

Tolane liquid crystals with piperidine, 3,3,4,4,5,5-hexafluoropiperidine as end group: Synthesis and properties



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ABSTRACT

A series of new tolane liquid crystals with piperidine and 3,3,4,4,5,5-hexafluoropiperidine as their terminal groups were synthesized via Sonogashira reaction by using Pd(PPh₃)₂Cl₂/CuI as the catalyst. Their structures were modified by varying the terminal N-heterocycles and/or the length of the alkyl/alkoxy chains on the benzene ring. Most of these new compounds exhibit Smectic B or G mesophases, good thermal stabilities and high clearing points. The molecule C₂H₅O₆F with 3,3,4,4,5,5-hexafluoropiperidine as the end group has a broader HOMO–LUMO energy gap and higher oxidation potential than piperidine derivative C₂H₅O₆H. The result indicates that the oxidation resistance of the tolane liquid crystals was improved by introducing the terminal fluorinated piperidine.

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1. Introduction

Liquid crystals (LCs) as soft materials have attracted considerable attention from both academic and industrial researchers in terms of their unique chemical and physical properties [1–4]. Especially, the super twisted nematic liquid crystal (STN-LCD) product was widely used in optical devices such as vehicles, cell phones and PDAs that carry intellectualization alphanumeric display terminals [5–7]. High optical anisotropy (Δn) of the tolane liquid crystal composition improves the efficiency of light modulation and brightness, and it serves to widen the viewing angle in the STN-LCD screen. The tolane liquid crystal possesses the terminal fluoro substituents which enhance the dielectric anisotropy, and confer a low melting point, low threshold voltage and a high N–I value [5,8–14].

Polar liquid crystal compounds, particularly fluorinated tolane, have been investigated as possible candidates in the development of new STN-LCD materials. Some of these reported liquid crystal molecules are shown in Scheme 1 [15,16].

These commercially available tolane-type liquid crystals with a mono, difluoro or cyano group as a substituent have large birefringence values and dielectric anisotropy. However, compound (a) has no liquid crystal phase, and when it is added to a liquid crystal composition, the

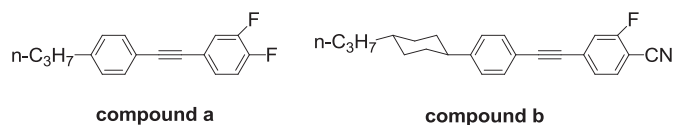
temperature range of the nematic phase was reduced. Compound (b) with cyano substituent in the terminal has higher viscosity than its fluorine derivative, and the cyano group usually attracts ions which confers a low resistivity (voltage holding ratio) to the liquid crystal material due to the high polarity and high polarizability. Based on this fact, the liquid crystal with cyano substituent can't completely satisfy the required characteristics for the AM-TFT displays based on active matrix (TFT) [17].

The shortcomings mentioned above can be overcome by introducing fluorinated heterocycle as terminal group. We have a continuing interest in fluorinated N, O-heterocycles for new building blocks in high performance liquid crystal materials [18]. The four features of tolane-type liquid crystals with 3,3,4,4,5,5-hexafluoropiperidine as the end group that make them attractive candidates for further investigation include the following: a) the introduction of 3,3,4,4,5,5-hexafluoropiperidine enhances the length to breadth ratio of molecule, which favors the formation of liquid crystal phase; b) replacement of the cyano group with polyfluoroalkyl group in the terminal location improved the resistivity; c) the polyfluoroalkyl group with high polarizability can enhance the overall polarizability anisotropy and hence provide high clearing points; d) in particular, fluorinated N-heterocycle with a strong electron-withdrawing group can impart novel characteristics.

Therefore, in this work, we report the synthesis and properties of some new tolane-type liquid crystals with piperidine, 3,3,4,4,5,5-hexafluoropiperidine as the end group. In an effort to establish the impact of different N-heterocycle groups on the physical and chemical properties of liquid crystal.

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Scheme 1. Structures of some typical fluorinated tolane-based Liquid Crystals.

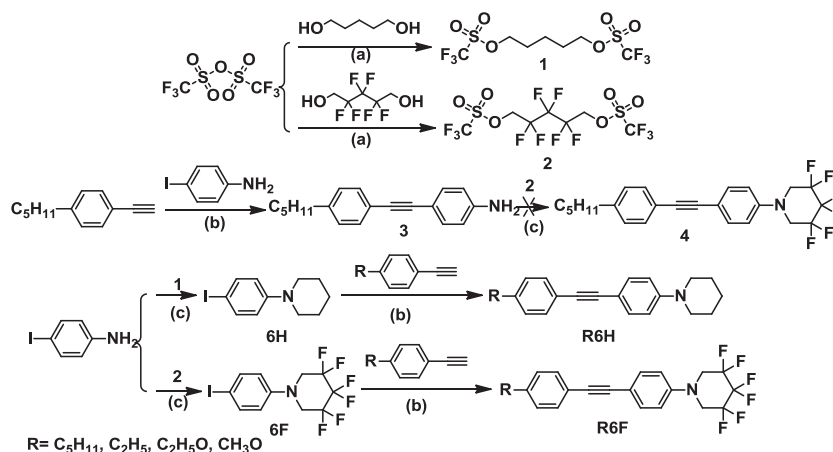
2. Results and discussion

2.1. Synthesis

Piperidine-, 3,3,4,4,5,5-hexafluoropiperidine-based tolan liquid crystals ($C_5H_{11}6F$, C_2H_56F , C_2H_5O6F , CH_3O6F , $C_5H_{11}6H$, C_2H_56H , C_2H_5O6H , CH_3O6H) were synthesized as shown in Scheme 2. Details of the synthesis and characterization of the materials are given in the Supplementary data.

Three synthetic routes for tolan-type liquid crystals have been described previously. These include the Fritsch–Buttenberg–Wiechell rearrangement [19], the 1,2-dibromo-1,2-diarylethane dehydrobromination reaction [20], and the Sonogashira coupling reaction [21]. The Sonogashira coupling reaction has been extensively used in recent years. The aryl iodides were reacted with terminal acetylenes under the Sonogashira coupling reaction condition to give a series of tolane in high yield.

Two synthetic protocols for preparation N-heterocyclic tolan-type liquid crystals have been employed in this article. In synthetic routine one, a) the key intermediate 4-amino-4'-pentyldiphenylacetylene (**3**) was synthesized by 4-iodobenzeneamine and 4-pentyl phenylacetylene under the Sonogashira coupling reaction condition in high yield. The trifluoromethanesulfonic acid alkyl or fluoroalkyldily ester (**1**) or (**2**) has been synthesized in our previous report [18a]. Upon cyclization of the 4-amino-4'-pentyldiphenylacetylene with (**2**) in ethanol using Et_3N as a base at 90 °C for 24 h, there is no desired product (**4**), which was observed by TLC. The strong P– π conjugation effect between the amino group and diphenylacetylene unit results in the decrease of the nucleophilicity of the amino group. In synthetic routine two, b) first, there was cyclization of trifluoromethanesulfonic acid alkyl or fluoroalkyldily esters with 4-iodobenzeneamine in ethanol using Et_3N as a base at 90 °C for 24 h to give aryl iodides **6H** or **6F**. The compound **6H** or **6F** further reacted with alkyl substituted phenyl acetylene in the CH_3CN by using $Pd(PPh_3)_2Cl_2/CuI$ as the catalyst to yield the new piperidine- or 3,3,4,4,5,5-hexafluoropiperidine-based tolan liquid crystals, **R6H** or **R6F**, in 85–90% yield.



Reagents and conditions: (a) $(CF_3SO_2)_2O$, CH_2Cl_2 , RT, 24h. (b) Et_3N , CuI , $PdCl_2(PPh_3)_2$, CH_3CN , N_2 , 85°C, 4h. (c) Et_3N , CH_3CH_2OH , reflux, 24h.

Scheme 2. Synthesis of the N-heterocycles tolan-type liquid crystals.

2.2. Liquid crystalline properties

The new compounds were investigated for their potential liquid crystalline properties by a combination of hot stage polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Their transition temperatures, mesophase morphology were modified by varying the terminal N-heterocycle and/or alkyl substituents on the benzene ring. The assignment of the mesophases was made based on their optical texture, which are presented in Fig. 1.

The new compounds containing piperidine as the end group display good liquid crystal properties. The transition temperatures and mesophase behaviors for the liquid crystals are shown in Table 1.

The structure of the N-heterocycles and the nature of the alkyl substituent have a strong influence on mesophase behaviors. When the substituent is C_2H_5 , CH_3O or C_2H_5O and the N-heterocycle is piperidine, liquid crystal compounds, C_2H_56H , CH_3O6H , C_2H_5O6H , display the mosaic texture of the SmB mesophase. Changing the length of the substituent from ethyl to n-pentyl gives rise to a decrease in ordered arrangement and the $C_5H_{11}6H$ shows a typical nematic phase.

The fluorinated N-heterocycle also plays a crucial role in determining the mesophase behaviors. Comparing with the piperidine compounds which show SmB mesophase, the compounds with 3,3,4,4,5,5-hexafluoropiperidine, $C_5H_{11}6F$, C_2H_56F , CH_3O6H and C_2H_5O6H , have the mosaic texture of the SmG mesophase. It can be seen that the polar character of the liquid crystals increases markedly by the introduction of a fluorinated heterocycle in the end, and the strong H...F inter, or intramolecular hydrogen bond favors the formation of the side hexatic SmG mesophase. e.g., C_2H_5O6H (Cr 154.5 °C SmB 173.5 °C), C_2H_5O6F (Cr 150.9 °C SmG 156.1 °C).

2.3. Thermal stability

Thermal stabilities, which range from 289 °C to 343 °C and depend on the N-heterocycle and the alkyl chain substituent, were determined by thermal gravimetric analysis (TGA). The decomposition temperatures of the new compounds are shown in Table 1, the correlation thermal stability of the new compounds is shown in Fig. 3. The decomposition temperatures were higher than the clearing points for these compounds. In general, the compounds with alkoxy group as the substituent are thermally less stable than the compounds with alkyl group as the substituent. e.g., C_2H_5O6H and CH_3O6H , at T_d 317 °C and T_d 289 °C, while C_2H_56H , $C_5H_{11}O6H$, at T_d 335 °C and T_d 343 °C.

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