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Synthesis and Characterization of New Banana Shape Molecules with PAH as Bend Central Cores*

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Abstract: Two new banana shape compounds with DBN (Dibenzo[fg,op]naphthalene) and triphenyl pyridine as bend central cores respectively were synthesized, their structures were confirmed by ^1H -NMR and ^{13}C -NMR and their mesophase behaviors were investigated by POM. No mesomorphic behavior is found in such two compounds.

Key words: banana shape; dibenzo[fg,op]naphthalene; synthesis

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The discovery by Niori et al. that banana shape mesogen with a bend central core can self assemble in polar phase is recently of great interest. However till now detailed knowledge about the relationship between such molecular structures and the mesogenic properties is unclear^[1]. During our research in the area of PAH (Polycyclic Aromatic Hydrocarbons), we become also interested in taking PAH as bend central core to cooperate with different rigid arms and different length of terminal groups to design new banana shape molecules, with a purpose to get more information between such molecular structures and their mesogenic properties. Therefore two new banana shape compounds were designed: one was with DBN as central bend core and octadecyloxy benzoic esters as lateral arms, and another was with triphenyl pyridine as bend central core and diene esters as lateral arms. Their structures were confirmed by ^1H -NMR, ^{13}C -NMR and HR-Mass, and their mesophase behaviors were investigated with POM (Polar Optical Microscopy).

1 Experimental

1.1 Apparatuses and Materials

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Commercially available chemicals were used as received; ^1H -NMR and ^{13}C -NMR spectra: Bruker-DRX-500 spectrometer; high resolution MS (HR-MS): Finnigan MAT 90 spectrometer, ionization potential 70 eV; field-desorption (FD) mass spectra: VG ZAB 2-SE-FPD; thin layer chromatography: aluminum plates precoated with 5 735 silica gel 60 PF254 (Merck); column chromatography: merck silica gel 60 (230~400 mesh).

1.2 Preparation

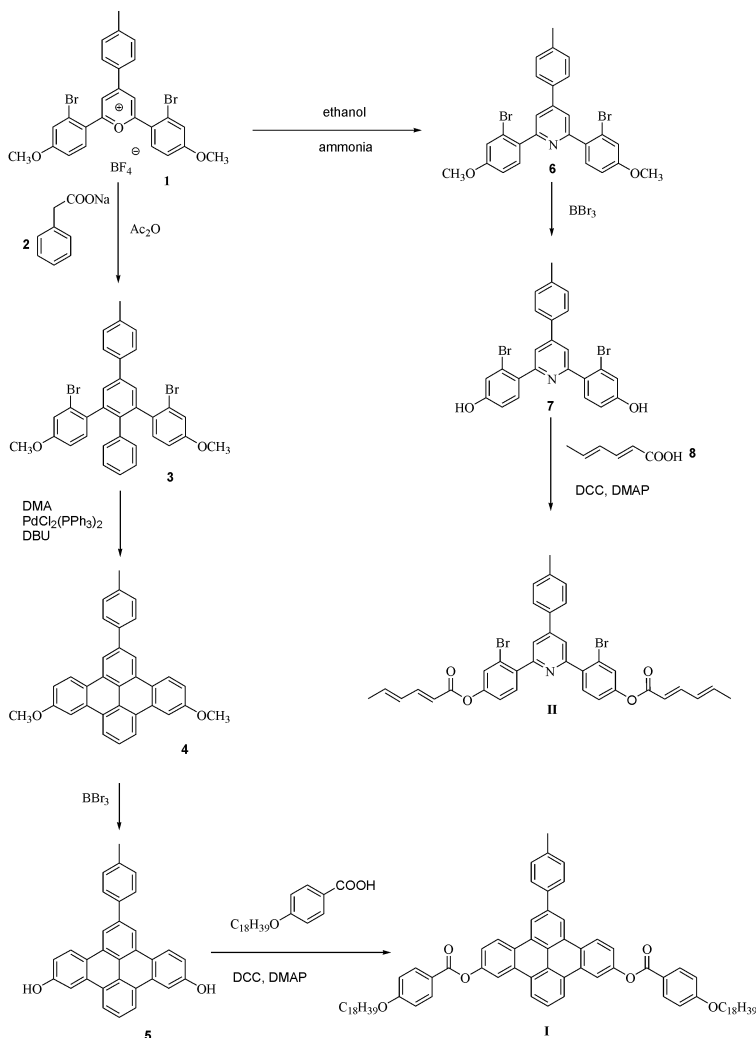
The synthesis of compounds 1, 3 and 4 were reported in reference^[3].

Preparation of 6: A mixture of pyrylium salt 1 (1 mmol) and ethanol (10 mL) was stirred at 78 °C for 5 min, then ammonia (25%, 2 mL) was added dropwise. The mixture was reflux for further 30 min, cooled to 4 °C. After 12 h, the colorless solid was filtered off and thoroughly washed with ethanol. The residue was purified by column chromatography. (PE/EE 7: 1). Colorless crystal, m. p. 108~109 °C, yield: 64%. ^1H -NMR (500 MHz in CDCl_3):

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Biography: CHENG Xiaohong (1968-), female, was born in Kunming City, Yunnan Province, Prof. Dr., PhD supervisor; research areas are organic chemistry and supramolecular chemistry.



Scheme 1 Synthesis of compounds I and II

$\delta = 7.79$ (s, 2 H, Ar—H), 7.67~7.64 (m, 4 H, Ar—H), 7.33~7.31 (d, $J = 7.6$ Hz, 2 H, Ar—H), 7.27~7.25 (d, $J = 8.8$ Hz, 2 H, Ar—H), 6.99~6.97 (d, $J = 7.6$ Hz, 2 H, Ar—H), 3.85 (s, 6 H, 2 ArOCH₃), 2.43 (s, 3 H, ArCH₃).

General procedure for preparation of 5 and 7: Appropriate methyl ether (4 or 6) (4.7 mmol) was dissolved in CH₂Cl₂ (45 mL) and cooled to -20 °C, BBr₃ (0.49 mL, 5.2 mmol) was added and the solution was stirred for 20 h at room temperature, water (30 mL) was carefully added, the solid was filtered off and thoroughly washed with methanol. The residue was used without further purification for the next reaction. Colorless crystal, yield: 100%.

General procedure for esterification: A suspension of biphenol (5 or 7) (0.1 mmol) in dry CH₂Cl₂ (5 mL), appropriately substituted benzoic acid (0.24 mmol), DCC (0.25 mmol), and a catalytic amount of DMAP were added. The mixture was stirred for 72 h at 20 °C. The solid was filtered off and washed with CH₂Cl₂, and the combined organic phase was washed with HCl (10%), NaOH (10%), H₂O respectively. The combined organic layers were dried over MgSO₄ and the solvent was removed in vacuo. The crude product was purified by column chromatography (PE/EE 20/1).

II: yellow crystal, m. p. 140~142 °C, yield: 63%. ¹H-NMR (500 MHz in CDCl₃): $\delta = 7.83$ (s, 2 H, Ar—H), 7.73~7.71 (d, $J = 8.4$ Hz, 2 H, Ar—H), 7.65~7.64 (d, $J = 8.1$ Hz, 2 H, Ar—H), 7.53~7.52 (d, $J = 2.2$ Hz, 2 H, Ar—H), 7.50~7.44 (m, 2 H, 2 O=C—CH=CH—CH=CH), 7.34~7.32 (d, $J = 7.9$ Hz, 2 H, Ar—H), 7.24~7.23 (d, $J = 8.2$ Hz, 2 H, Ar—H), 6.30~6.27 (m, 4 H, 2

$\text{CH}=\text{CH}-\text{CH}_3$), 5.98~ 5.95 (d, $J = 15.3$ Hz, 2 H, 2 $\text{O}=\text{C}-\text{CH}=\text{CH}$), 2.44 (s, 3 H, ArCH₃), 1.92~ 1.91 (d, $J = 5.3$ Hz, 6 H, 2 $\text{CH}_2=\text{CH}-\text{CH}_3$). HRMS (FAB): Calcd for $\text{C}_{36}\text{H}_{29}\text{Br}_2\text{NO}_4$ ($M^{+2} + 1$) 700.044 3 found 700.046 4.

I: yellow liquid, yield: 60%. ^1H -NMR (500 MHz in CDCl_3): $\delta = 8.78$ (s, 1 H, Ar—H), 8.75~ 8.73 (d, $J = 8.7$ Hz, 1 H, Ar—H), 8.44 (s, 1 H, Ar—H), 8.42 (s, 1 H, Ar—H), 8.24~ 8.22 (d, $J = 8.7$ Hz, 2 H, Ar—H), 8.20~ 8.18 (d, $J = 8.7$ Hz, 2 H, Ar—H), 7.80~ 7.78 (m, 2 H, Ar—H), 7.72~ 7.71 (d, $J = 8.0$ Hz, 2 H, Ar—H), 7.53~ 7.52 (d, $J = 8.5$ Hz, 2 H, Ar—H), 7.49~ 7.44 (m, 2 H, Ar—H), 7.33~ 7.32 (d, $J = 7.9$ Hz, 2 H, Ar—H), 7.30~ 7.29 (d, $J = 8.5$ Hz, 2 H, Ar—H), 7.15~ 7.13 (m, 1 H, Ar—H), 6.99~ 6.97 (m, 2 H, Ar—H), 4.07~ 4.03 (m, 4 H, 2 ArOCH₂), 2.44 (s, 3 H, ArCH₃), 1.84~ 0.84 (multi H in the alkyl chain). IR (KBr) ν : 3 129, 2 958, 2 924, 2 853, 1 733, 1 606, 1 400, 1 260, 1 165, 1 073 cm^{-1} . HRMS (FAB): Calcd for $\text{C}_{36}\text{H}_{29}\text{Br}_2\text{NO}_4$ ($M^{+} + 1$) 1 173.783 3 found 1 173.780 1.

2 Results and Discussion

Two compounds were synthesized according to the route shown in scheme 1. Pyrilium salt 1 was synthesized according to the route we recently reported^[1,3]. Condensation of 1 with the sodium (4-methyl) phenyl acetate 2 formed the aromatic dibromides 3 in good yield. The dehydrohalogenation was performed by heating 3 in dimethylacetamide (DMA) in the presence of DBU and $(\text{PPh}_3)_2\text{PdCl}_2$ at 160 °C for 12 h. The pure product was easily obtained by recrystallization of the crude product from Chloroform because of the different solubility between product and side products. Demethylation of 3 using BBr_3 at -78 °C yielded 4. 4 was esterified with benzoate acid to give out product I. 1 was also reacted with ammonia^[2] to give out the corresponding pyridine derivatives 6. Demethylation of 6 using BBr_3 at -78 °C yielded phenol 7, which was acylated with excess sorbic acid 8 yielding the target compounds II.

The mesophase behaviors of compounds I and II were investigated by POM. Unfortunately two compound were either crystal (II mp: 140~ 142 °C) or liquid (I) without mesomorphic properties. By comparison among the molecular structures of I and II and other banana mesogens reported^[4], it is easy to found that the main difference among them lies in that both compounds I and II have an extra tolyl group on the central bend core, and from our previous work on the single crystal X-structure of derivative of I and II, the tolyl group in such position is free rotatable^[5]. It seems that this free rotatable tolyl group strongly disturbs the effective packing between the molecules and therefore prevents the formation of the banana phase. Further work should be concentrated on the synthesis of comps without such tolyl group in the 4-position of the pyridine central core. Therefore, on designing banana shape molecules, beside the rigid arms and the flexible lateral chains etc, the effective packing between the molecules is also a key factor for the molecule to show liquid crystalline properties.

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Extraction of L- Arginine from Hair with Subzero Isoelectric Point Precipitation Method

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Abstract: Technological conditions on extracting L- arginine from hair with subzero isoelectric point precipitation method were researched in this paper. The influences of hair hydrolyzation conditions, the preapitant type and dosage, the pH value, temperature, and the concentration of chlorine ion on the extraction rate of L- arginine were investigated. The experimental results show that the extraction rate of L- arginine can reach 0. 139 g under the condition of pH 10, temperature at 0 °C, the bezaldehyde dosage of 2 mL, and the concentration of chlorine ion of 2. 1 mol/L in 30 mL hair hydrolysate.

Key words: L- arginine; isoelectric point precipitation method; hair

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含 PAH 弯曲核的香蕉型分子的合成及其结构

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摘 要: 设计合成了 2 个分别以 DBN(二苯并并四苯)及三苯基吡啶为中心弯曲核的 2 个香蕉型分子, 通过¹H- NMR, ¹³C HRMS 等手段对其结构进行了表征, 在偏光显微镜下, 没有观察到它们的液晶行为。

关键词: 香蕉型; 二苯并并四苯; 合成

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