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Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# New fluorescent N-heterocyclic liquid crystals with high birefringence



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# ARTICLE INFO

Article history: Received 8 January 2016 Received in revised form 6 September 2016 Accepted 14 October 2016 Available online 15 October 2016

Keywords: Fluorescence Birefringence Mesophase N-heterocycle Liquid crystal

# 1. Introduction

Liquid crystals (LCs) have attracted considerable attention owing to their fascinating properties and wide applications [1,2].

In microscopy techniques like near-field scanning optical, fluorescence and fluorescence confocal polarizing, the LC systems have been doped with some probe dye molecules to generate fluorescent characteristics. However, the dyes may lead to phase separation or complex formation with the host molecules, which may alter the properties of the mixed system. It is valuable to develop LC molecules with intrinsic fluorescence nature, some of which have been synthesized and reported in literature [3.4].

Tolane-type liquid crystal compounds with strong conjugation exhibit high birefringence value [5–7]. Their fluorescent properties can be modified by introducing the chromophore and/or the auxochrome on the terminal. Interest in modern high-performance display materials continues to grow and a large number of tolane-type liquid crystals have been reported [8]. Some tolane-type liquid crystals are shown in Fig. 1.

One of the promising approaches to increase birefringence  $(\Delta n)$  and dielectric anisotropy ( $\Delta \epsilon$ ) is to introduce a polar ring into the molecule. Large number of compounds containing heterocyclic unit have been reported [9–11]. A new class of fluorinated N-heterocycle based liquid crystals were synthesized by our group [12]. These compounds exhibit broad nematic phase range, good thermal stability and strongly positive dielectric anisotropy. Five-membered N-heterocycles, such as pyrrole,

ABSTRACT

A new series of tolane-based liquid crystals with different five-membered N-heterocycle as molecular rigid core have been prepared in good yield. All of these new compounds show mesomorphic behaviors, good thermal stability and intrinsic fluorescence nature. The physical and electro-optical properties of these liquid crystal materials were evaluated. Their properties can be adjusted by varying the alkyl/alkoxyl chain or N-heterocycles. Most of the new compounds exhibit high birefringence, and compounds with propyl chain display stronger fluorescence intensity than those with methoxyl. These tolane-based N-heterocyclic liquid crystals may be used as new high birefringence fluorescent liquid crystal materials.

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pyrazole, imidazole, 1,2,4-triazole are easy to obtain as the commercial available material with low cost. They are of great importance either as chromophore in fluorescent materials or polar terminal group in thermotropic liquid crystals.

Interest in combining the fluorescence and high polarity properties of N-heterocycle to develop high performance liquid crystal materials was aroused. In this work, a series of new tolane-type N-heterocyclic liquid crystals with high birefringence and intrinsic fluorescence nature have been prepared. Their mesomorphic behaviors, physicochemical properties such as UV and fluorescence, and thermal stability properties were investigated. They are expected to be used as new fluorescent liquid crystal materials with high birefringence.

# 2. Results and discussion

### 2.1. Synthesis

Synthetic routes of novel tolane-type liquid crystals are outlined in Scheme 1. Details of the synthesis and characterization of the materials are given in the experimental section.

Compound 2C<sub>3</sub>H<sub>7</sub> or 2CH<sub>3</sub>O was prepared through Sonogashira coupling reaction reported by Zheng [13] Coupling of 1-bromo-4iodobenzene with 1-ethynyl-4-propylbenzene, 1C<sub>3</sub>H<sub>7</sub>, or 1-ethynyl-4methoxybenzene, 1CH<sub>3</sub>O, by using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/CuI catalyst and Et<sub>3</sub>N as a base in THF at room temperature for 12 h, generated compounds, 2C<sub>3</sub>H<sub>7</sub> or 2CH<sub>3</sub>O, in high yields. And then, compound 2 was reacted with N-heterocycles by using CuI as the catalyst in the presence of Cs<sub>2</sub>CO<sub>3</sub> in DMF at 120 °C for 12 h, to give the novel tolane-type N-heterocyclic liquid crystals, C<sub>3</sub>H<sub>7</sub>-Nhet or CH<sub>3</sub>O-Nhet, in 45–85% yield.

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Fig. 1. Some tolane-type liquid crystal molecules.

#### 2.2. Liquid crystalline properties

The mesomorphic behaviors and thermodynamic data of the new compounds were investigated by a combination of hot stage polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The phase transitions and thermodynamic data are presented in Table 1. The assignment of the mesophases was made based on their optical texture, some of which are presented in Fig. 2.

All the new compounds were found to exhibit mesomorphic behavior. The enthalpy values are in the range of 3.66–46.94 kJ/mol by the differential scan calorimetry (DSC) thermograms. These liquid crystal molecules differ in structure at the N-heterocycle rigid core or terminal alky chain.

The new compounds with different five-membered N-heterocyclic rigid core exhibit different mesophases. Compounds  $C_3H_7$ -N1 and  $CH_3O$ -N1 with pyrrole as molecular rigid core display narrow nematic phase, which was evidenced by their schlieren texture shown in Fig. 2.

The other factor that affects the mesophase is the propyl or methoxyl substituent. Compound  $C_3H_7$ -N12 exhibits SmB phase, while CH<sub>3</sub>O-N12 displays SmA phase. The propyl causes stronger molecular packing arrangement which lead to the formation of smectic B phase.

The compounds prefer to form smectic phase as the number of the N atom increases. The melting point and clearing point are decreased, caused by molecular packing is lowering, e.g.,  $C_3H_7$ -N1 (Cr 173.1 °C, N 203 °C),  $C_3H_7$ -N12 (Cr 130.4 °C, SmB 145.5 °C),  $C_3H_7$ -N124 (Cr 128.6 °C, SmE 139 °C).

The transition points of most the compounds with methoxyl group are higher than those with propyl, e.g.,  $CH_3O-N1$  (Cr 193.4 °C, N 207 °C),  $C_3H_7-N1$  (Cr 173.1 °C, N 203 °C);  $CH_3O-N13$  (Cr 171.1 °C, N 193 °C),  $C_3H_7-N13$  (Cr 128.5 °C, SmB 160.6 °C). The transition point of the new compounds decrease when changing the N-heterocyclic rigid core from pyrrole to 1,2,4-triazole.

The shorter methoxyl substituent decreases the mesophase range. The longer propyl provides an appropriate length to width ratio, which is propitious to the stability of mesomorphism.



Reagents and cooditions: a)  $PdCl_2(PPh_3)_2$ , Cul,  $Et_3N$ , THF, rt, 12h; b) Cul,  $Cs_2CO_3$ , DMF, 120 , 12h.

Scheme 1. Synthesis of novel tolane-type N-heterocyclic liquid crystals.

Table 1	
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hermal behavior of the new compounds.	

Compound	Phase transition temperature/°C <sup>a</sup> enthalpies of transition [kJmol <sup>-1</sup> ]				
C <sub>3</sub> H <sub>7</sub> -N1	Cr 173.1 [26.83]	Ν	203 <sup>c</sup>	Ι	267.8
C <sub>3</sub> H <sub>7</sub> -N12	Cr 130,4 [24.65]	SmB	145.5 <sup>c</sup>	Ι	250.5
C <sub>3</sub> H <sub>7</sub> -N13	Cr 128.5 [3.66]	SmB	160.6 <sup>c</sup> [17.6]	Ι	248.3
C <sub>3</sub> H <sub>7</sub> -N124	Cr 128.6 [20.99]	SmE	139 <sup>c</sup>	Ι	280.8
CH <sub>3</sub> O-N1	Cr 193.4 [9.99]	Ν	207 <sup>c</sup>	Ι	221.7
CH <sub>3</sub> O-N12	Cr 95.6 [27.23]	SmA	158.6 <sup>c</sup>	Ι	272.7
CH <sub>3</sub> O-N13	Cr 171.1 [16.38]	Ν	193 <sup>c</sup>	Ι	251.7
CH <sub>3</sub> O-N124	Cr 163.3 [46.94]	Ν	179 <sup>c</sup>	Ι	287.6

<sup>a</sup> Transition temperature and enthalpy change (in square brackets) were determined by DSC (peak temperature, first heating scan, 10 Kmin<sup>-1</sup>) and confirmed by POM. Cr = crystalline solid, N = nematic phase, SmB = smectic B; SmC = smectic C; SmE = smectic E; I = isotropic liquid state.

<sup>b</sup> Td = decomposition temperature.

Transition temperatures were determined by POM.

#### 2.3. Thermal stability

The novel compounds are thermally stable up to 221.7–287.6 °C determined by thermal gravimetric analysis (TGA). The decomposition temperatures of the new compounds are shown in Table 1. Data shows the decomposition temperatures are higher than the clearing points. The new tolane-type compounds with N-heterocycles as end group exhibit good thermal stability. The stability of compounds with methoxyl substituent increases as the number of the N atom increases, e.g., CH<sub>3</sub>O-N124 (287.6 °C), CH<sub>3</sub>O-N12 (272.7 °C), CH<sub>3</sub>O-N1 (221.7 °C).

#### 2.4. UV/Vis absorption, photoluminescence spectroscopy and birefringence

The UV absorption spectra data for solutions of the new tolane-type N-heterocyclic compounds in dichloromethane are presented in



Fig. 2. Optical texture (a) for CH<sub>3</sub>-N1 schlieren of nematic phase upon cooling to 197 °C, (b) for CH<sub>3</sub>O-N1 schlieren of nematic phase upon cooling to 204 °C.

V-visible, fluorescence spectra analysis data and birefringence of new compounds.					
Compounds	$\lambda_{max}[nm]^a$	$\lambda_{exc}[nm]^a$	$\lambda_{em}[nm]^a$	Birefringence <sup>b</sup>	
C <sub>3</sub> H <sub>7</sub> -N1	305	310	338	0.37	
C <sub>3</sub> H <sub>7</sub> -N12	309	310	336	0.31	
C <sub>3</sub> H <sub>7</sub> -N13	298	310	330	0.20	
C <sub>3</sub> H <sub>7</sub> -N124	302	310	336	0.27	
CH <sub>2</sub> O-N1	307	310	340	_c	

309

302

307

<sup>a</sup> The spectra were recorded from a dilute solution in dichloromethane  $(1.5 \times 10^{-5} \text{ mol/L})$ .

346

349

359

0.35

0.33

0.34

310

310

310

<sup>b</sup> Extrapolated from 5 wt% solution in nematic host mixture 1C40200-000 ( $\Delta n = 0.131$ ).

<sup>c</sup> Poor solubility.

CH<sub>3</sub>O-N12

CH<sub>3</sub>O-N13

CH<sub>3</sub>O-N124

Table 2



Fig. 3. Absorption spectra (left) and fluorescence spectra (right) of tolane-type liquid crystals.

Table 2. The position of N atom in N-heterocyclic rigid core influences the max absorption wavelength, for example, changing the position from 1,3 to 1,2, gives a red shift, e.g., C<sub>3</sub>H<sub>7</sub>-N13,  $\lambda_{max} = 298$  nm, C<sub>3</sub>H<sub>7</sub>-N12,  $\lambda_{max} = 309$  nm, CH<sub>3</sub>O-N13,  $\lambda_{max} = 302$  nm, CH<sub>3</sub>O-N12,  $\lambda_{max} = 309$  nm.

Recently, adding the property of liquid crystallinity to emissive materials is of increasing interest [14]. The emission fluorescence spectra data of new compounds are shown in Table 2. All spectra were recorded from a dilute solution in dichloromethane ( $1.5 \times 10^{-5}$  mol/L).

As shown in Fig. 3, the intensities of compounds with propyl group are stronger than that of compounds with methoxyl group. The double peak phenomenon of fluorescence spectra for compounds with propyl group result from the marketed difference between the excited state and the ground state [15]. Compound  $C_3H_7$ -N12 exhibited the strongest



Fig. 4. The optimized geometry of C<sub>3</sub>H<sub>7</sub>-N1 (a), C<sub>3</sub>H<sub>7</sub>-N12 (b), C<sub>3</sub>H<sub>7</sub>-N13 (c), C<sub>3</sub>H<sub>7</sub>-N124 (d).



Fig. 5. HOMO of C<sub>3</sub>H<sub>7</sub>-N12 (a) and LUMO of C<sub>3</sub>H<sub>7</sub>-N12 (b); HOMO of CH<sub>3</sub>O-N12 (c) and LUMO of CH<sub>3</sub>O-N12 (d).

# Table 3

Tuble 5							
Geometr	rical parame	ters of new	compounds	calculated	with	Gaussian	03

Compounds	Molecular length $(10^{-1} \text{ nm})$	L/D	Energy (a.u.)	HOMO (ev)	LUMO (ev)	EHL (ev)	Dipole (D)
C <sub>3</sub> H <sub>7</sub> -N1	18.48	4.30	-866.17	-0.048	-0.202	0.154	2.04
C <sub>3</sub> H <sub>7</sub> -N12	18.48	4.30	-882.19	-0.051	-0.202	0.151	2.09
C <sub>3</sub> H <sub>7</sub> -N13	18.33	4.26	-882.20	-0.056	-0.211	0.155	5.17
C <sub>3</sub> H <sub>7</sub> -N124	18.13	4.21	-893.49	-0.047	-0.234	0.187	4.81
CH <sub>3</sub> O-N1	17.47	4.06	-862.74	-0.045	-0.197	0.152	2.86
CH <sub>3</sub> O-N12	17.44	4.05	-878.75	-0.048	-0.197	0.149	3.68
CH <sub>3</sub> O-N13	17.50	4.07	-878.79	-0.053	-0.205	0.152	5.43
CH <sub>3</sub> O-N124	17.30	4.02	-894.78	-0.059	-0.205	0.146	5.18

intensity at 336 nm, which makes it new liquid crystal materials with intrinsic fluorescene nature possible.

As shown in Fig. 3, the intensities of compounds with propyl group are stronger than that of compounds with methoxyl group. The double peak phenomenon of fluorescence spectra for compounds with propyl group result from the marketed difference between the excited state and the ground state [15]. Compound C<sub>3</sub>H<sub>7</sub>-N12 exhibited the strongest intensity at 336 nm, which makes it new liquid crystal materials with intrinsic fluorescene nature possible.

New tolane-type N-heterocyclic compounds have high  $\Delta n$  value, which range from 0.20 to 0.37. The N-heterocyclic rigid core has influence on  $\Delta n$  value. As the number of N atoms increases, the  $\Delta n$  value of compound with propyl decreases, e.g.,  $C_3H_7$ -N1 ( $\Delta n = 0.37$ ),  $C_3H_7$ -N12 ( $\Delta n = 0.31$ ), C<sub>3</sub>H<sub>7</sub>-N124 ( $\Delta n = 0.27$ ). It can be illustrated by the polarity that N-atom brings. The propyl and methoxyl substituent also influence the  $\Delta n$  value, e.g., C<sub>3</sub>H<sub>7</sub>-N12 ( $\Delta n = 0.31$ ), CH<sub>3</sub>O-N12  $(\Delta n = 0.35)$ . Compound C<sub>3</sub>H<sub>7</sub>-N1 containing molecular rigid core pyrrole ring has the largest  $\Delta n$  value (0.37). It can be employed as new fluorescent liquid crystal materials with high birefringence.

#### 2.5. Theoretical study

The geometry optimization of the structures were performed by density functional theory (DFT) Becke's three-parameter hybrid function with non-local correlation of Lee-Yang-Parr (B3LYP) method in gas phase [16]. The corresponding frequency analyses were computed at the same level of theory to characterize them as minima (no imaginary frequencies) with help of Gaussian03 (Revision D.01) suite of programs [17]. All of above calculations used a 6 - 31 + G basis set [18]. The computed structures were visualized using the GaussView program. The optimized geometry of compounds with propyl were shown in Fig. 4, and the HOMO, LUMO of compounds C<sub>3</sub>H<sub>7</sub>-N12 and CH<sub>3</sub>O-N12 were shown in Fig. 5. The HOMO, LUMO of other compounds were shown in the Supplementary data.

As shown in Table 3, the length to width ratios (L/D) of the new compounds is larger than 4, which is an important factor that affects the formation of liquid crystal.

The energy of compound C<sub>3</sub>H<sub>7</sub>-N124 is the lowest among compounds with propyl, and that of compound CH<sub>3</sub>O-N124 is also the lowest among compounds with methoxyl. This indicates that compounds with 1,2,4-triazole as end group is more stable than those with other five-membered N-heterocycles. It may result from the intrinsic dipole moment of 1,2,4-triazole which lead to the increase of the molecular polarity.

The energy of compound C<sub>3</sub>H<sub>7</sub>-N12 is close to compound C<sub>3</sub>H<sub>7</sub>-N13, and that of compound CH<sub>3</sub>O-N12 is nearly the same as CH<sub>3</sub>O-N13, while their dipole moments are different. The difference in mesophase of the compounds may depend on their different dipole moments.

# 3. Conclusions

A new class of tolane-based liquid crystals with different N-heterocyclic rigid core has been prepared in high yield. All of the new compounds show mesomorphic behaviors and good thermal stability. Their melting points, decomposition temperatures, UV/Vis absorption, photoluminescence spectroscopy and birefringences were measured. Their properties can be adjusted by varying the terminal chain or N-heterocycles. The melting points of the compounds with methoxyl are higher than those with propyl. As the number of the N-atom increases, compound prefers to form smectic phase. The longer propyl substituent causes the liquid crystal compounds to have stronger fluorescene intensity. Compound C<sub>3</sub>H<sub>7</sub>-N12 exhibited the strongest fluorescene intensity and high  $\Delta n$  value ( $\Delta n = 0.31$ ), hence it was suggested as new fluorescent liquid crystal materials with high birefringence.

#### 4. Experimental section

The experimental details, synthesis, structural characterization of new compounds and their liquid crystal properties, geometrical parameters and frontier orbitals were seen in the Supplementary data.

# Acknowledgements

The authors gratefully acknowledge the support of National Natural Science Foundation of China (21272080), Department of Science and Technology, Guangdong Province (2010A020507001-76, 5300410, FIPL-05-003). The Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.molliq.2016.10.071.

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