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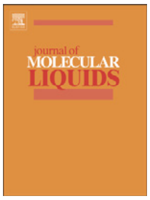

New U-shaped liquid crystals azobenzene derived from catechol for photoswitching properties

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ABSTRACT

A new series of liquid crystals whose molecular structure consists of a U-shaped unit as a central core and two rod-like azobenzenes as the peripheral units are synthesized. The mesomorphic properties were investigated by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. The existence of nematic and smectic A phase was confirmed by textures and X-ray diffraction. The *trans*-form of azo compounds showed a strong band in the UV region at ~365 nm for the π–π* transition, and a weak band in the visible region at ~450 nm due to the n–π* transition. These molecules exhibit a strong photoisomerization behavior in which *trans–cis* take 50 and 55 s for compounds L4/5 and L4/6, respectively, whereas *cis–trans* take place almost 29 and 30 h, respectively. Long thermal back relaxation allows us to realize that optical storage devices with these materials which need longer periods.

1. Introduction

In principle, the thermotropic liquid crystals (LCs) constructed by rod-like molecules exhibit nematic and/or smectic mesophases, whereas LCs with flat disc-shaped molecules display nematic and/or columnar mesophases [1,2]. A new class of LCs whose anisotropic shape of the molecules is distorted away from the classical rod or disc shapes so called 'non-conventional LCs', for instance oligomeric LCs, bent-core molecules, polycatenars, and dendrimers [1,3]. Indeed, the non-classical molecular architectures may exhibit mesophases even though their molecular geometry deviate substantially from the classical rod or disc shapes [1]. In reality, since the time of Vorlander who is famous in LCs synthesis and design, his colleague Apel [4,5] reported the first synthesis of bent-core molecules. Disubstitution of the benzene ring either 1,2 or 1,3-positions derived into U-shaped or bent-shaped molecules that deviates significantly from classical rod-shaped molecules.

Although Yelamaggad et al. [1] described that bent core V-shaped molecules of 1,2-phenylene bis[*N*-(2-hydroxy-4-*n*-alkoxyloxybenzylidene)-4′-aminobenzoate]s and other reported compounds having 1,2-subsitution of benzene ring, also termed as bent core V-shaped molecules [5–7]. However, several reports [8–11] are available on the 1,2-subsituted phenylene compounds showing U-shaped molecular architectures which are very relevant to this work. Therefore, we desire to designate the term U-shaped molecules in this paper. It is well-established that U-shaped molecules exhibit mesophases which are similar to classical calamitic LCs, whereas banana-shaped mesogens exhibit a new type of smectic phases, which are not comparable to the phases formed by calamitics [1]. U-shaped molecule, viz. 1,2-phenylene bis[4-(ethoxyphenylazoxy)benzoate] was first reported by Vorlander and Apel [5] and later Pelzl et al. [6] hence identified this compound that exhibit a nematic phase. Some reports also showed that bent-core compounds are found as fused twins [8] or U-shaped molecules [9]. A homologous series of U-shaped dimeric liquid crystals in which two mesogenic groups are connected via catechol is reported [10]. These compounds show the nematic and smectic C phases of the even members, whereas the odd members favor the nematic and smectic A phases. They discussed the transition behavior of the U-shaped compounds in terms of molecular shape [10].

Some interesting reports on new types of bent-core structure in which two mesogenic segments are connected to a benzene ring at the 1,2-positions through alkylene spacers, which are relevant to this study. In this connection, Attard and Douglass [11] reported such U-shaped dimeric liquid crystals, the benzene-1,2-di(4-carboxybenzyliedene-4′-*n*-alkylanilines) in which the spacers incorporated 3 to 6 methylene units, whilst terminal aliphatic chain lengths varied from 1 to 12 units. In the two homologous series, an odd number of methylene units in the spacer form nematic and smectic phases as a function of terminal chain length whereas an even number of methylene units in the spacer are purely smectogenic and in both series the first two homologues form only

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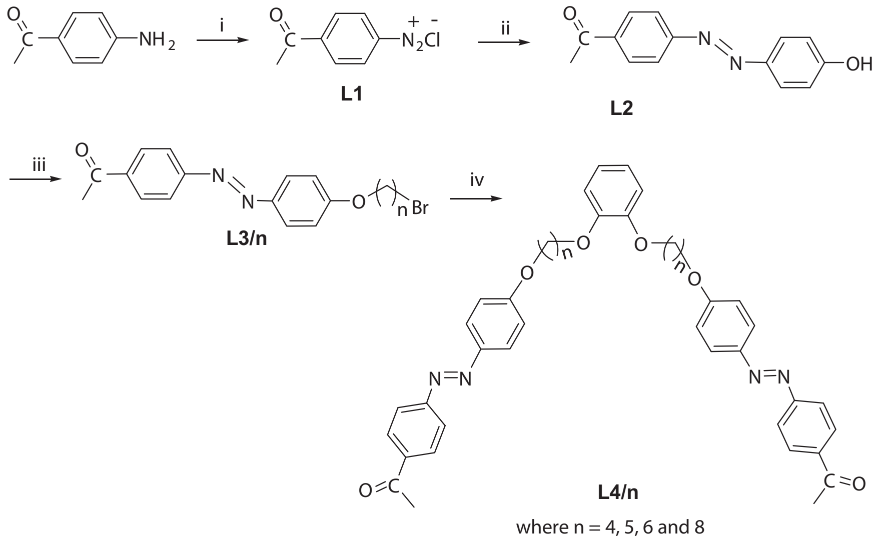

Scheme 1. Synthesis of U-shaped liquid crystals. Reagents and conditions: i, $NaNO_2$, HCl, 2 °C; ii, NaOH, C_6H_5OH; iii, K_2CO_3, KI, $Br(CH_2)_nBr$; iv, $C_6H_6O_2$ catechol, K_2CO_3.

smectic B phases. Their X-ray diffraction studies have shown that these smectic phases are composed of molecules arranged in bilayers [11].

On the other hand, a field of research is growing steadily on the photoinduced phenomenon, in which the incident light itself brings about molecular ordering/disordering of the liquid–crystalline system [12]. This particular aspect of photonics, in which light can be controlled by light as a stimulus, is being proposed as the future technology for high-speed information processing. The heart of the phenomenon in such systems is the reversible photoinduced shape transformation of the molecules containing the photochromic azo groups [13,14]. Liquid crystals having low or high molar mass containing an azo-linkage have attention due to their unique photoswitchable properties induced by light [15–19]. Upon absorption of UV light (~365 nm) the energetically more stable E configuration (*trans*) converts to the Z configuration (*cis*). The reverse transformation of the Z isomer into the E isomer can be brought by irradiation with visible light (in the range of 400 to 500 nm). This reverse process is known as thermal back relaxation which occurs in the dark and this reverse process (*cis* to the *trans*) can occur thermally or photochemically with visible light [20–27].

To the best of our knowledge, the 1,2-bis{[4-(4-acetylphenylazo)phenoxy]alkyloxy}benzene moieties have not been employed to realize such U-shaped dimeric mesogens. The introduction of flexible spacers between mesogenic units can have a profound effect on the liquid crystal properties and the phase transition behavior of U-shaped dimeric materials are related with the parities of the spacer chains and terminal alkyl chains showing nematic and smectic phases [10,11]. In this paper, we have synthesized a series of new molecules in which two rod-shaped photoswitchable azobenzene moieties, each carrying a short electron withdrawing acetyl group at the terminals [12c], are attached to a 1,2-phenylene unit via alkylene spacers and ether linkage which exhibits nematic and smectic A phases irrespective of chain length and parity.

Table 1
Phase transition temperatures (*T*/°C) and associated transition enthalpy values [Δ*H*/J g^{-1}] from the DSC scans of **L4/n** (n = 4, 5, 6 and 8).[a]

Compound	n	Heating cycles	Cooling cycles
L4/4	4	Cr 148.8 SmA 154.3 N 167.5 I [49.4] [5.0] [1.0]	I 165.4 N 151.8 SmA 82.4 Cr [1.3] [5.8] [25.9]
L4/5	5	Cr 131.3 SmA 136.8 N 149.5 I [11.1] [1.8] [0.76]	I 147.1 N 134.8 SmA 70.1 Cr [0.87] [2.3] [7.3]
L4/6	6	Cr 139.6 SmA 142.5 N 154.3 I [45.9] [2.4] [1.1]	I 152.2 N 141.1 SmA 83.6 Cr [1.3] [4.0] [31.6]
L4/8	8	Cr 135.1 SmA 138.8 N 152.4 I [32.5] [4.5] [1.0]	I 149.6 N 135.8 SmA 73.5 Cr [1.2] [4.8] [21.5]

[a] Abbreviations: Cr = crystal, SmA = smectic A, N = nematic and I = isotropic phase.

2. Characterization

The structures of the intermediates and final products were confirmed by spectroscopic methods. FT-IR spectra were recorded with a PerkinElmer (BX 20) spectrometer. ^1H NMR spectrum were recorded with a Jeol (ECA 600) and ^{13}C NMR was also recorded with a Jeol (150 MHz) spectrometer. The transition temperatures and their enthalpies were measured by differential scanning calorimetry (Mettler Toledo Star, SW 7.01), heating and cooling rates were 10 °C min^{-1}. Optical textures were determined by using a Mettler FP 82 hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing optical microscope. The compositions of the compounds determined by CHNS elemental analyzer (Leco & Co) confirmed molecular structures.

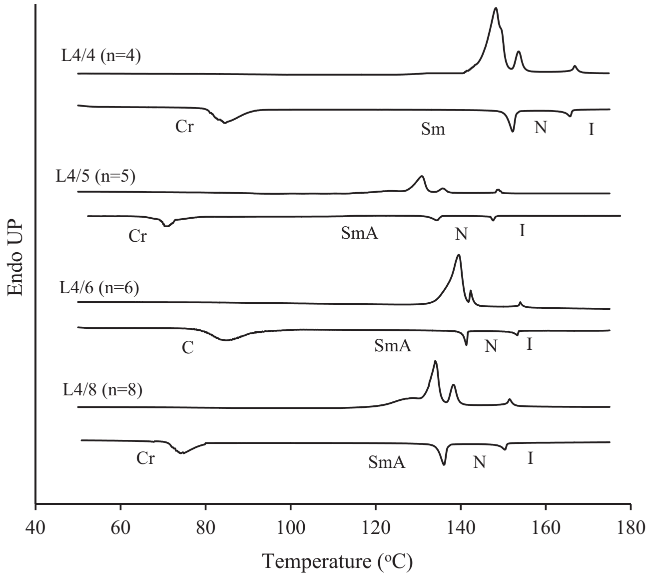

Fig. 1. DSC heating and cooling traces of compound **L4/n** (n = 4, 5, 6 and 8) at 10 °C min^{-1}.