Liquid-crystalline properties of 4-octyloxybenzylidene-4′-alkyloxyanilines and their mixtures with 4-pentyloxybenzylidene-4′-heptylaniline

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ABSTRACT

Liquid-crystalline properties of the homologous series of 4-octyloxybenzylidene-4′-alkyloxyanilines are described. Based on the polarization microscopy (POM and TOA methods) and the calorimetric (DSC) measurements a rich polymorphism was detected. Investigated compounds exhibit nematic, smectic C, smectic I and smectic G mesophases with their characteristic configurations. The presence of all mesophases was confirmed by the miscibility method, using 4-heptyloxybenzilidene-4′-pentylaniline (I), 4-octyl-4′-decyloxyazobenzene (II) and 4-octyl-4′-undecyloxyazobenzene (III) as the mesophase standards. The influence of an alkyl chain length on the mesophase sequence and the entropic effects are extensively discussed.

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1. Introduction

Schiff bases are one of the oldest groups of liquid crystals. Derivatives with the short alkyl chains (methyl and ethyl groups) were already synthesized at the beginning of the XX century. Only the nematic mesophase was detected among these derivatives. Since the 1970s the series of 4-alkyloxybenzylidene-4′-alkylanilines, showing very rich polymorphism, were extensively investigated. This type of compound is especially important, because they are acclaimed as the mesophase standards. Even hexamorphism of GBICAN type, meaning according to Demus and Richter [1], the presence of the six different mesophases, was found in the 4-pentyloxybenzylide-4′-decylaniline.

Properties similar to those mentioned above were expected in the group of 4-alkyloxybenzylidene-4′-alkyloxyanilines, which was investigated since the 1960s. However, only derivatives with short alkyl chains were synthesized and their mesophases were not assigned.

Recently, we published detailed investigations, with the special attention devoted to the proper recognition of the smectic phases, of the following series of Schiff bases: 4-decyloxybenzylidene- [2], 4-dodecyloxybenzylidene- [3], 4-nonyloxybenzylidene- [4], 4-heptyloxybenzylidene- [5] and 4-hexyloxybenzylidene-4′-alkyloxyanilines [6].

This publication gives a detailed analysis of the mesomorphic behavior of the 4-octyloxybenzylidene-4′-alkyloxyanilines. Only derivatives with short alkyl chains (from ethyl to hexyl) and one with a longer chain (octyl) are described in literature. In 1938, Weygand and Gabler published for the first time an article describing 4-octyloxybenzylidene-4′-alkyloxyanilines [7]. They synthesized ethyl ($n = 2$) derivative, which exhibited only a nematic phase. Propyl ($n = 3$), butyl ($n = 4$) and pentyl ($n = 5$) derivatives were described in 1967 by Dave and Patel [8]. The propyl ($n = 3$) derivative showed only a nematic phase. The nematic and one unknown smectic phase were detected in butyl ($n = 4$) derivative. In the pentyl ($n = 5$) derivative the nematic and three unknown smectic phases were observed. Ten years later, in 1976 Malthête et al. [9] published an article describing butyl ($n = 4$) derivative, for which nematic and smectic A phases were recognized. In 1983, Gandolfo and Grasso [10] described pentyl ($n = 5$) and hexyl ($n = 6$) derivatives. They confirmed the presence of the nematic and three unknown smectic phases in the pentyl ($n = 5$) and the nematic with two unknown smectic phases in the hexyl ($n = 6$) derivative. In 1996, Buey et al. [11] reported the presence of the nematic and smectic C phases in the octyl ($n = 8$) derivative.

This paper describes the liquid-crystalline properties of the full homologous series of 11 derivatives of 4-octyloxybenzylidene-4′-alkyloxyanilines. Four of them are for the first time presented in
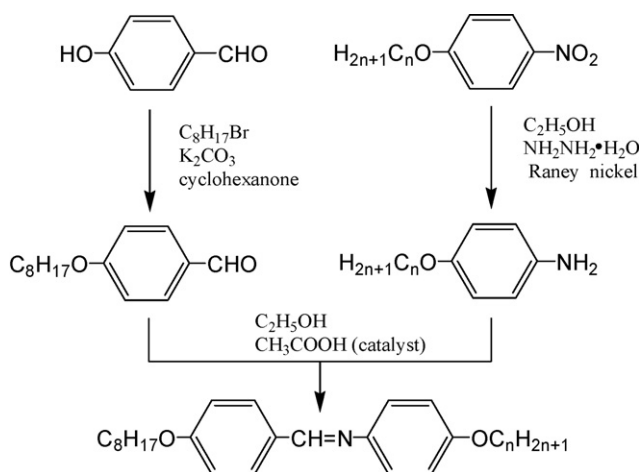
Scheme 1. Synthesis of 4-octyloxybenzylidene-4′-alkyloxyanilines (8-*n*).

literature (n = 7, 9, 10 and 12). The main aim of this work is a detailed description of the phase transition parameters based on polarizing microscopy and DSC calorimetry. The observed mesophases were confirmed by the miscibility Sackmann–Demus method [12]. The phase diagrams showing the induction of, unobserved in pure compounds, new mesophases are extensively discussed. The influence of the alkyl chain length on the temperature and entropy of phase transitions and the topology of a phase diagram are discussed.

2. Experimental

2.1. Synthesis

The synthesis of 4-octyloxybenzylidene-4′-alkyloxyanilines is outlined in Scheme 1. The detailed standard synthetic procedures are described elsewhere [13,14]. All final products were purified by chromatography on silica gel (Fluka 60 Mash) with chloroform as an eluent, followed by recrystallization from ethanol and heptane. The purity of all investigated compounds was confirmed by the elemental analysis (Table 1) with the error limit less than 0.3%.

2.2. Equipment

The phase transition parameters of all compounds were obtained by combining differential scanning calorimetry (DSC) and polarization optical microscopy (POM) results. DSC measurements were performed by using PerkinElmer DSC7 set-up. Typical heating

Table 1
Elemental analysis of 4-octyloxybenzylidene-4′-alkyloxyanilines (8-*n*).
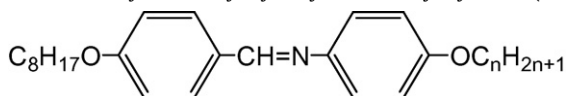
n	Calculated			Found		
	C	H	N	C	H	N
1	77.88	8.55	4.13	77.91	8.58	4.10
2	78.19	8.78	3.97	78.33	8.69	3.99
3	78.47	8.99	3.82	78.39	8.87	3.95
4	78.74	9.19	3.67	78.83	9.31	3.83
5	78.99	9.37	3.54	78.97	9.24	3.51
6	79.22	9.54	3.43	79.00	9.83	3.56
7	79.43	9.69	3.31	79.27	9.71	3.41
8	79.63	9.84	3.20	79.79	9.99	3.31
9	79.82	9.98	3.10	79.84	10.07	3.21
10	80.00	10.11	3.01	80.18	10.25	2.98
12	80.33	10.35	2.84	80.25	10.41	3.01
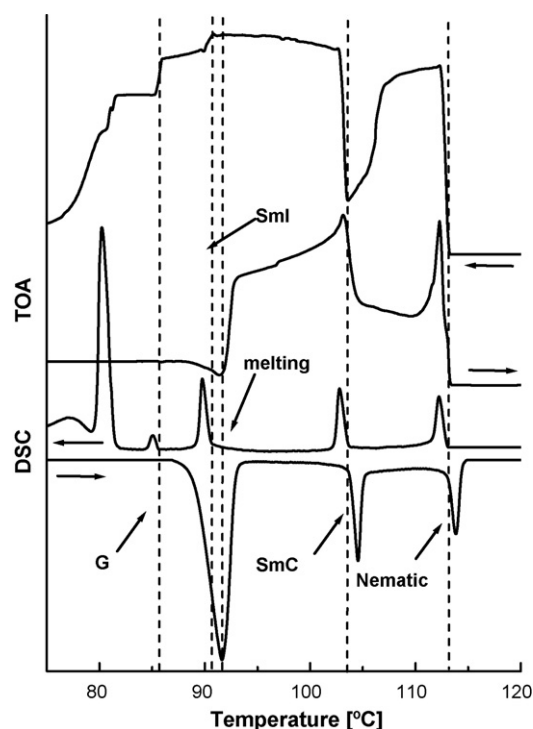
Fig. 1. DSC and TOA spectra of pentyl (n = 5) derivative.

and cooling rates were 5 °C min^{-1}. Indium was used as a calibration standard.

Textures were identified by using OLYMPUS BX60 microscope equipped with LINKAM HTM600 hot stage device with a TMS93 temperature regulator and additionally with CCD Moticom 1000 camera connected to the PC computer. The communication between PC computer and microscope was obtained by RS232 connections. Detailed description of the set-up and experimental procedures are published elsewhere [15].

In phase diagram investigations only mixtures of exact composition were prepared and studied. Very small samples were prepared (~10 mg) using Mettler AT20 balance with accuracy of 2 × 10^{-6} g. All mesophases identified by POM were additionally confirmed by the Sackmann–Demus miscibility method [12].

3. Results and discussion

3.1. Liquid-crystalline properties

The phase transition parameters (Table 2) were detected by the DSC calorimetry and the polarization microscopy (POM and TOA). Both methods gave the same results of phase transitions temperatures. Typical DSC and TOA traces are shown in Fig. 1 for pentyl (n = 5) derivative. In the heating mode three phase transitions were detected in this compound. The first one at 92 °C is associated with the transition from the crystal to smectic C mesophase. This type of mesophase can be synonymously recognized by texture observations. At 104 °C both applied methods allowed for the detection of the SmC–N phase transition showing the change of texture, which was also observed as the significant change of the light intensity running through the microscope. At 113 °C the isotropisation process was detected. The lowest value of light intensity in polarizing microscopy was associated with a disappearance of the refractive index anisotropy. SmC and N mesophases were observed also in the cooling mode. Both DSC and TOA traces showed the same signal anomalies in the opposite order. The temperature hysteresis of melting in the cooling mode allowed us to observe an

Table 2
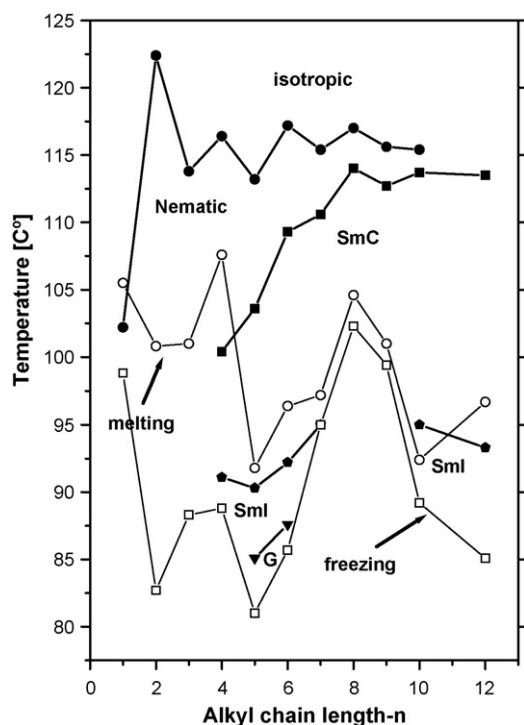Phase transition parameters of 4-octyloxybenzylidene-4′-alkyloxyanilines (8-*n*).

n	Melting (°C)	Recrystallization	G		SmI		SmC		N		Iso
1	105.5 [47.74]	98.8 [41.83]							•	(102.2) [0.56]	•
2	100.8 [40.43]	82.7 [35,60]							•	122.4 [1.12]	•
3	101.0 [37.82]	88.3 [20.44]							•	113.8 [1.02]	•
4	107.6 [44.38]	88.8 [30.10]			•	(91.1)[a]	•	(100.4) [1.18]	•	116.4 [1.80]	•
5	91.8 [29.42]	81.0 [14.93]	•	(85.1) [0.32]	•	(90.3) [2.03]	•	103.6 [1.89]	•	113.2 [1.64]	•
6	96.4 [33.46]	85.7 [20.48]	•	(87.6)[a]	•	(92.2) [1.89]	•	109.3 [1.99]	•	117.2 [2.20]	•
7	97.2 [34.25]	95.0 [32.49]			•	(95.0)[a]	•	110.6 [2.53]	•	115.4 [2.34]	•
8	104.6 [39.07]	102.3 [38.60]					•	114.0 [2.27]	•	117.0 [3.00]	•
9	101.0 [43.71]	99.4 [41.51]					•	112.7 [1.78]	•	115.6 [1.91]	•
10	92.4 [44.00]	89.2 [37.07]			•	95.0 [2.03]	•	113.7 [8.43][b]	•	115.4	•
12	96.7 [59.37]	85.1 [50.72]			•	(93.3) [2.70]	•	113.5 [10.09]			•

Abbreviations assigned to phase transitions: Iso—isotropisation, N—nematic phase, SmC—smectic C phase, SmI—smectic I phase, G—crystal G mesophase, enthalpy of the phase transition in kJ mol^{-1} are in square brackets and monotropic phase transition temperatures are in round brackets.

[a] Phase transition observed only in TOA.

[b] Summary enthalpy of two phase transitions: SmC–N and N–Iso.

additional phase transition at 90 °C. The enthalpy of this phase transition was relatively low, but the change of texture was unique. This mesophase was identified as the smectic I by the miscibility methods. At 85 °C next phase transition with relatively small value of enthalpy was detected. This phase transition was observed especially clearly by the TOA method. Basing on miscibility method this mesophase was identified as the smectic G. At 81 °C both methods showed very strong anomaly with the significant enthalpy effect, which is characteristic for the recrystallization. The observed freezing process was complex. Both methods showed an additional phase transition in the solid state. Detailed description of this process was not trivial due to the fact that both phase transitions take place at the same time.

The complete phase situation for the homologous series is shown in Fig. 2. The nematic mesophase was found in the derivatives with the alkyloxy chains from methyl (*n* = 1) to decyl (*n* = 10). The even–odd effect for the temperature of isotropisation, which is connected with the relation between the length of the alkyl chain on its conformation, was very characteristic. This effect was explained in details by Marcelja in 1974 [16] by the simulation of all possible conformations of alkyl chains and recently in 2004 confirmed by Zannoni group [17], in more precise experiment (MD simulations).

The next detected mesophase was smectic C, observed in derivatives from butyl (*n* = 4) to dodecyl (*n* = 12). Most probably the recrystallization process in propyl (*n* = 3) derivative prevented the existence of smectic C mesophase. The temperature of the appearing of the smectic C phase increased relatively strongly from butyl (*n* = 4) to octyl (*n* = 8) derivative and for derivatives with longer alkyl chains was almost constant. The highest value was observed for octyl (*n* = 8) derivative. Also for this parameter (temperature) a weak even–odd effect was detected.

The third observed mesophase was smectic I. It was observed similarly among the derivatives from butyl (*n* = 4) to dodecyl (*n* = 12) except for octyl (*n* = 8) and nonyl (*n* = 9). The absence of smectic I in octyl (*n* = 8) and nonyl (*n* = 9) derivatives was associated with the high melting and freezing temperatures.

Unexpectedly, smectic G was observed only in pentyl (*n* = 5) and hexyl (*n* = 6) derivatives.

Fig. 2. Influence of the alkyl chain length on the mesophase sequence.
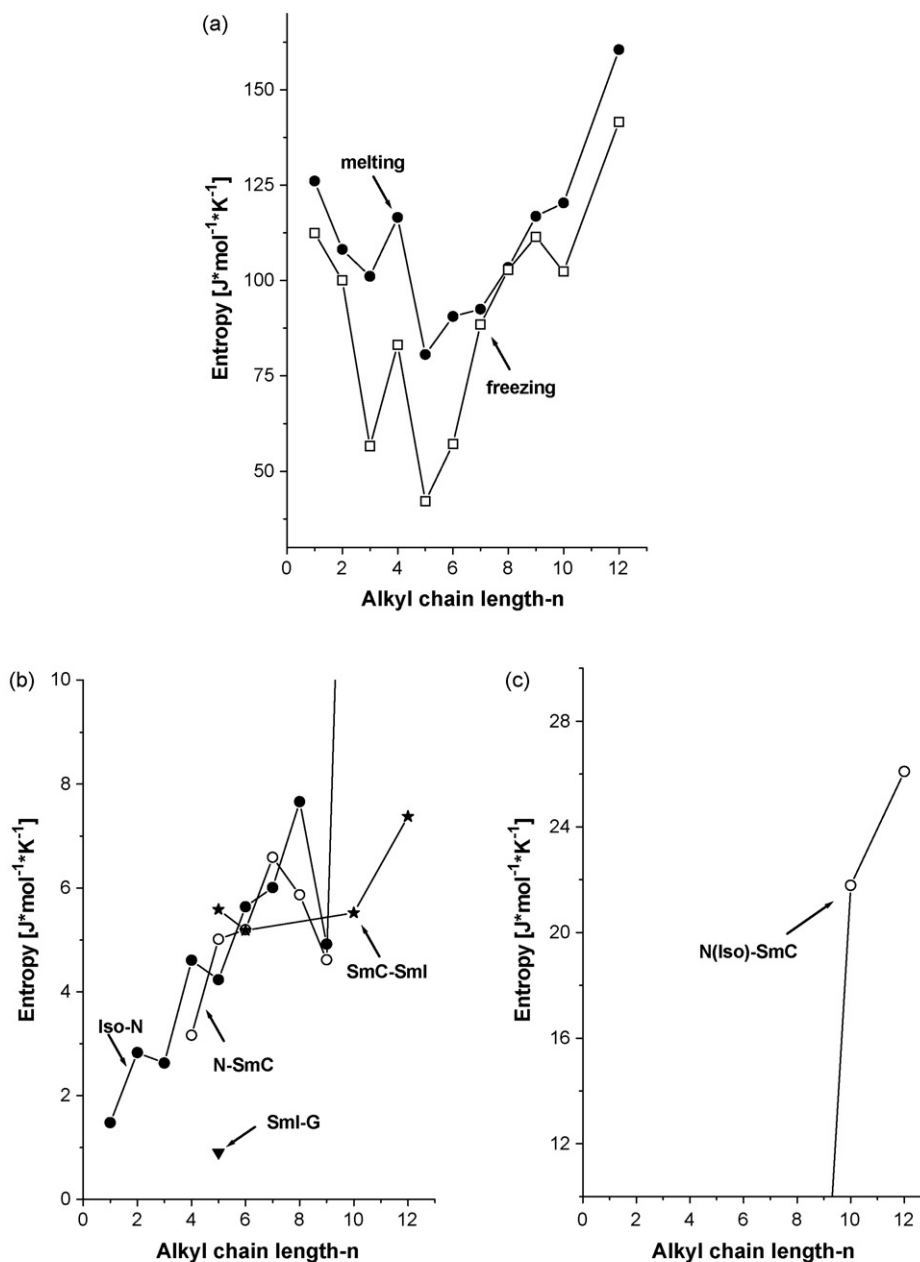
Fig. 3. Influence of the alkyl chain length on the entropy changes of 4-octyloxy-benzylidene-4′-alkyloxyanilines (8-*n*).

3.2. Entropic effects

All observed phase transitions can be quantitatively analyzed basing on their entropy values (Fig. 3). Presented phase transitions can be divided into three categories shown in Fig. 3a–c.

The entropies of melting process strongly depended on the alkyl chain length (Fig. 3a). The methyl (*n* = 1) derivative has the entropy value of 126 J mol^{-1} K^{-1}. The decrease of the entropy down to 80 J mol^{-1} K^{-1} for pentyl (*n* = 5) derivative was caused by the increase of the alkyl chain length. Next, monotonous increase of entropy value with alkyl chain length up to 160 J mol^{-1} K^{-1} for dodecyl (*n* = 12) derivative was observed. Melting entropy curve shows a small even–odd effect. The entropies of freezing showed similar properties. However, the values of entropy were especially low comparing with the melting ones observed for propyl (*n* = 3), butyl (*n* = 4), pentyl (*n* = 5) and hexyl (*n* = 6) derivatives.

The influence of the alkyl chain length on the entropy of phase transition N–Iso (Fig. 3b) was typical. This parameter increased from 1.5 J mol^{-1} K^{-1} for methyl (*n* = 1) derivative to 7.6 J mol^{-1} K^{-1} for octyl (*n* = 8) derivative. For the first six derivatives regular even–odd effect was observed. In this series entropy of phase transition SmC–N had similar value as the phase transition N–Iso (Fig. 3b). This was not a typical effect. Unusual entropic effect of isotropisation was observed for decyl (*n* = 10) derivative in which the nematic mesophase was very narrow (Δ*T* ≈ 1 K), and dodecyl (*n* = 12) derivative in which a nematic phase was not observed at all. The entropic effect of isotropisation for derivatives with longer alkyl chains was about four times larger than for derivatives with short
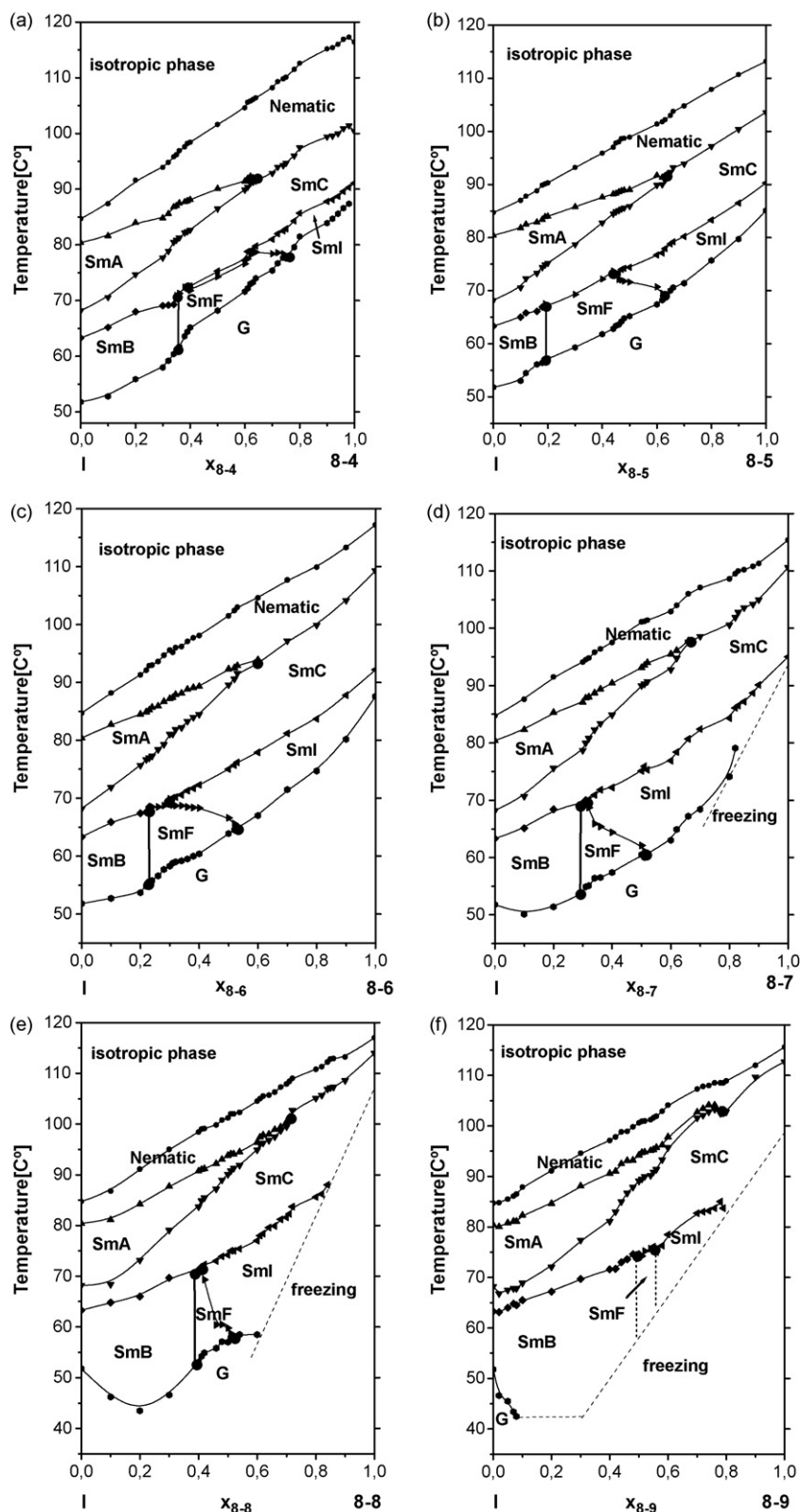
Fig. 4. Phase diagrams of butyl (*n* = 4), pentyl (*n* = 5), hexyl (*n* = 6), heptyl (*n* = 7), octyl (*n* = 8), nonyl (*n* = 9), decyl (*n* = 10) and dodecyl (*n* = 12) derivatives with 4-heptyloxybenzylidene-4′-pentylaniline.

alkyl chains (Fig. 3c). These phase transitions follow the relation: $\Delta S_{N-Iso} + \Delta S_{N-C} \neq \Delta S_{Iso-C}$.

Phase transition SmC–SmI had similar value of entropy as phases transitions N–SmC and N–Iso (Fig. 3b).

3.3. Phase diagrams

Three standards of mesophases were used in the phase diagram investigations. 4-Heptyloxybenzylidene-4′-pentylaniline (I)
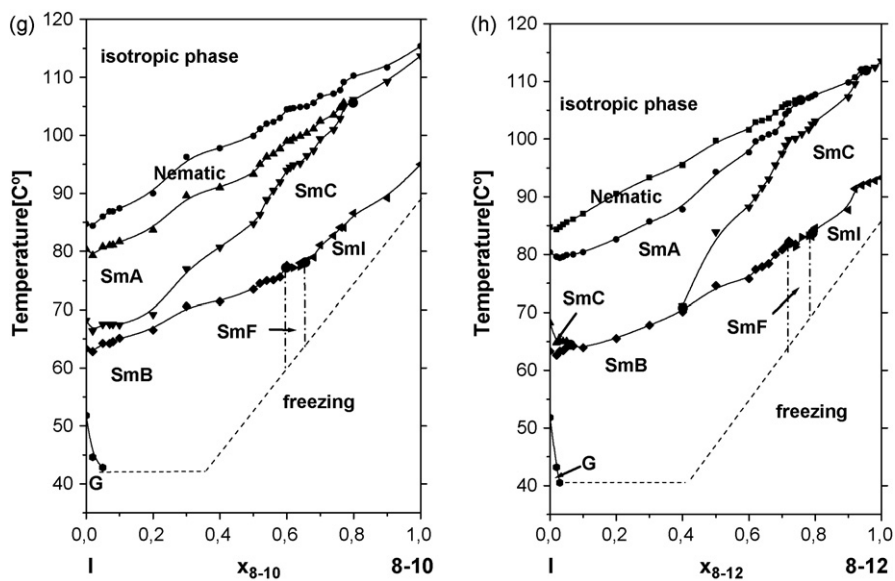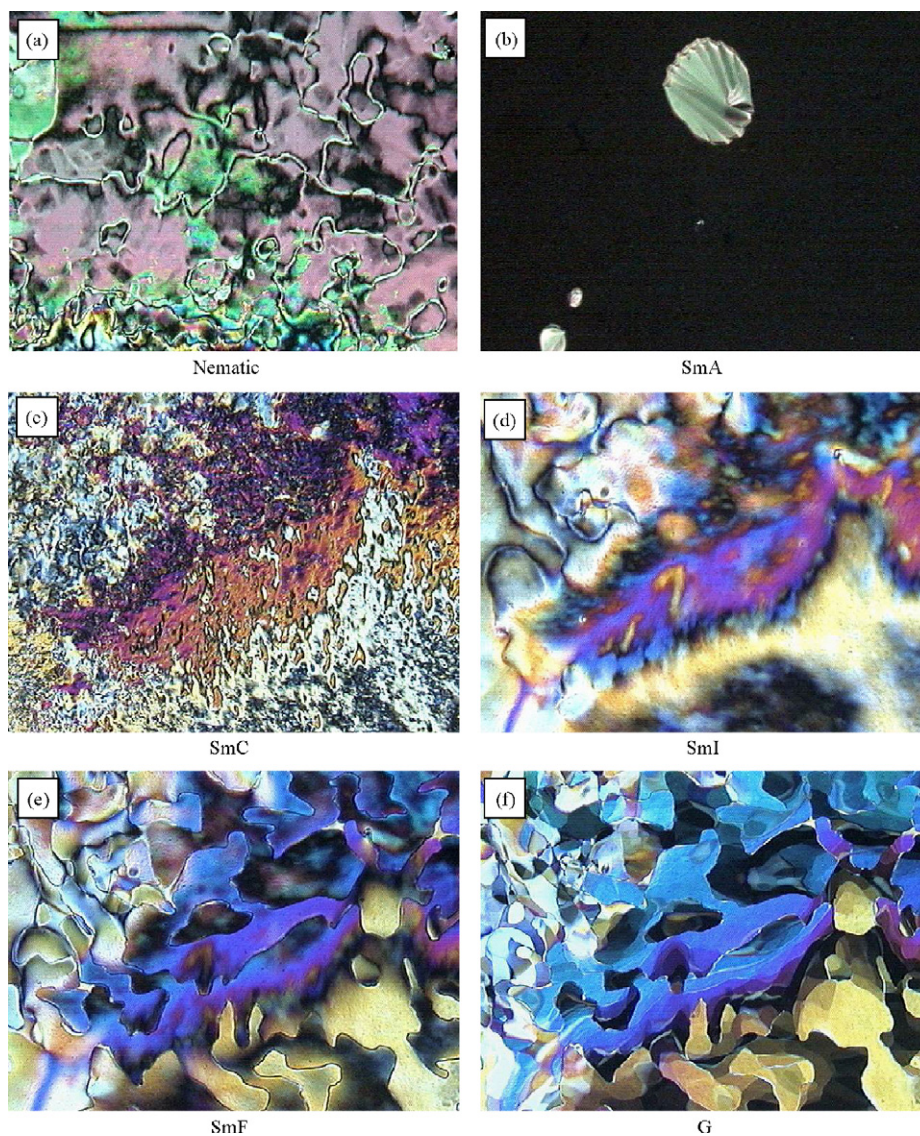
Fig. 4. (*Continued*).

Fig. 5. Textures of mixture of pentyl (*n* = 5) derivative with 4-heptyloxybenzylidene-4′-pentylaniline.
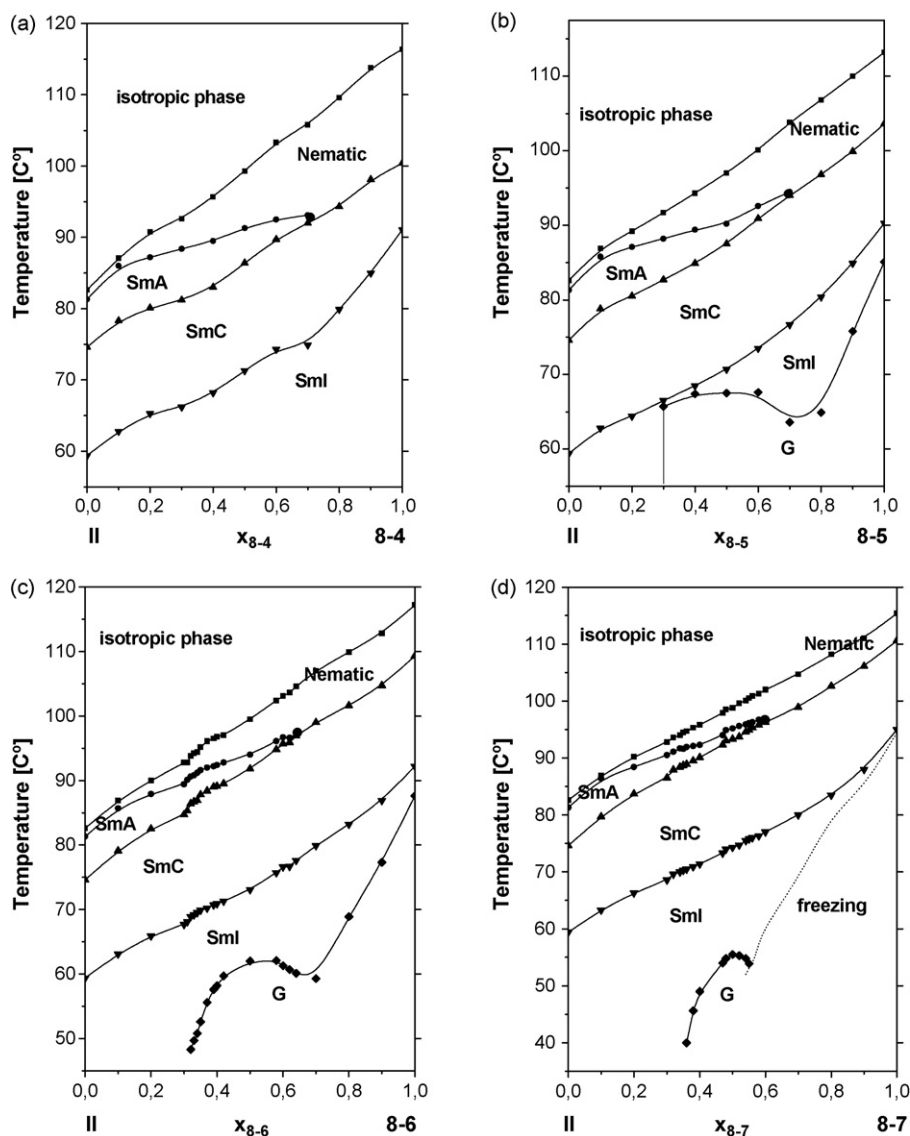
Fig. 6. Phase diagrams of butyl ($n = 4$), pentyl ($n = 5$) and heptyl ($n = 7$) derivatives with 4-octyl-4′-decyloxyazobenzene.

was used as the standard of the smectic A, smectic B and G mesophases [18], 4-octyl-4′-decyloxyazobenzene (II) [19] and 4-octyl-4′-undecyloxyazobenzene (III) were applied as the standard of smectic C and I [19].

In Fig. 4, phase diagrams of eight derivatives from butyl ($n = 4$) to dodecyl ($n = 12$) with standard I are shown. The mesophases of the standard exist in the similar temperature range to those of investigated compounds. The phase diagrams confirmed the presence of nematic and smectic C mesophases in derivatives from butyl ($n = 4$) to decyl ($n = 10$) (Fig. 4a–g). Fig. 4b and c shows an appearance of the smectic G mesophase in pentyl ($n = 5$) and hexyl ($n = 6$) derivatives. Most probably this mesophase could be observed also for butyl ($n = 4$) derivative, but its significantly high melting and freezing temperatures made it impossible (Fig. 4a).

These phase diagrams showed the induction of smectic F which was restricted to four triple points: CBF, CFI, BFG, FGI and four lines which connected these points. Smectics B, F and I created one area along the concentration axes. This is related to the similarity in disorder of these phases [20]. Temperature of phase transition from the smectic B to tilted smectic F phase weakly depended on the concentration. A complete concentration range of these phase transitions was not possible to measure because of the high melting temperatures of some pure components.

The presented diagrams show also other important results. Especially interesting appears to be the influence of the alkyl chain length on the thermodynamic parameters. The first five phase diagrams (Fig. 4a–e) display five triple points: NAC, CBF, CFI, BFG and FIG. The phase transition line SmB-SmF strongly depends on the alkyl chain length. The stability of the smectic B phase with an increase of alkyl chain ends was observed. The phase transition line SmF–SmI depends on the concentration and on the alkyl chain length. The latter was less pronounced than for the SmB-SmF phase transition line and, as a result, the range of stability of smectic F decreased with alkyl chain increase. The disappearance of smectic F can be expected in the diagrams with longer alkyl chains (possibly tetradecyl).

The phase diagram with the dodecyl derivative shows different properties (Fig. 4h). The triple point NAC disappeared and two additional triple points can be observed: IsoNA and IsoAC. This phenomenon is observed due to the lack of the nematic and the smectic A mesophases in the investigated derivative. Interesting appears to be the disappearance of the smectic C phase on both sides of diagram, which was observed for other diagram as additional two triple points of ACB type. Thus six triple points are observed.

Typical textures of the mixture of pentyl ($n = 5$) derivative with 4-heptyloxybenzylidene-4′-pentylaniline (molar fraction of pentyl

derivative $x_{8-5} = 0.5$), which were observed during investigation of phase diagram (Fig. 4b), are shown in Fig. 5. For these concentration, due to the presence of two triple points, six mesophases were detected. The nematic with a characteristic schlieren type texture containing many disclination lines appeared first on cooling (Fig. 5a). At lower temperature this texture disappeared and an almost black area of the homeotropic orientation was observed (Fig. 5b). Next the small oval with the fan texture was characteristic for the smectic A mesophase. The third mesophase in cooling mode was smectic C with a characteristic schlieren type texture and small loops of disclination lines (Fig. 5c). These three textures synonymously prove the mentioned mesophases. The sudden change of schlieren type texture (Fig. 5d) revealed the appearance of the smectic I phase. The small loops disappeared and bigger ones appeared. The continuous change of colors was very characteristic. Futher decrease of temperature induced the fifth mesophase with characteristic polygonal texture and continuous change of a color inside a domain (Fig. 5e). This mesophase was recognized as the smectic F basing on the type of texture and miscibility stud-

ies in the 4-hexyloxybenzylidene-4′-alkiloxyaniline series [6]. The last observed mesophase was the smectic G, which had characteristic polygonal texture with discontinuous change of color inside the domains (Fig. 5f). These phase recognitions confirmed mesophase assignation in the following phase diagrams.

The diagram in Fig. 6 shows the presence of the nematic, smectic C and smectic I mesophases in derivatives from butyl ($n = 4$) to heptyl ($n = 7$). 4-Octyl-4′-decyloxyazobenzene (II) was used as a standard. In these phase diagrams only one type of triple point was observed—NAC. Unexpectedly, the smectic G mesophase appeared in pentyl ($n = 5$) and hexyl ($n = 6$) derivatives (Fig. 6b and c). In diagrams in which the amount of pentyl ($n = 5$) and hexyl ($n = 6$) increased the decrease of the temperature of the phase transition SmI–G was observed. The minimum temperature occurred for the molar ratio x_{6-5} about 0.7. In addition, the maximum of this temperature appeared for the equimolar mixtures. This maximum was present even for the heptyl ($n = 7$) derivative, in which smectic G was not observed due to the freezing process (Fig. 6d). In these mixtures glass transitions appeared at temperature range of smectic G, thus
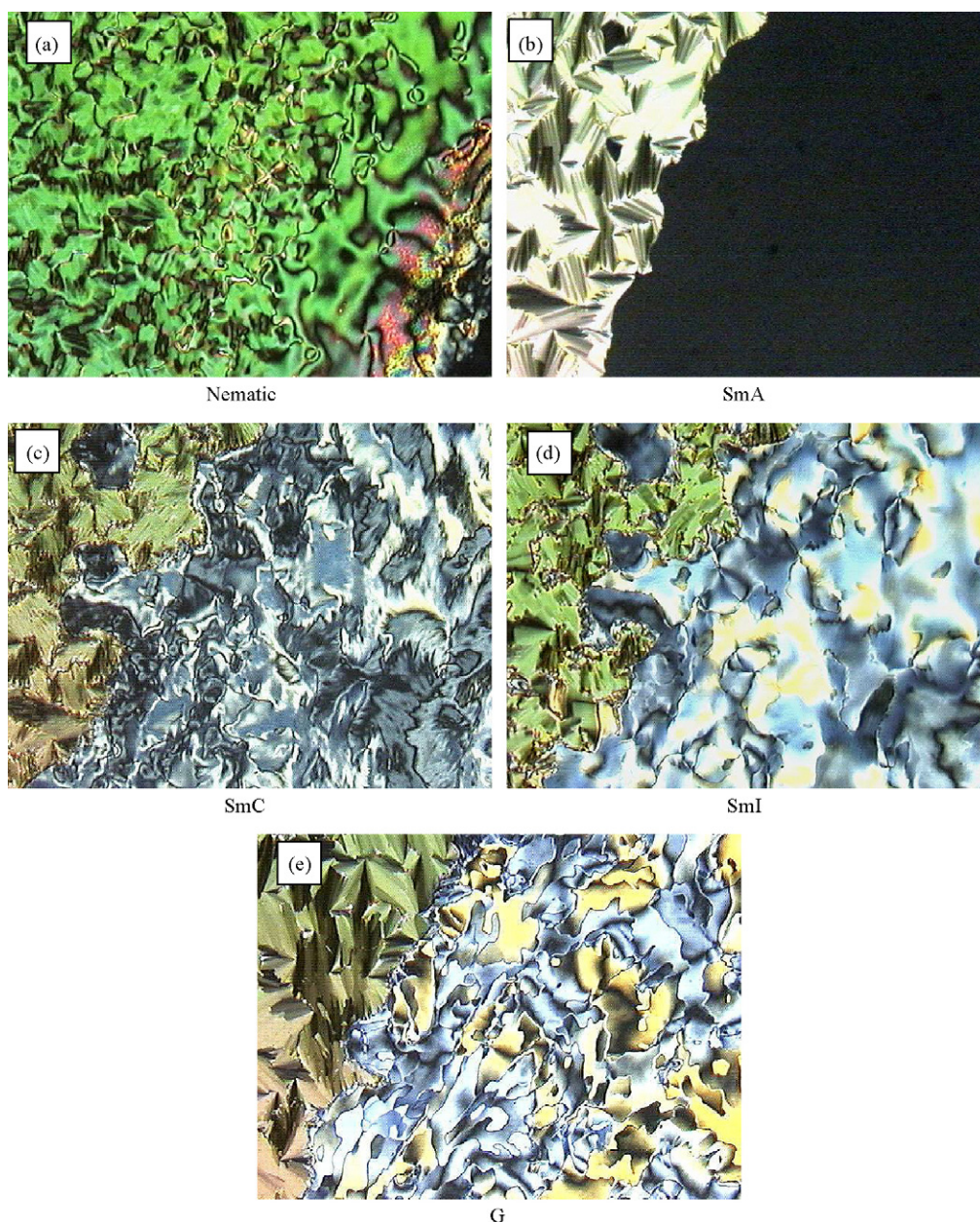

(a) Nematic

(b) SmA

(c) SmC

(d) SmI

(e) G

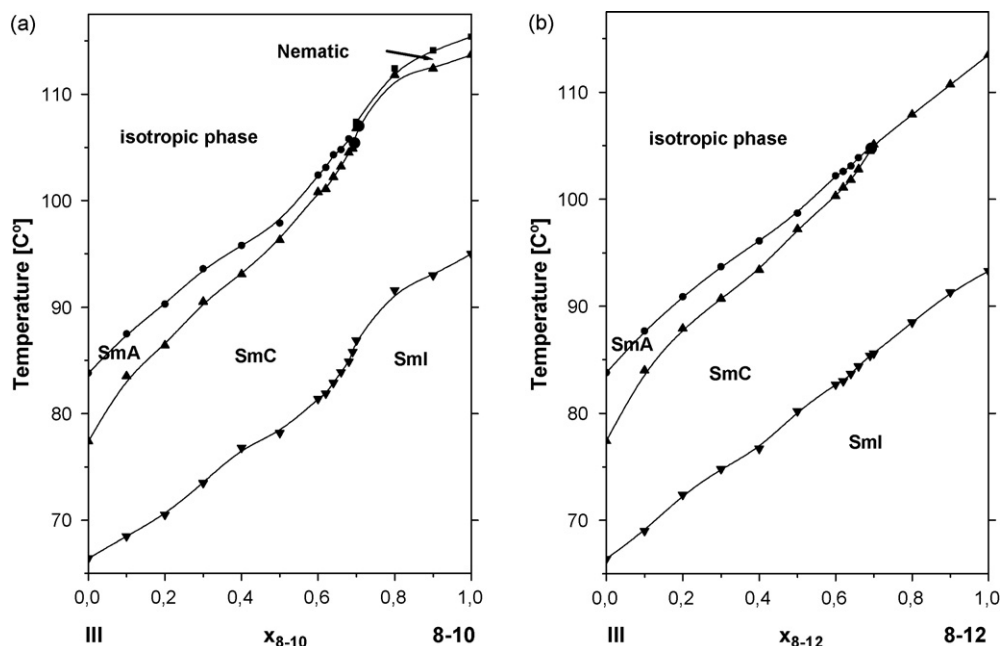**Fig. 7.** Textures of mixture of pentyl ($n = 5$) derivative with 4-octyl-4′-decyloxyazobenzene.

Fig. 8. Phase diagrams of decyl ($n = 10$) and dodecyl ($n = 12$) derivatives with 4-octyl-4′-undecyloxyazobenzene.

the phase transition line SmI–G on the left side of the diagram ends without any characteristic point.

The textures of equimolar mixture of pentyl ($n = 5$) derivative with 4-octyl-4′-decyloxyazobenzene observed under a microscope are shown in Fig. 7. All liquid-crystalline phases were detected in the cooling mode for the same sample. Fig. 7a shows a typical schlieren texture, characteristic for the nematic phase. Fig. 7b presents a fan texture, which is typical for the smectic A mesophase. A black area on the right side of the diagram is caused by homeotropic orientation of molecules. In the next figure (Fig. 7c) fan texture of the smectic A changed into a broken fan texture, which is typical for the smectic C. The black area observed for the smectic A is replaced by a schlieren texture, which is very specific and found only in the smectic C phase. The SmC–SmI phase transition proceeded in a very characteristic way (Fig. 7d). All the defect points of a schlieren part remained the same, but the change of the orientation of molecules was relatively slow, which was observed as a slower change of colors. Broken fan texture areas of the smectic C changed into a polygonal texture, which is typical for the smectic I. Textures of G mesophase are shown in Fig. 7e. Polygonal areas of the smectic I become sharper and the schlieren part changes also into a polygonal texture but with a different pattern. All observed liquid-crystalline textures are typical according to the Demus and Richter [1], Gray and Goodby [21] and Dierking [22] books of liquid-crystalline texture.

The last two diagrams shown in Fig. 8 confirm the presence of the smectic C and the smectic I mesophases in decyl ($n = 10$) and dodecyl ($n = 12$) derivatives. 4-Octyl-4′-undecyloxyazobenzene (III) was used as a standard of smectics C and I. In Fig. 8a two types of triple points: IsoAC and IsoNC are shown. The diagram in Fig. 8b has only one triple point—IsoAC.

4. Conclusion

1. A rich polymorphism in 4-octyloxybenzylidene-4′-alkyl-oxyaniline series was detected: tetramorphism for pentyl ($n = 5$) and hexyl ($n = 6$) derivatives, trimorphism for butyl ($n = 4$), heptyl ($n = 7$) and decyl ($n = 10$) derivatives, dimorphism for octyl ($n = 8$), nonyl ($n = 9$) and dodecyl ($n = 12$) derivatives and monomorphism for methyl ($n = 1$), ethyl ($n = 2$) and propyl ($n = 3$) derivatives.
2. Only pentyl ($n = 5$) and hexyl ($n = 6$) derivatives showed the presence of G mesophase.
3. All phase diagrams confirmed the mesophase sequence for the derivatives from butyl ($n = 4$) to hexyl ($n = 6$).
4. In the mixtures of the same type of molecules (Schiff bases) there was induced a mesophase (smectic F) unobserved for the pure components.

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