihydroxybenzene. Long hydrocarbon chains are still needed, however, which would provide enough space and possibility for interdigitation, and stabilize the packing of the molecular columns.

CONCLUSION

The compound, 1,3,5-trihydroxybenzene, can be employed as the central core for constructing discotic mesogens, provided that each arm consists of two benzoate units in series and with hydrocarbon chain longer than 12 carbon atoms.

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