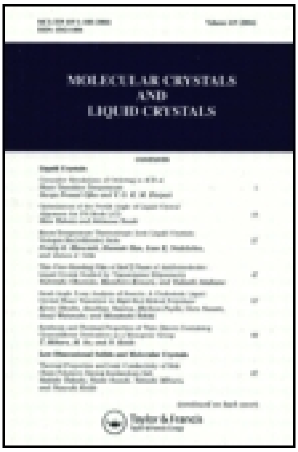

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DSC and POM Study of New Thermotropic Unsymmetrical Azomethines Derived from 4-Octadecyloxybenzaldehyde

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New thermotropic liquid crystals containing long octadecyloxy chain, one mesogen (Schiff base) and different functional end-groups such as biphenyl-4-carbonitrile, ethylcarbazole, 4-phenoxy, or 4-(heptadecafluoroctyl) were synthesized via an one-step route. Transition temperatures and phase characterization were studied by differential scanning calorimetry (DSC) and polarizing optical microscope (POM) techniques. The amine had an effect on the mesomorphic properties of the azomethines. As a result of DSC and POM investigations it was shown that liquid-crystalline properties of the azomethines exhibit a strong dependence of the end-groups. Based on the POM and DSC measurements the following mesophases were detected: smectic A, smectic B, and smectic G. In this article, we will present characterization of the liquid-crystalline azomethines of great interest for the emerging field of molecular electronics.

Keywords Azomethines; mesomorphic properties; Schiff bases; smectic mesophases; thermotropic properties

Introduction

Azomethines (Schiff bases) belong to the classic type of molecules with liquid-crystalline (LC) properties. 4-Methoxybenzylidene-4′-butylaniline was the first azomethine that exhibit the nematic phase at room temperature (Cr 22°C N 47°C I) [1]. In the present time the scientists investigated LC behavior of the azomethines and polyazomethines [2–4]. Moreover, many papers are dedicated to the polyazomethines or symmetrical azomethines [2,4]. On the other hand, less attention is paid to the mesomorphic behavior of the unsymmetrical azomethines with one azomethine bond. For example, Godzwon *et al.* [5] investigated smectic polymorphism of 4-nonyloxybenzylidene-4′-alkyloxyanilines based on polarizing optical microscope (POM), thermo-optic experiments (TOA), and differential scanning calorimetry (DSC) techniques. Smith *et al.* [6] obtained the azomethines based on

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Address correspondence to Dr. Agnieszka Iwan, Electrotechnical Institute, Division of Electrotechnology and Materials Science, M. Sklodowskiej-Curie 55/61 Street, 50-369 Wroclaw, Poland. E-mail: a.iwan@iel.wroc.pl fluorinated carbon chains that exhibit nematic and smectic A phase transitions. A new traceless linker was developed by Hioki *et al.* [7] to synthesize a library of 42 azomethines with one azomethine bond and different terminal groups by using combinatorial solid-phase parallel synthesis, these azomethines exhibit smectic mesomorphism. Narasimhaswamy *et al.* [8] synthesized novel thermotropic LC containing a terminal dimethylamino group and additionally one ester and one azomethine group, and an enantiotropic nematic phase was detected for all compounds. New amido-ether Schiff bases were investigated by Stamatoiu *et al.* [9], but only the 2,4-substituted azomethines show, LC behavior (nematic phase). Very interesting unsymmetrical azomethines in which an achiral bent-core is covalently tethered to a bulky chiral rod-like mesogen through an odd-even parity alkylene spacer were obtained by Yelamaggad *et al.* [10]. Blue phase and smectic fluids were observed for the chiral bent-rod imines [10]. Eran *et al.* [11] investigated thermotrophic properties of a new chiral salicylaldimine compound. The compound exhibits the chiral smectic C mesophase. Chiral Schiff bases derived from cholesterol were investigated also by Majumdar *et al.* [12]. They found that the compounds show a smectic A phase and/or a chiral nematic phase or an unknown mesophase. Thermotropic properties of 4-hexyl-N-(4-hexadecyloxysalicylidene)aniline were investigated by Nesrullajev *et al.* [13] and a Sm C mesophase was found.

Studies reported here investigate four unsymmetrical azomethines with a long octadecyloxy aliphatic chain and different functional end-groups. The molecular structures of the title compounds were characterized by proton and carbon nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) techniques and by elemental analysis. Their liquid crystal properties were investigated by DSC and POM. To the best of our knowledge the LC behavior of the unsymmetrical azomethines with biphenyl-4-carbonitrile, ethylcarbazole, 4-phenoxy, or 4-(heptadecafluoroctyl) have not been investigated so far.

Experimental

Materials

Acetone (POCh), ethanol (POCh), N,N-dimethylacetamide (DMA) (Aldrich), and 4-octadecyloxybenzaldehyde (TCI), 4′-aminobiphenyl-4-carbonitrile (Aldrich), 3-amino-9-ethylcarbazole (Aldrich), 4-phenoxyaniline (Aldrich), and 4-(heptadecafluoroctyl)aniline (Fluka) were used without any purification.

General Synthetic Procedure of the A1–A5

A mixture of 4-octadecyloxybenzaldehyde (1.0 mmol) and amine (1.0 mmol) in N,N-dimethylacetamide (DMA) solution, with the presence of *p*-toluenesulfonic acid (PTS) (0.06 g) was refluxed with stirring for 10 h. After cooling, the mixture was precipitated with 50 mL of methanol. The crude product was washed three times with methanol (3 × 500 mL) and twice with acetone (2 × 350 mL) to remove unreacted monomers. Then the compound was dried at 60°C under vacuum for 12 h.

Azomethines yields were in the range of 84–88% in dependence on the amine structures. The compounds were soluble at room temperature in chloroform ($CHCl_3$), tetrahydrofuran (THF), N,N-dimethylacetamide (DMA), hexamethylphosphoramide (HMPA). These azomethines were characterized by various spectroscopic methods; *e.g.*, proton and carbon NMR ($CDCl_3$), and elemental analysis. The proposed structures are in full agreement with these spectroscopic data. In particular the signal in the range 158–161 ppm, present in the ^{13}C NMR spectra of the compounds, confirms the existence of the azomethine group. The changes in the chemical shift, observed upon the modification of the chemical constitution of the amine, are clearly observed. For example, in the case of A1 and A2, the presence of carbonitrie group or carbazole unit results in an up-field shift of the line related to the azomethine carbon atom in comparison with A3 and A4.

In proton NMR spectra of the investigated compounds the imine proton signal in the range 8.36–8.57 ppm was observed. For example, in the azomethhines A1 and A3 the signal from the imine group at 8.42 ppm was observed, and the presence of the fluorooctyl chain in A4 caused significant up-field shift of the imine proton signals to 8.36. In the case of A2, the presence of the carbazol unit results in a down-field shift of the line related to imine proton in comparison with another azomethines. Up-field shift of the imine signals indicates less conjugation of the compound chain.

The structural formulas of the unsymmetrical azomethines are presented in Fig. 1.

Methods

All synthesized compounds were characterized by ^{1}H, ^{13}C NMR, and elemental analysis. The phase transitions and mesogenicity were studied by DSC and POM. DSC was measured on a TA-DSC 2010 apparatus (TA Instruments, New Castle, DE) using sealed aluminium pans under nitrogen atmosphere at a heating/cooling

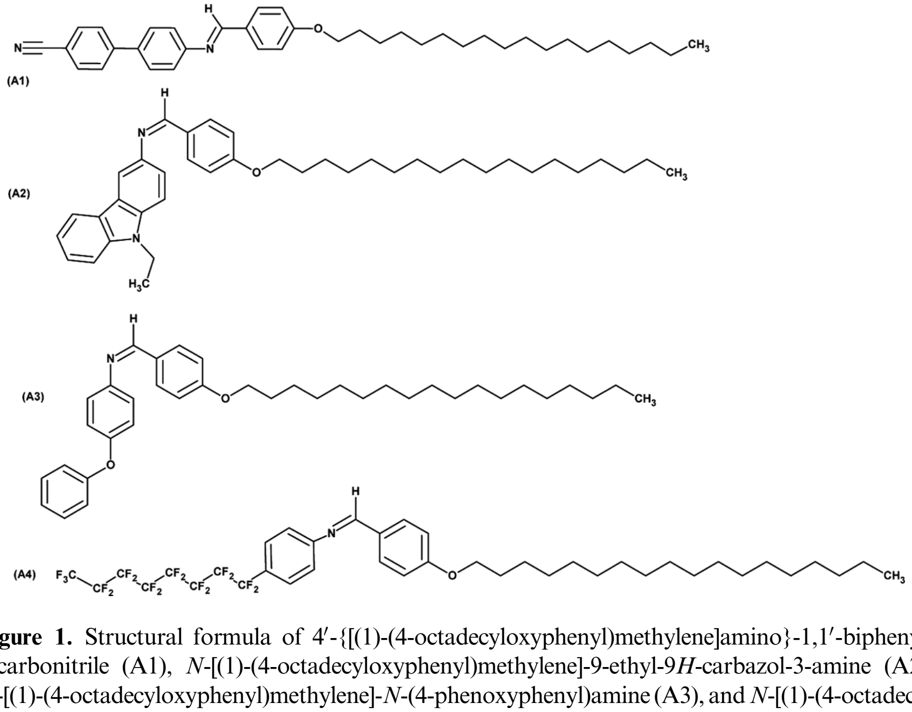


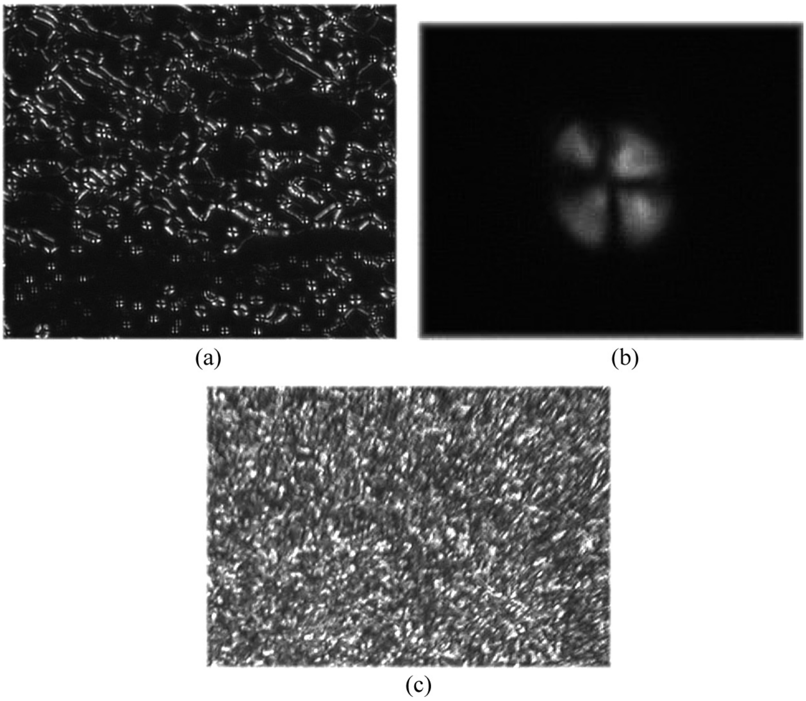
Figure 1. Structural formula of 4′-{[(1)-(4-octadecyloxyphenyl)methylene]amino}-1,1′-biphenyl-4-carbonitrile (A1), *N*-[(1)-(4-octadecyloxyphenyl)methylene]-9-ethyl-9*H*-carbazol-3-amine (A2), *N*-[(1)-(4-octadecyloxyphenyl)methylene]-*N*-(4-phenoxyphenyl)amine (A3), and *N*-[(1)-(4-octadecyloxyphenyl)methylene]-*N*-[4-(4,4,4-trifluorooctyl)phenyl]amine (A4) liquid-crystalline compounds.

rate 0.5°C/min in a temperature range from −20°C to over the clearing point. The textures of the liquid-crystalline phase were observed with POM.

Results and Discussion

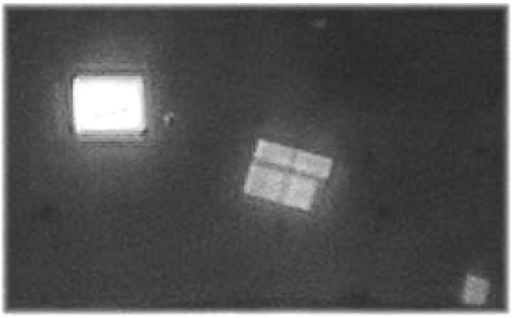
Investigations by DSC and POM showed that all compounds exhibit only one liquid-crystalline mesophase. The POM and DSC observations revealed that all of the compounds exhibit enantiotropic liquid crystal phases. The investigations by POM show that the compound A1 during a cooling scan exhibited the following thermal scenario: full isotropization (ISO) at 215.0°C, SmA at 210.0°C, and crystallization at 86°C (growth of spherulites). Only for this azomethine we found a Tg at about 40°C. During a heating scan the following thermal scenario was found: Tg at 35–40°C, mp at 94.0°C, and full ISO at 215.0°C.

By POM, only textures typical of the SmA mesophase of A1 were observed. More particularly, we observed the typical "oily streaks" textures and homeotropically aligned (with a few defects) were found. On heating scans we always saw a change from a majority of the surface of the sample studied covered by an oily streaks texture to a majority of the surface of the sample studied covered by an homeotropically aligned (black) texture at 150°C. On cooling scans, the homoetropically aligned (black) texture of SmA mesophase, which appeared at 210°C, was invariably the only texture of SmA mesophase of A1 observed. In Fig. 2 POM

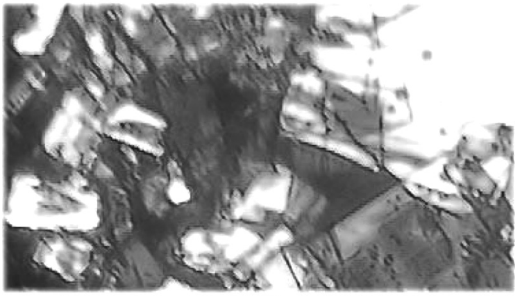

(a) (b)

(c)

Figure 2. (a) POM pictures of the planar texture (oily streaks) of the SmA mesophase of A1 (at 100°C) taken during a heating scan. (b) POM picture of the homeotropically aligned (black) texture of the SmA mesophase (at 100°C) with one defect taken during a cooling scan. (c) Texture of smectic A mesophase of A4.



(a)



(b)

Figure 3. Photomicrographs of the optical textures of mesophase obtained for A2.

pictures of the planar texture of SmA mesophase of A1 (at 100°C) taken during a heating scan (Fig. 2a) and a POM picture of the homeotropically aligned (black) texture of the SmA mesophase (at 100°C) with one defect taken during a cooling scan (Fig. 2b) are presented.

By POM the smectic A mesophase was also observed for the azomethine A4 with perfluorinated chain (Fig. 2c). The investigations by POM show that during a cooling scan compound A4 exhibited the full isotropization at 89.7°C and the

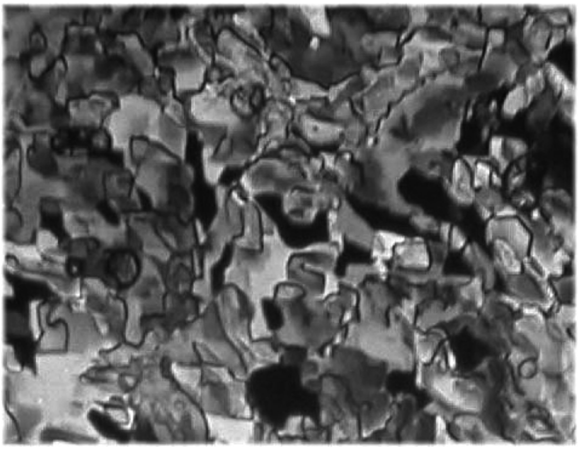
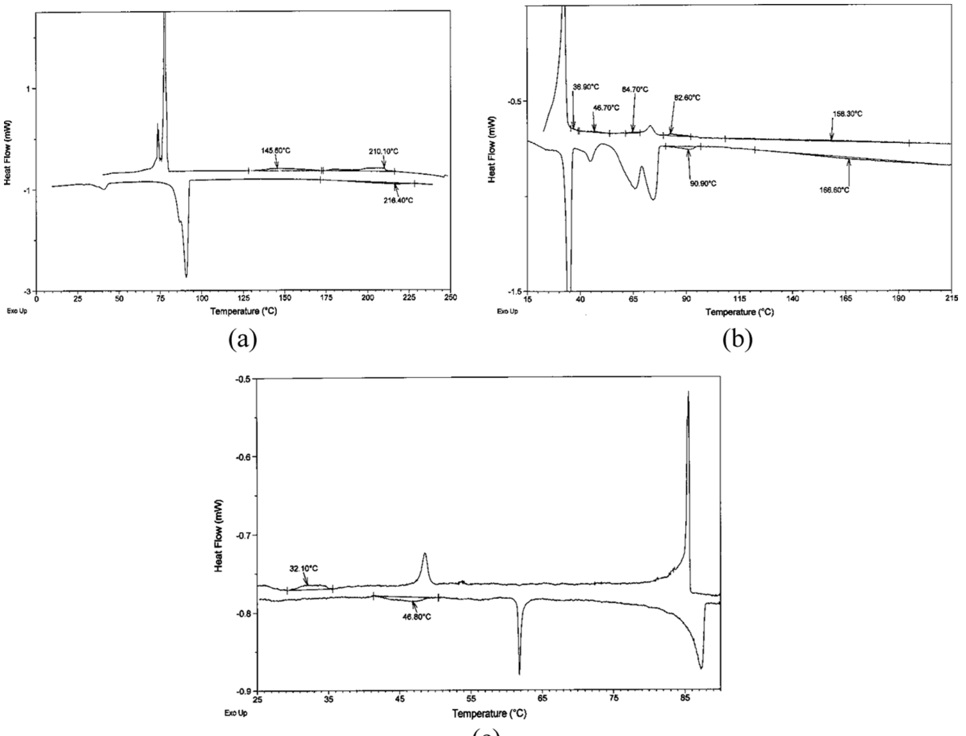


Figure 4. Photomicrograph of the optical texture of mesophase obtained for A3 (at 101°C).



(a) (b)

(c)

Figure 5. DSC traces of the azomethines at a heating/cooling rate of 1°C/min. (a) A1, (b) A2, (c) A4.

SmA phase from 89.4°C to 87.4°C. During a heating scan the same scenario was found. The smectic A phase of A4 shows a sanded texture as shown in Fig. 2c.

In the POM study, the compound A2 exhibited stable enantiotropic smectic B (SmB) liquid crystal phase (Fig. 3). Hexatic liquid crystal phases, such as the orthogonal SmB phase, often exhibit a mosaic-like appearance.

The compound A3 exhibits stable smectic G (SmG) liquid crystal phase (Fig. 4). Higher ordered, or so-called crystalline smectic or soft crystal phases, generally show

Table 1. Thermal parameters of the azomethines determined by DSC

	Phase transition behavior, detected by DSC	
	Phase transitions (°C) (corresponding enthalpy changes) (J/g)	
Code	Heating	Cooling
A1	40.9 (7.1), 90.7 (92.1), 216.4 (6.2)	210.1 (20.4), 145.6, 77.9 (88.2)
A2	34.6 (24.9), 44.8 (3.2), 65.6, 74.4 (32.7), 90.9 (1.2), 166.6 (2.5)	158.3 (1.7), 82.6 (0.9), 73.0 (2.7), 64.7, 46.7, 36.9, 32.4 (41.2)
A3	32.9 (4.8), 107.7 (134.7)	102.6 (110.3), 94.5 (4.8), 40.0 (1.7), 29.6 (3.9)
A4	46.8 (6.0), 61.8, (12.1), 87.3 (46.1)	32.1 (4.7), 48.6 (9.9), 85.6 (46.4)

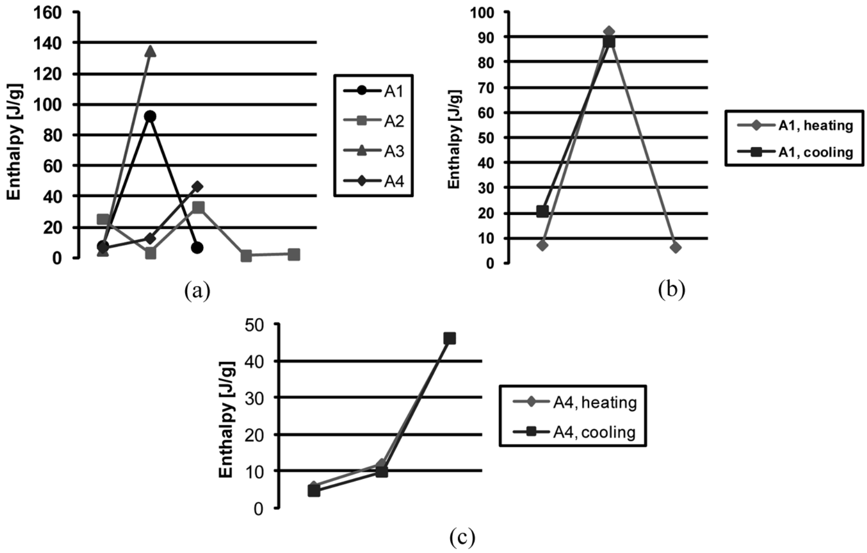


Figure 6. Influence of the amine structure on the enthalpy of the azomethines during (a) heating and (b, c) heating and cooling process of A1 and A4, respectively.

a mosaic texture. A smectic mesophase, as detected by POM, was observed from 106°C to 108°C, this phase in likely to be a SmG but can only be distinguished by X-ray diffraction.

DSC thermograms of the compounds obtained on the second heating and the second cooling, at a heating and cooling rate 1°/min under N_2 atmosphere are presented in Fig. 5. Details of transition temperatures of the all compounds as determined by DSC are summarized in Table 1.

Table 1 reveals that the all compounds exhibit a clearing point temperature in the range 87–216°C and show different thermal ranges of the mesophase. For example, the thermal range of the Sm A phase of the A1 exceeds 125°C and that of the mesophase of A4 exceeds 25°C, whereas the thermal range of the Sm G phase of A3 exceeds only 2°C. For the investigated azomethines different mesomorphic properties were observed. This behavior indicates the role of the rigid mesogenic core structure in creating their mesomorphic properties.

The phase transitions were additionally analyzed based on their enthalpy values (Fig. 6). The melting process has the highest enthalpy values. The enthalpy values decrease from 92.1 J/mol K for A1 to the minimal value 4.8 J/mol K for A3. The parameters of the heating and cooling process are similar (Fig. 6).

All transitions of the azomethines observed by POM are in good agreement with the DSC analyses.

Conclusion

Four new unsymmetrical azomethines were synthesized and thermotropic properties of these compounds have been investigated. The compounds are monomorphic and exhibit an enantiotropic smectic liquid-crystalline mesophase, however, the type of mesophase is dependent on the amine moiety. The azomethines with a carbonitrile and a heptadecafluoroctyl group exhibit the smectic A mesophase, whereas the compound with an ethylcarbazole group shows the smectic B phase. The azomethine with a phenoxy group exhibits the smectic G phase. It should be mentioned that such LC compounds that exhibit a mesophase over a broad or short temperature range could be used in: (i) color information technology-based applications for thermally stable glassy derived from cholesterol LC molecules (realize rewritable full-color recording in a thermal and photon mode) and (ii) organic electronic devices (organic light-emitting devices, organic solar cells). Obtained compounds could be utilized in devices for which operating temperature is much higher than room temperature. Moreover, such types of LC compounds have been used in mixtures with other LCs for LC displays. Particularly important are twisted nematic (TN) cells, which rely on calamitic mesogens and usually exhibit high clearing temperatures.

Acknowledgments

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