Synthesis and Properties of Liquid Crystalline Y-shaped Molecules Containing 1,3,4-Oxadiazole

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Abstract

New liquid crystalline Y-shaped molecules containing 1,3,4-oxadizoles have been synthesized with variation of terminal groups (R = H, OCH_3 or OC_8H_{17}). The structures of obtained compounds were identified by FT/IR and NMR spectrometry, and their thermal and liquid crystalline properties were investigated by DSC and polarizing optical microscope.

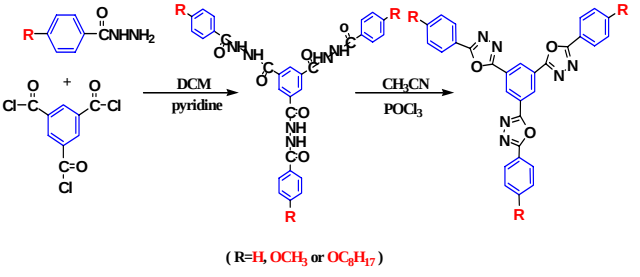
1. Introduction

Aromatic compounds with 1,3,4-oxadiazoles are known to show fascinating properties which can be applied for charge transfer layers and light-emitting materials.[1, 2] Recently, it has been reported that banana-shaped molecules containing heteroaromatic rings could form the biaxial nematic phase.[3] In this study, we have synthesized and characterized the new liquid crystalline Y-shaped molecules containing 1,3,4-oxadizoles with variation of terminal groups (R = H, OCH_3 or OC_8H_{17}). The structures of Y-shaped molecules were identified by FT/IR and NMR spectrometry, and their thermal and mesogenic properties were investigated by DSC and polarizing optical microscope.

2. Experimental

Synthesis. Synthetic route to Y-shaped molecules containing 1,3,4-Oxadiazole is shown in Scheme 1. First, 1,3,5-benzenetrihydrazide was prepared by conden-sation reaction of 1,3,5-benzenetricarboxylic-chloride and 4-alkoxybenzohydrazide in DCM with pyridine. The final product was prepared by substitution reaction of the 1,3,5-benzenetrihydrazide with $POCl_3$, which was purified by chromatography on silica gel by eluting with 8:2 $CHCl_3$/EtoAc.

Synthesis of compound with R = OC_8H_{17}. IR (KBr pellet, cm^{-1}): 3079 (aromatic = CH, st), 2928, 2852 (aliphatic CH, st), 1255 (C-O, st), 1600 (C=C, st), 1686 (C=N, st). ^1H NMR ($CDCl_3$, δ in ppm): 8.98-8.81 (3H, d, ArH), 8.27-7.82 (6H, m, ArH), 7.06-6.85 (6H, m, ArH), 4.11-3.97 (6H, m, OCH_2), 1.81-0.85 (45H, m, C_7H_{17}).



Scheme 1. Synthetic route to Y-shaped molecules.

Characterization. IR and NMR spectra were obtained by Jasco 300E FT/IR and Bruker DPX 200 MHz NMR spectrometers, respectively. The phase transition temperatures were determined by DSC

(NETZSCH DSC 200 F3) and polarizing optical microscope (Zeiss, Jenapol). DSC measurements were performed in a N_2 atmosphere, and the heating and cooling rates were 10°C/min. Optical textures were observed by the polarizing microscope equipped with a camera and a thermo-controller (Mettler FP82HT).

3. Results and discussion

The structures of obtained Y-shaped compounds were identified by FT/IR and NMR spectrometry. The results were in accordance with expected formulae.

The properties of the Y-shaped molecules are summarized in Table 1. The melting tempera-ture (T_m) of the compounds are in the range of 205-310℃ depending on the structure of therminal alkoxy groups (R = OCH_3, OC_8H_{17}). The compounds with R = H and OCH_3 show relatively high melting temperature of 307°C and 310°C respectively. It is not cleared that compound with R = OCH_3 can form mesophase intrinsically because it undergo thermal degradation just after melting. By introducing the longer alkyl chain end such as OC_8H_{17}, the melting temperature of Y-shaped molecules was observed decrease into 205°C (Figures 4). However, such molecule could not form the mesophase. The isotropiczation temperature of compound with R = H is 330°C. Using an optical microscope for compound with R = H, the optical textures corresponding to nematic phase was observed (Figures 2 and 3).

Table 1. Yields and transition temperatures of compounds

R	Yield (wt%)	T_m (°C)	T_i (°C)
H	85	307	330
OCH_3	83	310	--
OC_8H_{17}	67	205	--

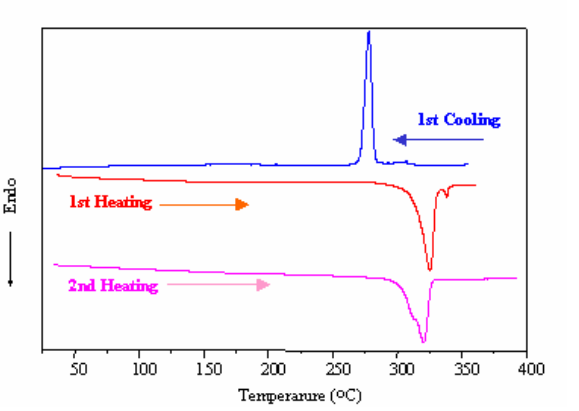


Fig 2. DSC Thermograms of compound with R=H (Heating and cooling rates = 10℃/min).

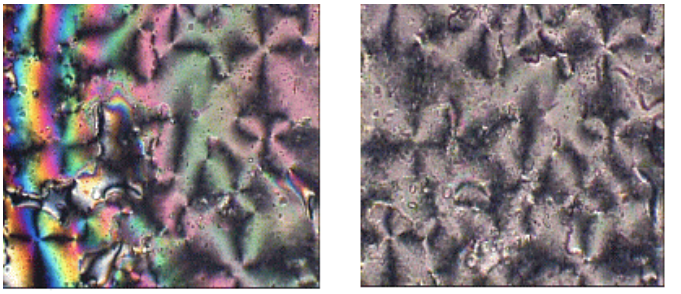


Fig 3. Optical textures of compound with R = H taken at (a) heating and (b) cooling cycles.

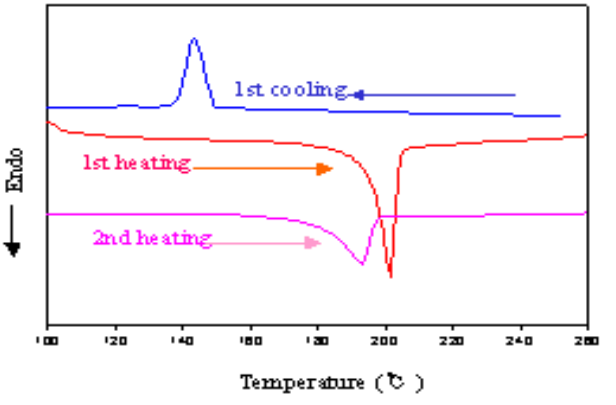


Fig 4. DSC Thermograms of compound with R = OC_8H_{17} (Heating and cooling rates = 10℃/min).

4. Summary

Three new Y-shaped molecules have been synthesized. The values of melting temperature were in the range 205-310^{o}C. Compound without a substituent produced a nematic mesophase enantiotropically on heating, while two compounds with R = OCH_3 and OC_8H_{17} were not a thermotropic liquid crystal.

5. References

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