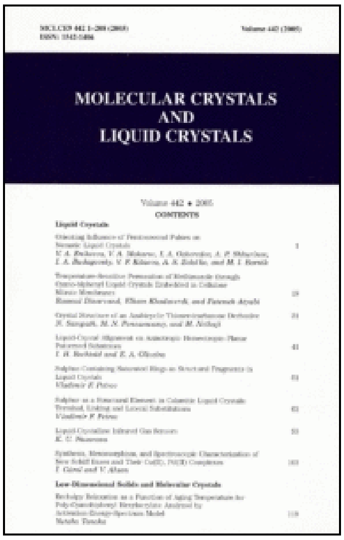

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Characterisation and Mesomorphic Behavior of Rod-Shaped Unsymmetrical Imine with a Fluorinated Chain and a Carboxylic Group

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The synthesis and thermal properties of unsymmetrical imine with a fluorinated chain and a carboxylic group are described. The mesomorphic behavior was investigated via differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) studies. Additionally, we compared the mesomorphic behavior of the azomethine presented in this work with other azomethines.

Keywords Azomethines; fluoro compounds; imines; mesomorphic behavior; Schiff bases

Introduction

Liquid crystals (LCs) composed of rod-shaped molecules are still widely investigated [1–22]. Among the large group of liquid-crystalline compounds imines with a fluorinated chain are the subject of this investigation. Surprisingly, literature data concerning LC properties of imines with a fluorinated chain (also called *azomethines* or *Schiff bases*) are rather scarce [8,19]. Unsymmetrical imines with a perfluorinated chain were investigated by Bilgin-Eran *et al.* [8] and Iwan *et al.* [19]. Bilgin-Eran *et al.* [8] found that the thermal behavior of the semiperfluorinated imines depends on the length of the chain, the substitution pattern, and the number of fluorine atoms in the fluoroalkyl chains. Along with increasing the number of F atoms in the fluoroalkyl chains, stabilization of smectic and columnar mesophases was observed [8]. We recently reported the synthesis, characterization, and mesomorphic properties of unsymmetrical imines based on 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)-benzaldehyde [19], and enantiotropic smectic phases were observed for all the systems studied.

Studies reported here investigate synthesis and thermal characterization of usymmetrical rod-shaped imine with a long alkoxysemiperfluorinated chain (-O-$(CH_2)_3$-$(CF_2)_7$-CF_3) derived from an aldehyde and a carboxylic group (COOH) derived from an amine. The liquid-crystal properties of the imine were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy

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(POM). The investigated compound has not been described previously and shows the mesophase behavior. These imine Az could be used as a monomer to syntheze various imines with ester groups (-O-CO-) from the reaction of the COOH group of the imine with a hydroxyl group (OH) of a different type of compounds.

It should be mentioned that such LC compounds that exhibit a mesophase or a sequence of mesophases over a broad temperature range could be used in (i) color information technology [22] for thermally stable glassy derived from cholesterol LC molecules and (ii) organic electronic devices (organic light-emitting devices, organic solar cells). The obtained compounds could be utilized in devices with an operating temperature 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.

Experimental

Materials

All starting chemicals were used as purchased without any purification.

Characterization Techniques

All compounds were characterized by proton and carbon nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. NMR was recorded on a Bruker AC 200 MHz. Chloroform-*d* ($CDCl_3$) containing tetramethylsilane (TMS) as an internal standard was used as solvent. Elemental analyses (C, H, N) were carried out on a 240 C Perkin-Elmer analyzer.

The phase transitions and mesogenicity were studied by DSC and POM observations. DSC were measured on a TA-DSC 2010 apparatus (TA Instruments) using sealed aluminum pans under nitrogen atmosphere at different heating/cooling cycles. The textures of the liquid-crystaline phase were observed with a polarized optical microscope (POM) Zeiss (Opton-Axioplan) equipped with a Nikon Coolpix 4500 color digital camera, and Mettler FP82 hot plate with Mettler FP80 temperature controller.

Synthetic Procedure of Imine Az

A mixture of 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)-benzaldehyde (1.0 mmol) and 4-aminobenzoic acid (1.3 mmol) in N,N-dimethylacetamide (DMA) solution in the presence of *p*-toluenesulfonic acid (PTS) (0.06 g) was refluxed with stirring for 12 h. The reaction was conducted in an argon atmosphere. After cooling, the mixture was precipitated with 100 mL of ethanol. The crude product was washed three times with methanol (3 × 500 mL) to remove unreacted compounds. Then the compound was dried at 70°C under vacuum for 12 h.

Yield: 80%; ^{1}H NMR (200 MHz, DMSO-d_6, TMS) [ppm]: δ 9.87 (s, 1H, COOH); 8.53 (s, 1H, CH=N–); 7.86–7.97 (m, 4H, H_{Ar}), 7.06–7.09 (d, 2H, H_{Ar}); 7.24–7.27 (d, 2H, H_{Ar}); 4.17–4.21 (m, 2H, CH_2–O); 2.47 (m, 2H, CH_2-CH_2-CH_2-CF_2); 2.01–2.06 (m, 2H, CH_2-CF_2). ^{13}C NMR (50 MHz, DMSO-d_6, TMS) [ppm]: δ 190.58 (COOH), 166.94, 166.55 (HC=N), 162.91, 160.99, 160.67, 155.36, 152.61, 131.27, 130.71, 130.36, 130.11, 129.69, 128.68, 127.44, 120.37, 114.69, 114.61, 112.36, 66.27, 66.09, 26.96, 26.63, 26.35, 19.69. Anal. Calcd: C, 42.80%; H, 2.28%; N, 2.00%. Found: C, 42.50%; H, 2.30%; N, 1.87%. UV-vis (THF, nm): 294, 334.

Results and Discussion

The structure of the imine **Az** along with the synthetic route is depicted in Fig. 1, whereas the principle spectroscopic and molecular characteristics are provided in the Experimental section. The reaction between 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde and 4-aminobenzoic acid in DMA at 160°C gave the imine **Az**. The compound was characterized by ^{1}H and ^{13}C NMR spectroscopy and additionally by elemental analysis. The spectral data were in accordance with the expected formula. A one-proton singlet at about $\delta = 8.53$ ppm showed the formation of the imine. In the carbon NMR spectrum the signals at $\delta = 166.94$, 166.55 ppm confirm the existence of the azomethine group carbon atoms. In the case of the imine structure, two isomers are possible (*E* and *Z*), even though the *Z* (trans) structure is always supposed to be thermodynamically more stable. A splitting of the signals in ^{13}C NMR spectrum seems to confirm the coexistence of the isomers. ^{1}H and ^{13}C NMR spectra of the **Az** are presented in Fig. 2. Elemental analysis showed good agreement of the calculated and found contents of carbon, nitrogen, and hydrogen atoms in the **Az**.

The UV-vis absorbance spectrum of the azomethine in solution (THF) displayed two absorption maxima at 294 and 334 nm (4.22 and 3.71 eV). The former band can be assigned to the π-π^* transition, whereas the second band is characteristic of

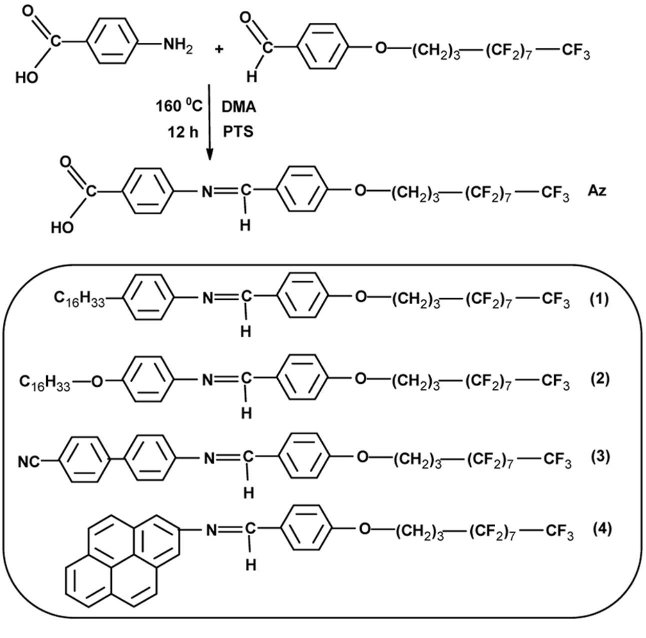
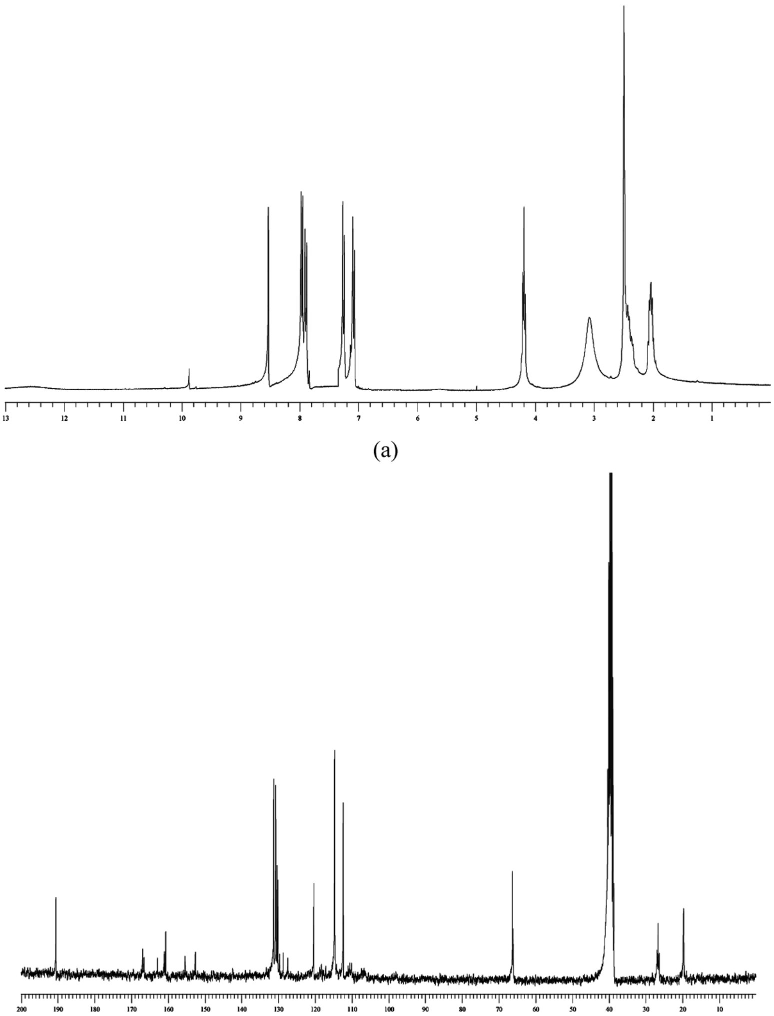


Figure 1. Synthetic route of the imine **Az** and chemical structure of the selected azomethines with different type of side groups.



(a)

(b)

Figure 2. ^{1}H (a) and ^{13}C (b) NMR spectra of **Az** in DMSO-d_6 solution.

the imine group in **Az** and its position and intensity are dependent on the chemical constitution of the compound [19].

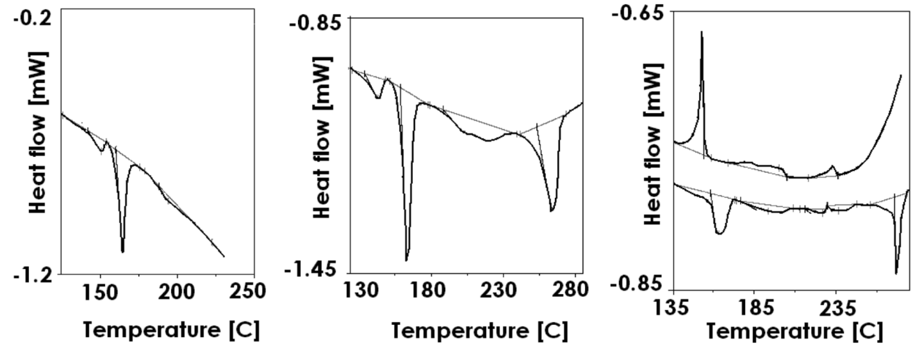
The transition temperatures and enthalpies of the **Az** determined by DSC are presented in Table 1. The compound **Az** was investigated by DSC during different heating cycles, that is, 10°C/min, 4°C/min and 2°C/min. Upon DSC analysis the **Az** exhibited three enantiotropic transitions such as crystal to mesophase (Cr/M), mesophase to mesophase (M/M) and mesophase to isotropic state (M/I). DSC thermographs of the Az during heating at 10°C/min showed double peaks with maxima at 150.42°C ($\Delta H = 3.28$ J/g) and 164.32°C ($\Delta H = 15.87$ J/g) and a small endotherm at 194.34°C ($\Delta H = 1.63$ J/g). During heating of the **Az** at 4°C/min two peaks at 143.48°C (3.39 J/g) and 163.90°C ($\Delta H = 18.63$ J/g) along with a broad endotherm with two not well-separated peaks at 204.66°C and 217.16°C ($\Delta H = 9.28$ J/g) were found. Additionally, isotropization at 265.19°C ($\Delta H = 18.34$ J/g) was observed.

Table 1. Transition temperatures and enthalpies of the azomethines detected by DSC along with POM observations

Heating	Cooling	Ref.
Phase transitions (°C) (corresponding enthalpy changes) (J/g), DSC		
Az^a: 163.49 (4.54), 193.78 (1.39), 226.80 (0.25), 236.38 (0.72), 271.46 (4.09)	153.62 (4.30), 183.21 (1.62), 232.63 (0.67), 270.52 (4.02)	This work
(1): 108.3 (15.08), 128.9 (2.68), 131.9 (13.00)	106.9 (14.55), 128.7 (2.62), 131.5 (12.70)	[19]
(2): 109.0 (138.84), 111.3 (0.22), 113.9 (10.17), 142.1 (15.17)	105.9 (13.01), 110.3 (0.1), 113.2 (10.59), 141.2 (15.2)	[19]
(3): 135.0 (33.55), 309.7 (11.50)	106.9 (23.71), 309.9 (7.00)	[19]
(4): 106.1 (22.52), 250.3 (4.78)	46.9 (7.69), 56.1 (1.60), 250.2 (4.69)	[19]
Phase transitions (°C), POM, cooling		
Az: Cr, 162.5 Sm, 168 N, 275 I		This work
(1): Cr 107, Sm C 129, Sm A 131, I		[19]
(2): Cr 106, Sm X2 110, Sm X1 113, Sm C 140, I		[19]
(3): Cr 110, Sm C 130, Sm A 320, I		[19]
(4): Cr 107, Sm A 253, I		[19]

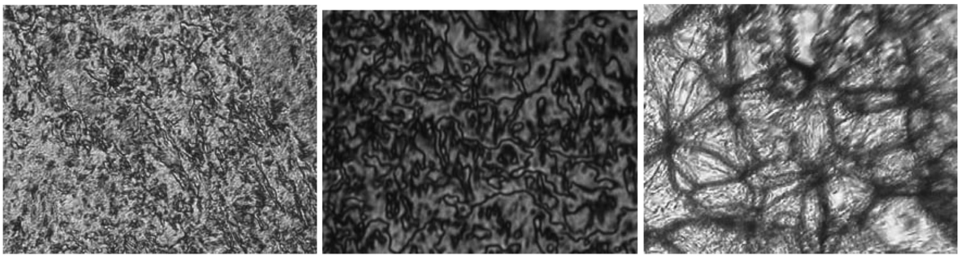
Cr, Sm, and I indicate crystal, smectic, and isotropic phases, respectively.
^{a}2°C/min rate of heating and cooling.

During the heating of the sample with 2°C/min three small peaks were found with the enthalpies 1.39, 0.25, and 0.72 J/g (Table 1). Compound **Az** showed a liquid crystal to isotropic transition at 271.46°C with a $\Delta H = 4.09$ J/g during heating. During heating of sample with 2°C/min, two not well-separated peaks observed during heating of **Az** with 4°C/min were separated and were found at 193.78°C and 226.80°C. During cooling of the sample with 2°C/min one exotherm at 153.62°C along with two small peaks appeared at 183.21°C and 232.63°C, with



(a) (b) (c)

Figure 3. DSC traces of the **Az** obtained during (a) heating rate 10°C/min, (b) 4°C/min and (c) heating and cooling rate 2°C/min under N_2 atmosphere.



(a) (b) (c)

Figure 4. Photomicrographs of the optical textures of mesophases obtained for **Az**: (a) SmX, Schlieren and sharkskin texture (seen at 195°C), (b) nematic (seen at 250°C), and (c) SmX1 (seen at 190°C).

the enthalpy values at 1.62 and 0.67 J/g were detected. DSC thermograms of **Az** are shown in Fig. 3.

In our opinion **Az** exhibited three mesophases, probably two smectic with Schlieren and sharkskin texture and nematic mesophase (Fig. 4). A tentative scenario of phase transitions for the LC behavior of **Az** detected by POM are presented in Table 1. The microphotographs of the smectic and nematic phases obtained for the compound **Az** are shown in Fig. 4.

To show the influence of the amine on the mesomorphic properties of the imines with a perfluorinated chain in Fig. 1 we presented the structure of the responsible azomethines that were the subject of our previously work [19], and in the Table 1 the thermal characteristics of the compounds are shown. Taking into consideration the temperature of isotropization, the following scenario was observed: 132°C (1) >141°C (2), 250°C (4) >270°C (**Az**) and 310°C (3). It was a surprise that introduction the carboxylic group as in the case of (**Az**) influenced on increase of the temperature of isotropization in comparison with imines (1)–(3). On the contrary, the presence of cyjano group as in the case of (3) influenced on increase of the temperature of isotropization in comparison with **Az**. Different amines used in the synthesis of the azomethines influenced on the kind of mesophases (Table 1). Imines (1)–(4) exhibit smectic mesophases, whereas compound **Az** additionally, exhibites a nematic mesophase.

Conclusions

In conclusion, a new unsymmetrical imine with one fluorinated chain and a carboxylic group was synthesized and investigated by proton and carbon NMR spectroscopy, elemental analyses and additionally by DSC and POM measurements. The compound probably exhibited two smectic mesophases and a nematic mesophase. Additionally, synthesis and investigation of new mesogens is one of the important and interesting fields for the materials research community.

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