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Liquid Crystals

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Synthesis and mesomorphic properties of two series of new azine-type liquid crystals

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Two series of symmetrical azine-type liquid crystals were synthesised and their chemical structures identified by FTIR, ^1H NMR and elemental analysis. Their mesomorphic properties were investigated by polarising optical microscopy, differential scanning calorimetry and X-ray diffraction. The characteristic of these liquid crystals is that they have a high clearing point (most were higher than 320°C) and a broad thermal range in the mesophase. The end groups of the liquid crystals had an effect on their mesomorphic properties. The series with alkoxy end groups all exhibited both smectic A (SmA) and a nematic phase, whereas the series with alkyl end groups showed only nematic phase at their lower analogues and showed both SmA and nematic properties at their higher analogues.

Keywords: azine-type liquid crystals

1. Introduction

It is well-known that thermotropic nematic liquid crystals are the most technologically important liquid crystal compounds. They are usually composed of rigid rod-like or disc-shaped molecules (*I*) and are widely used as the operating fluid in liquid crystal displays (LCDs). Actually, the operating fluids used in LCDs are all mixtures because no single liquid crystal can meet the diverse demands of different display modes. Sometimes some LCDs must operate at high temperatures, which will require a high clearing point and broad thermal range of nematic phase of their operating liquids. The most important and widely used way to meet these demands is to add liquid crystals of high clearing point to the mixtures. Therefore, the development of liquid crystals of high clearing point, broad thermal range of nematic phase and appropriate melting point has significant importance.

Azine compounds have interesting chemical and pharmacological properties. They are attracting increased interest for their potential in medical and biological applications (2–4), the design of metal complexes (5, 6) and other material applications (7, 8). In 1959, a series of azine-type liquid crystals were synthesised by Wilfrid and Glenn (9) and were found have high clearing points. For example, the clearing point of 4,4'-ethoxylbenzalazine is as high as 197°C . Since then, many experimental and theoretical studies (10–16) have been carried out on the synthesis and mesomorphic properties of azine-type liquid crystal compounds. Chudgar *et al.* (16) reported a series of azine-type liquid crystals with ester group and lateral substituents in the rigid core and alkoxy end groups. In this paper, we report two series of new symmetrical

azine-type liquid crystals, 4,4'-(4-alkylbenzoyloxy)-benzalazine and 4,4'-(4-alkoxybenzoyloxy)benzalazine, that contain only ester groups in their linear mesogenic core and alkyl or alkoxy end groups.

2. Experimental

Characterisation

FTIR spectra were recorded on a Nicolet 510P instrument and ^1H NMR spectra (in CDCl_3) on a Bruker AV400 instrument. Elemental analysis measurements were carried out on a Thermo Finnigan Flash EA1112 elemental analyser. Thermogravimetric analysis (TGA) curves were recorded on a Netzsch-Sta 409C thermal analyser. The mesomorphic properties were studied by polarising optical microscopy (POM) using an Olympus BX-51 equipped with a Linkam Scientific LTS 350 hot stage. The smectic phase was determined by its optical texture and was further confirmed by a Philips 1700 type X-ray diffraction (XRD) instrument. For differential scanning calorimetry (DSC), a Perkin-Elmer DSC 6 instrument was used, with a scanning rate of $10^\circ\text{C min}^{-1}$ when heating and 5°C min^{-1} when cooling, the samples were sealed in aluminium capsules in air and the holding atmosphere was dry nitrogen.

Synthesis

All starting materials were commercially available and used without further purification. Figure 1 shows the structure of the target compounds and their synthetic route, procedures of which are summarised

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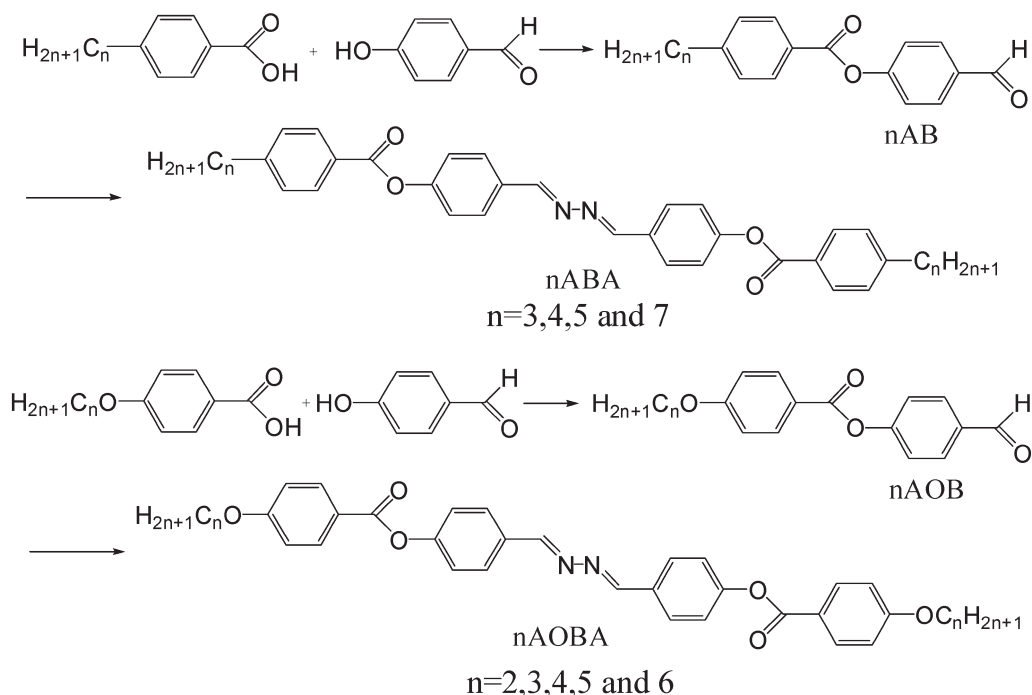


Figure 1. Synthetic route for the target compounds.

below. Processes for the preparation of 7ABA and 6AOBA are described in full as examples.

Synthesis of 4-heptylbenzoic acid 4-formylphenyl ester (7AB).

Dicyclohexylcarbodiimide (10.3 g, 50 mmol) and *N,N*-dimethylaminopyridine (20 mg) were added to a solution of 4-heptylbenzoic acid (11.1 g, 50 mmol) and 4-hydroxybenzaldehyde (6.1 g, 50 mmol) in 120 ml of dichloromethane (DCM). The mixture was stirred for 12 h. The dicyclohexylurea was filtered off and the solvent from the filtrate was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM). IR (ν/cm^{-1}): 2957, 2922, 2850 (CH₃-, -CH₂-), 1738 (C=O of ester), 1696 (C=O of aromatic aldehyde), 1600, 1500 (aromatic C=C), 1262 (C-O-Ar). ¹H NMR (CDCl₃): δ 0.87–1.68 (m, 13H, alkyl), 2.69–2.73 (m, 2H, Ar-CH₂), 7.32–7.34 (d, 2H, aromatic), 7.40–7.42 (d, 2H, aromatic), 7.96–7.98 (d, 2H, aromatic), 8.10–8.12 (d, 2H, aromatic), 10.03 (s, H, Ar-CHO). Elemental analysis: calculated for C₂₁H₂₄O₃, C 77.75, H 7.46; found, C 77.69, H 7.48%.

Synthesis of target compound 7ABA.

A mixture of 3.24 g (0.01 mol) 7AB and 1.12 g (0.01 mol) semicarbazide hydrochloride and 20 ml of DMF was stirred in a round-bottom flask under reflux for 6 h. After cooling, water (200 ml) was

added to the reaction mixture. The precipitate was allowed to stand overnight, collected by suction filtration and recrystallised by DMF. Yield: 46%. IR (ν/cm^{-1}): 2963, 2928, 2855 (CH₃-, -CH₂-), 1740 (C=O), 1627 (C=N), 1601, 1502 (aromatic C=C). ¹H NMR (CDCl₃): δ 0.86–1.68 (m, 13H, alkyl protons), 2.69–2.73 (m, 2H, Ar-CH₂), 7.32–7.34 (d, 4H, aromatic), 7.94–7.96 (d, 2H, aromatic), 8.11–8.13 (d, 2H, aromatic), 8.72 (s, H, Ar-CH=N). Elemental analysis: calculated for C₄₂H₄₈N₂O₄, C 78.23, H 7.50, N 4.34; found, C 78.17, H 7.52, N 4.38%.

Synthesis of 4-hexyloxybenzoic acid 4-formylphenyl ester (6AOB).

The procedure was similar to that for 4-heptyloxybenzoic acid 4-formylphenyl ester. IR (ν/cm^{-1}): 2960, 2872, 2932, 2850 (aliphatic C-H), 1735 (C=O of ester), 1695 (C=O of aromatic aldehyde), 1605, 1579, 1510 (aromatic C=C), 1265 (C-O-Ar). ¹H NMR (CDCl₃): δ 0.92–1.85 (m, 11H, alkyl protons), 4.03–4.08 (d, 2H, -CH₂-O), 6.97–7.00 (d, 2H, aromatic), 7.39–7.42 (d, 2H, aromatic), 7.96–7.98 (d, 2H, aromatic), 8.13–8.16 (d, 2H, aromatic), 10.03 (s, H, Ar-CHO). Elemental analysis: calculated for C₂₀H₂₂O₄, C 73.60, H 6.79; found, C 73.46, H 6.81%.

Synthesis of target compound 6AOBA.

The procedure was similar to that for 7ABA. IR (ν/cm^{-1}): 2958, 2932, 2872, 2854 (CH₃-, -CH₂-), 1735

(C=O), 1627 (C=N), 1606, 1579, 1510 (aromatic C=C). ^1H NMR (CDCl_3): δ 0.94–1.90 (m, 11H, alkyl), 4.07–4.10 (m, 2H, O-CH₂), 6.96–6.98 (d, 2H, aromatic), 7.38–7.45 (d, 2H, aromatic), 7.95–7.98 (d, 2H, aromatic), 8.16–8.20 (d, 2H, aromatic), 8.70 (s, H, Ar-CH=N). Elemental analysis: calculated for C₄₀H₄₄N₂O₆, C 74.05, H 6.84, N 4.32; found, C 73.86, H 6.85, N 4.33%.

3. Results and discussion

All the target compounds were investigated by POM and DSC to determine their mesomorphic properties. The POM observations revealed that all of the compounds were enantiotropic liquid crystals.

3ABA, 4ABA and 5ABA showed similar mesomorphic properties; they exhibited only a nematic phase characterised by the formation of small droplet textures, followed, on further cooling, by the formation of schlieren textures (Figure 2(a)). In contrast, 7ABA exhibited both enantiotropic nematic (Figure 2(b)) and smectic (Figure 2(c)) properties, which implies a significant effect of the length of the alkyl chain on the mesomorphic properties. For the *n*AOBA series, both enantiotropic smectic (Figure 2(d)) and nematic (Figure 2(e)) properties were observed in all samples.

The smectic phases of 7ABA and 6AOBA were further studied by temperature-dependant XRD to confirm their smectic A (SmA) natures as well as to

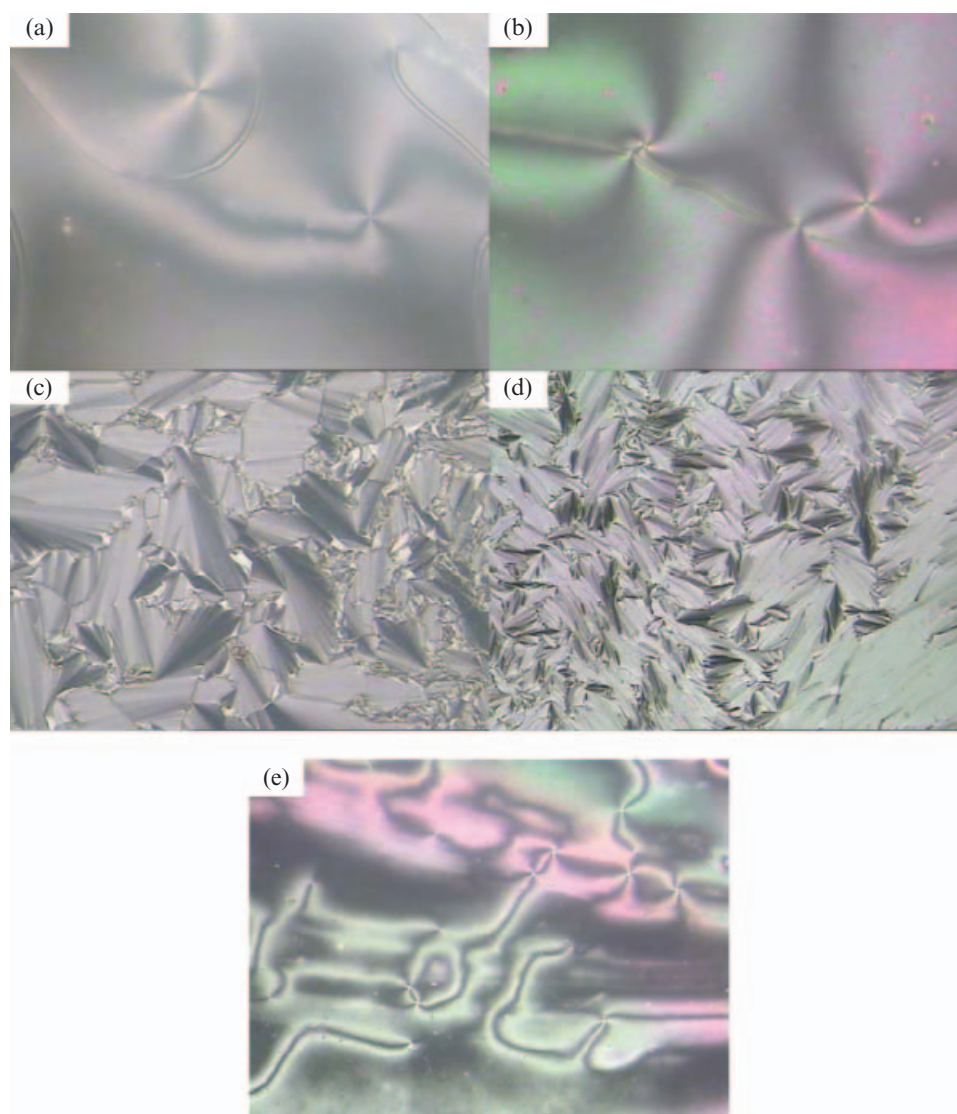


Figure 2. Optical textures of typical target compounds on cooling: (a) 5ABA, schlieren textures at 288°C; (b) 7ABA, schlieren textures at 254°C; (c) 7ABA, fan-shaped textures at 158°C; (d) 6AOBA, fan-shaped textures at 197°C; (e) 6AOBA, schlieren textures at 330°C.

Table 1. XRD results for 7ABA and 6AOBA. The parameter d is the smectic layer thickness and L is the molecular length estimated from Dreiding stereomodels for a fully extended conformation.

Compound	Temperature/°C	Phase	d /nm	L /nm
7ABA	162	SmA	42.1	45.7
6OABA	178	SmA	41.2	45.4

determine the layer spacing at the operating time on cooling. The XRD patterns of both compounds contain a single sharp maximum at small angles, due to the reflection of X-rays on the smectic layers, and a diffuse broad scattering peak at large angles, related to the liquid-like packing inside the layers. From Bragg's law, the layer spacing d in the smectic structure was calculated, and the values determined for this parameter are listed in Table 1 for 7ABA and 6AOBA, together with the length, L , of the molecules in their fully extended conformation, as measured using Dreiding stereo models.

It can be seen from Table 1 that for both compounds the measured layer thickness d is slightly smaller than the calculated molecular length L , which confirms that the smectic phase has a structure involving vertical molecules. The above-mentioned diffuse and broad peaks at large angles that arise from short-range order within the smectic layer provided estimates of the mean intermolecular distance by using the Bragg's law. The two distances were about 0.44 nm for 7ABA and about 0.46 nm for 6AOBA, which are typical values for a calamitic mesophase. This means that there is no regular intermolecular distance inside the layers, which also confirmed their SmA phase (17).

Table 2. Phase transition temperatures (°C) and associated enthalpy changes (in parentheses, J g^{-1}) of the target compounds (Cr, SmA, N and I indicate crystal, smectic A, nematic and isotropic phases, respectively).

Compound	Phase transitions
3ABA	Cr 196.6 (45.98) N 311.7 (4.94) I
4ABA	Cr 186.1 (44.66) N 323.0 (5.34) I
5ABA	Cr 180.3 (57.30) N 328.8 (5.17) I
7ABA	Cr ₁ 140.6 (6.15) Cr ₂ 151.5 (49.45) SmA 178.1 (2.19) N 310.6 (5.53) I
2AOBA	Cr 232.7 (63.94) SmA 325.6 (0.25) N 346.9 (3.41) I
3AOBA	Cr 214.9 (70.02) SmA 324.6 (0.10) N 343.9 (2.53) I
4AOBA	Cr 199.0 (38.43) SmA 300.8 (0.08) N 335.5 (3.27) I
5AOBA	Cr 186.7 (62.57) SmA 322.7 (0.13) N 342.7 (2.90) I
6AOBA	Cr 169.4 (52.06) SmA 324.4 (0.22) N 333.7 (2.85) I

DSC studies revealed that traces of most target compounds in cooling cycle exhibited no distinct exothermic peaks due to partial decomposition (the decomposition was confirmed by TGA at a scanning rate of $10^\circ\text{C min}^{-1}$ in an argon atmosphere; see Figure 3). Details of transition temperatures and associated enthalpy changes of both series, as determined by DSC, are summarised in Table 2, together with their phase variants, as determined by POM and XRD.

Table 2 reveals that most of the target compounds exhibited a clearing point temperature higher than 320°C and broad thermal range of mesophase (for example, the thermal range of nematic phase of 5ABA exceeds 150°C and that of the mesophase of 6AOBA exceeds 164°C). In n ABA series, members with propyl, butyl and pentyl end groups had only crystal–nematic and nematic–isotropic transitions and their clearing points increased and melting point decreased with an

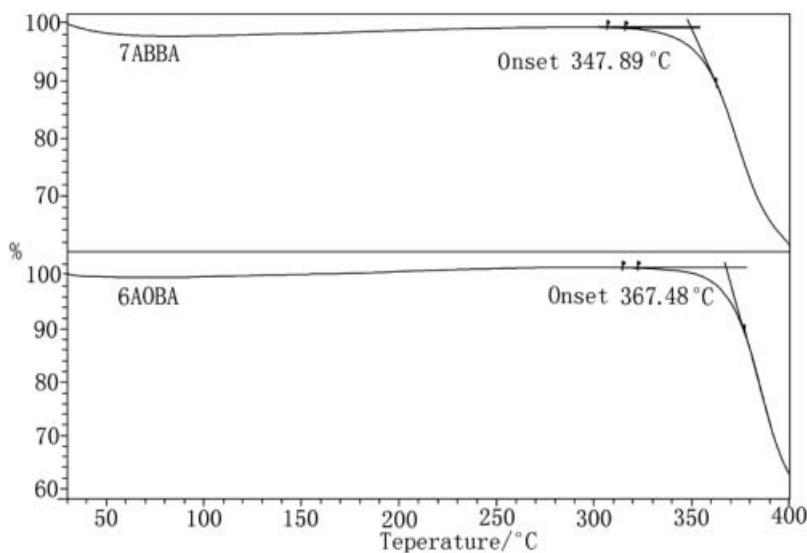


Figure 3. TGA curves of typical target compounds.

increase of the alkyl chains. In contrast, 7ABA exhibited an additional smectic–nematic transition, indicating the existence of a smectic phase. For the *n*AOBA series, all members showed similar mesomorphic properties. They all exhibited both smectic and nematic phases, which indicates the leading role of the rigid mesogenic core structure in shaping their mesomorphic properties. Their melting point temperatures decreased with the length of their alkoxy chains, as in the *n*ABA series, but their clearing point temperatures showed no distinct regularity. When comparing *n*ABA with their corresponding *n*AOBA, it was found that the melting point and clearing point temperature of *n*ABA were always lower than their corresponding compounds in the *n*AOBA series.

4. Conclusion

We have successfully synthesised and characterised two series of azine-type liquid crystals. It was found that 3ABA, 4ABA and 5ABA exhibit only a nematic phase, whereas 7ABA showed both SmA and nematic properties. All members of the *n*AOBA series exhibited SmA and nematic properties. Additionally, when comparing *n*ABA with their corresponding *n*AOBA of same length of end group, it was found that the melting point and clearing point temperature of *n*ABA were always lower than their corresponding compounds in the *n*AOBA series. These results indicate that the alkoxy end groups are of benefit for the formation and stability of the smectic phase of these compounds.

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