Liquid crystalline properties of 4-hexyloxybenzylidene-4'-alkyloxyanilines

Joanna Godzwon[a]; Monika J. Sienkowska[a]; Zbigniew Galewski[a]

[a] Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

PLEASE SCROLL DOWN FOR ARTICLE

Liquid crystalline properties of 4-hexyloxybenzylidene-4′-alkyloxyanilines

JOANNA GODZWON, MONIKA J. SIENKOWSKA* and ZBIGNIEW GALEWSKI**

Faculty of Chemistry, University of Wrocław, 14, Joliot-Curie, 50-383 Wrocław, Poland

The liquid-crystalline polymorphism of the homologous series of 4-hexyloxybenzylidene-4′-alkyloxyanilines is investigated. Basing on the polarization microscopy (POM, TOA), the DSC calorimetry and miscibility studies the following mesophases were detected: nematic, smectic A, smectic C and smectic I. The phase diagrams of the compounds of these series with 4-hexyloxybenylidene-4′-pentylaniline (as the standard of mesophases) show induction of the smectic F mesophases. Their dependence on the alkyl chain length and mole fraction is shown.

1. Introduction

Azomethanes (Schiff bases) are a well known group of liquid crystalline compounds. 4-Methoxybenzylidene-4′-methylaniline, the first compound from this group, was described by Bertleff in 1908 [1]. Two other derivatives, 4-methoxybenzylidene-4′-methoxyaniline and 4-methoxybenzylidene-4′-ethoxyaniline were described by Haberland [2] in 1925 and broadly studied by Weygand and Gabler [3, 4] before World War II. In their investigations, the methoxy, ethoxy, and propoxy derivatives of 4-alkyloxybenzylidene-4′-alkoxyanilines were described and their polymorphism was characterized. Since the studied derivatives contain one relatively short alkyl chain, only the nematic phase was detected. The above-mentioned studies also discuss the interesting problem of liquid crystalline polymorphism and the different kinds of mesophases named by Vorlaender as Pl-, Bz- and Rs-Formen [5].

The influence of different substituents in the 4 and 4′ positions on the mesomorphic behaviour of benzylideneanilines was investigated by Castellano [6]. He obtained derivatives exhibiting the nematic phase over nearly 100°C.

The synthesis of 4-methoxybenzylidene-4′-butylaniline (MBBA) by Kelker and Scheurle [7] yielded the first liquid crystalline compound with a nematic phase at room temperature. Currently, this compound is one of the three most extensively studied liquid crystalline substances.

The discovery of MBBA inspired extensive studies of 4-alkoxybenzylidene-4′-alkoxyanilines. In particular the most important appears to be their rich and unusual polymorphism, which for example in case of 4-pentyloxybenzylidene-4′-hexylaniline occurs as GFBCAN hexamorphism [8], which means that this compound has 6 different mesophases as follows: G, SmF, SmB, SmC, SMA and N. In 1980 4-pentyloxy-4′-hexylaniline was assigned as a standard reference for the smectic phases, due to its rich polymorphism [9]. This is very important in the identification of mesophases by the Sackmann-Demus miscibility method [10].

One of the first twisted nematic liquid crystalline displays was built with 4-octyloxybenzylideno-4′-nitroaniline [11] and the first banana-shaped liquid crystal (LC) material synthesized by Niori *et al.* [12] was a Schiff base.

Also the LC polymorphism of 4-alkoxybenzylidene-4′-alkoxyanilines is very interesting. The studies by Wegand and Gabler [3, 4], as well as work done by Dave and Patel [13] in 1967, describe liquid crystalline properties of 4-alkoxybenzylidene-4′-alkoxyanilines where one of the alkyloxy chains is shorter than the hexyloxy chain. Therefore, studies of 4-alkoxybenzylidene-4′-alkoxyanilines with longer alkyl chains are of interest. These compounds are expected to exhibit a broader smectic polymorphism.

The aim of this work was focused on the characterization of the polymorphic behaviour of 4-alkyloxybenzylidene-4′-alkyloxyanilines with longer alkyloxy chains. We have chosen the hexyloxy series since the series with shorter chains exhibits poor polymorphism. In addition due to the subtle intermolecular interactions of the azomethine group, the 4-alkyloxybenzylidene-4′-alkyloxyanilines provide very interesting phase diagrams

*Present address: Department of Chemistry, University of Pennsylvania, 231 South 34th St., Philadelphia, PA 19104, USA

**Corresponding author. Email: ZG@chem.uni.wroc.pl

Table 1. Elemental analysis for 4-hexyloxybenzylidene-4′-alkyloxyanilines.

	Calculated /%			Found /%		
n	C	H	N	C	H	N
1	77.17	8.04	4.50	77.15	8.04	4.74
2	77.54	8.31	4.31	77.53	8.32	4.51
3	77.88	8.55	4.13	77.73	8.77	4.21
4	78.19	8.78	3.97	77.96	9.05	4.04
5	78.47	8.99	3.82	78.47	9.03	3.98
6	78.74	9.19	3.67	78.72	9.20	3.82
7	78.99	9.37	3.54	78.93	9.43	3.71
8	79.22	9.54	3.43	79.11	9.48	3.55
9	79.43	9.69	3.31	79.31	9.82	3.41
10	79.63	9.84	3.20	79.65	9.84	3.36
12	80.00	10.11	3.01	80.10	10.21	3.13

with the induction of new liquid crystalline phases, the shift of the phase's stability with increasing length of alkyl chain, and the nonlinearity of studied phase diagrams. We used Schiff bases and azobenzene derivatives as standards in our studies.

2. Experimental

The 4-hexyloxybenzylidene-4′-alkyloxyanilines were prepared from the appropriate amine and aldehyde.

4-Hexyloxybenzaldehyde was synthesized according to the Gray procedure by etherification of 4-hydroxybenzaldehyde with 1-bromohexane in cycloxanone with K_2CO_3 as a base [14].

Similarly 4-propyloxynitrobenzene was prepared by etherification of 4-nitrophenol with bromopropane in cyclohexanone in the presence of K_2CO_3 as a base [15].

4-Propyloxyaniline was synthesized by reduction of 4-nitro-4′-propoxybenzene with hydrazine in the presence of Raney nickel [15].

The purity of all compounds was confirmed by elemental analysis (table 1).

Calorimetric measurements were performed using a Perkin Elmer DSC7. Metallic indium was applied as a standard for latent heats.

Phase transition temperatures and liquid crystalline textures were investigated using a Linkam THMS 600 hot stage and TMS 93 control unit in conjunction with an Olympus BX60P polarizing microscope. This set-up with a multimeter Black Star 4503 and a PC computer was applied in the thermo-optical measurements [16].

In phase diagram investigations, very small samples were employed ($\sim$10 mg), using a Mettler AT20 balance, which has an accuracy 2×10^{-6} g.

3. Liquid crystalline properties

All phase transition parameters (table 2) were determined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM, thermo-optical technique). Both methods showed identical phase transition temperatures in the cooling and heating modes. Differences occurred only in recrystallization due to strong supercooling effects. In the investigated family, four mesophases were detected: nematic (N), smectic A (SmA), smectic C (SmC) and smectic I (SmI). The complete range of phases is shown in figure 1.

Mesophases were identified by LC texture analysis; representative examples of the LC textures are shown in figure 2. Figures 2a–2c show photomicrographs of a sample mounted between two microscope cover glasses, which were covered with thin film of nylon 6-6. This procedure induces a planar orientation of molecules and the characteristic textures of the N, SmA and SmC phases can be observed under the microscope. Figure 2a shows a marbled texture, which is very characteristic of an N phase. A decrease in temperature changes the texture into the fan-shaped type (figure 2b), most often found for SmA phases. The change into SmC is

Table 2. Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}, in square brackets) of 4-hexyloxybenzylidene-4′-alkyloxyanilines (monotropic phase transition temperatures in brackets).

n	Melting	Recryst.	SmI		SmC		SmA		N		I
1	105.7 [39.49]	93.7 [33.13]							•	(105.2) [0.67]	•
2	97.6 [33.08]	88.4 [25.85]							•	124.3 [1.07]	•
3	93.7 [31.67]	91.2 [21.69]							•	115.4 [0.94]	•
4	104.6 [36.21]	101.4 [24.27]							•	121.2 [1.03]	•
5	104.4 [25.65]	103.4 [24.91]							•	114.7 [1.06]	•
6	107.1 [30.28]	105.5 [30.60]							•	118.5 [1.30]	•
7	102.7 [29.65]	100.8 [24.74]			•	103.1 [1.90]			•	115.7 [1.30]	•
8	95.3 [29.76]	95.1 [13.18]			•	104.6 [2.09]			•	116.6 [1.90]	•
9	92.0 [44.07]	89.3 [11.62]			•	104.8 [2.23]			•	112.8 [2.00]	•
10	92.5 [43.62]	88.2 [24.01]	•	(88.9)[a]	•	107.3 [1.11]			•	114.1 [2.32]	•
12	93.7 [50.42]	86.3 [30.06]	•	(86.7)[a]	•	106.8 [0.12]	•	107.7 [0.28]	•	111.0 [2.99]	•

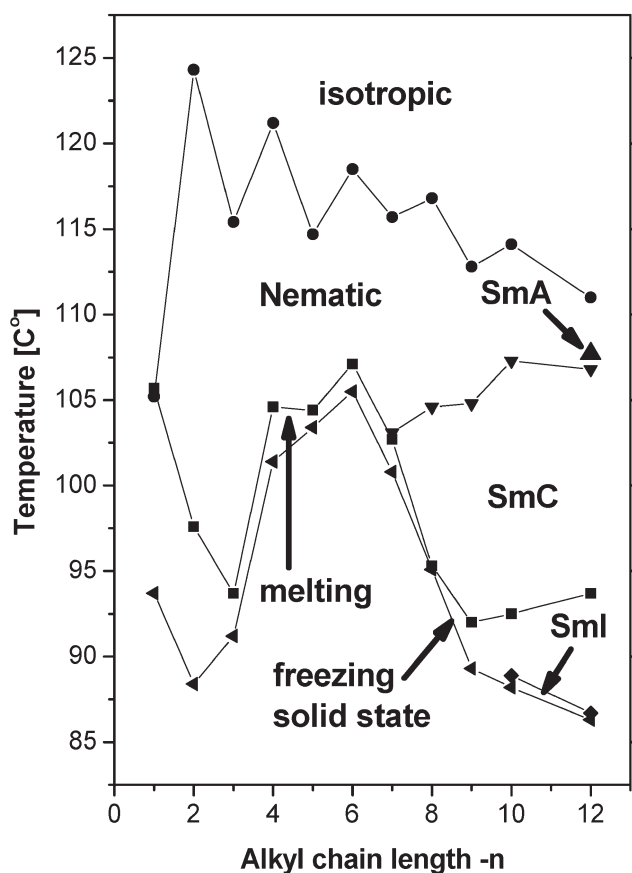[a] Phase transition observed only in TOA.

Figure 1. Influence of alkyl chain length on the mesophase sequence in 4-hexyloxybenzylidene-4'-alkyloxyanilines.

observed as a breaking of this texture, which gives the broken fan-shaped texture (figure 2c). These types of texture are typical and clearly identify the SmA and SmC phases. In the case of a cover glass, without surface modification, a homeotropic orientation was induced. This caused the perpendicular orientation of the molecules and N, SmA and SmB phases are not visible under the microscope. This circumstance confirms the presence of the orthogonal mesophases and the proper identification of the tilted SmC and SmI phases, which show characteristic schlieren textures (figures 2d and 2e). The schlieren textures have different patterns. The SmI phase has a much more regular pattern with longer distances between singular points. The texture in figure 2f shows additional regions of solid matter, and indicates the freezing process.

The influence of the alkyl chain length on the phase situation is shown in figure 1. The odd-even effect for the clearing temperature is characteristic, with an unusually low temperature for the methyl derivative. The average value is nearly 120°C and decreases with alkyl chain length to 110°C for the dodecyl derivative.

The alternation phenomenon was first recognized by Weygand and Gabler [3] and broadly discussed by Gray [17, 18]. A recent article by Berardi *et al.* [19] also describes application of modern simulation techniques to such odd–even effects. For the homologues series of esters, ω-phenylalkyl 4-(4'-cyanobenzylidene)aminocinnamates, they suggest that the simple increase of alkyl chain length does not monotonically change the ratio length/breadth; for $n = 1$ the terminal ring is not able to align the CH_2 group against the director and finally that non-fully stretched conformations are very important and could be responsible for the decrease of the phase transition temperatures. The alternation effects in the clearing temperatures that we have observed are in agreement with these earlier observations.

The second smectic mesophase which appears in the investigated series of compounds is SmC. It was detected in derivatives with heptyl and longer chains. Taking into account the high melting and recrystallization temperatures for the hexyl, pentyl and butyl derivatives, the occurrence of the monotropic SmC phase in these compounds is possible. Two members of the investigated family, with the longest alkyl chains (the decyl and dodecyl), have an additional SmI mesophase.

Based on phase diagrams (see figures 3b and 3c), it is possible to identify a virtual SmI phase in the nonyl derivative [20], and the presence of two tilted smectics is an expected behaviour. Similar properties were found in the series of 4-alkyloxy-4'-alkyloxyazobenenes. An unexpected result is the appearance of a SmA phase in the dodecyl derivative. It is possible that the derivatives with longer alkyl chains will have a similar polymorphism, ICAN type.

The melting temperature is also very interesting. The highest value is that for the hexyl derivative, which is a quasi-symmetric molecule. Butyl, pentyl, heptyl and octyl derivatives have also higher than expected melting temperatures.

4. Phase diagrams

For proper mesophase identification, the Sackmann–Demus miscibility method was applied [10]. Figure 3 shows phase diagrams of heptyl, octyl, nonyl, decyl and dodecyl derivatives with 4-heptyloxybenzylidene-4'-pentylaniline (A), used as a standard for GBCAN mesophases. The mesophases of this standard material exist in a similar temperature range to the investigated compounds [9]. Other members of the investigated group of compounds were not studied, because of their rather poor polymorphism (only nematic phase). The phase diagrams in figure 3 confirm the presence of N and SmC mesophases.
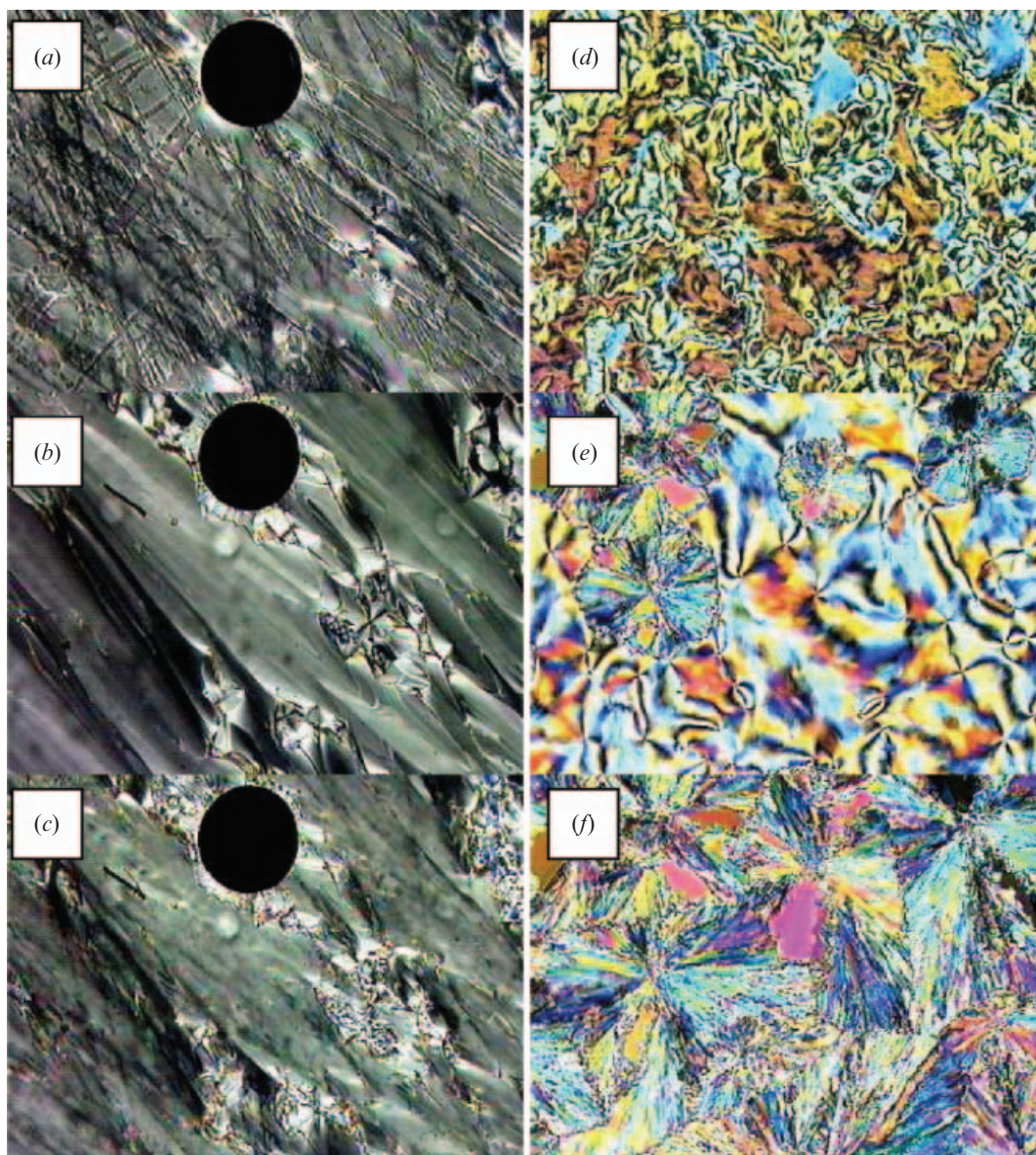
Figure 2. Textures of 4-hexyloxybenzylidene-4′-dodecyloxyaniline: (a) marble texture of nematic phase; (b) fan-shaped texture of SmA phase; (c) broken fan-shaped texture of SmC phase; (d) schlieren texture of SmC phase; (e) schlieren texture of SmI phase; (f) texture of solid state.

The occurrence of the SmI mesophase is also proven via the phase diagrams in figure 4. For the confirmation of this mesophase, 4-octyl-4′-decyloxyazobenzene was applied as the standard (B), which was fully investigated in our previous paper [21] and independently by Pelzl *et al.* [22] with the help of X-ray measurements.

The investigated phase diagrams show a very interesting result, which is the induction of a SmF mesophase, absent in the pure components. Identification of induced mesophases is confirmed also by the miscibility method, as shown in figure 5.

4-Nonyloxybenzylidene-4′-butylaniline (C) was used as a SmF standard [23].

Moreover, the phase diagrams in figure 3 show other interesting results, especially the influence of the alkyl chain length on the thermodynamic parameters. The first phase diagram (figure 3a) has five triple points, of which the types are NAC, CBF, CFI, BFG and FIG. The same topology exists in the next three diagrams with the octyl, nonyl and decyl derivatives (figures 3b–3d).

Especially important is the triple point of the NAC type, for which the critical properties have been fully
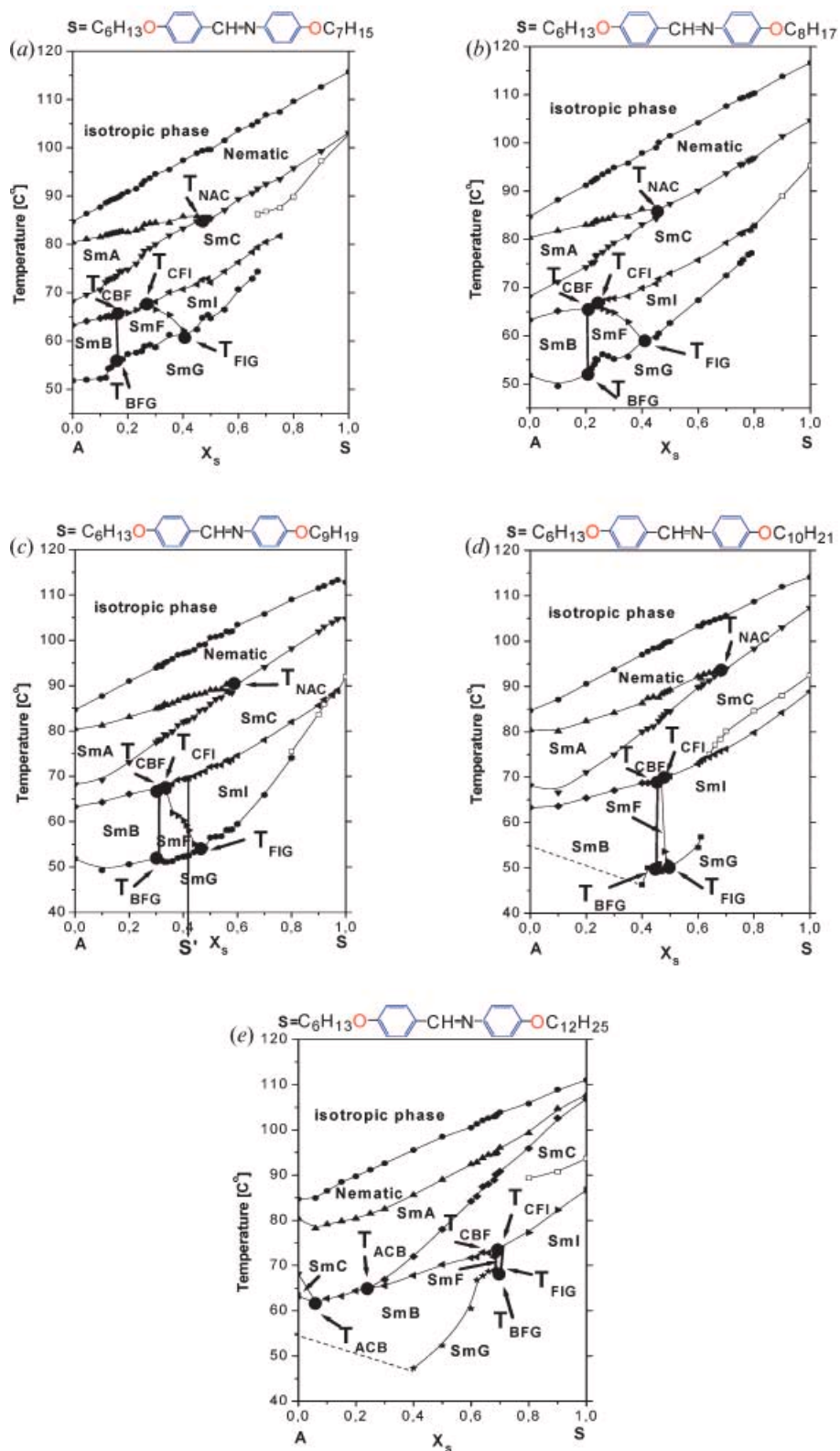
Figure 3.   Phase diagrams of 4-hexyloxybenzylidene-4'-pentylaniline (standard compound, A) and 4-hexyloxybenzylidene-4'-alkyloxyanilines (S) (see text).
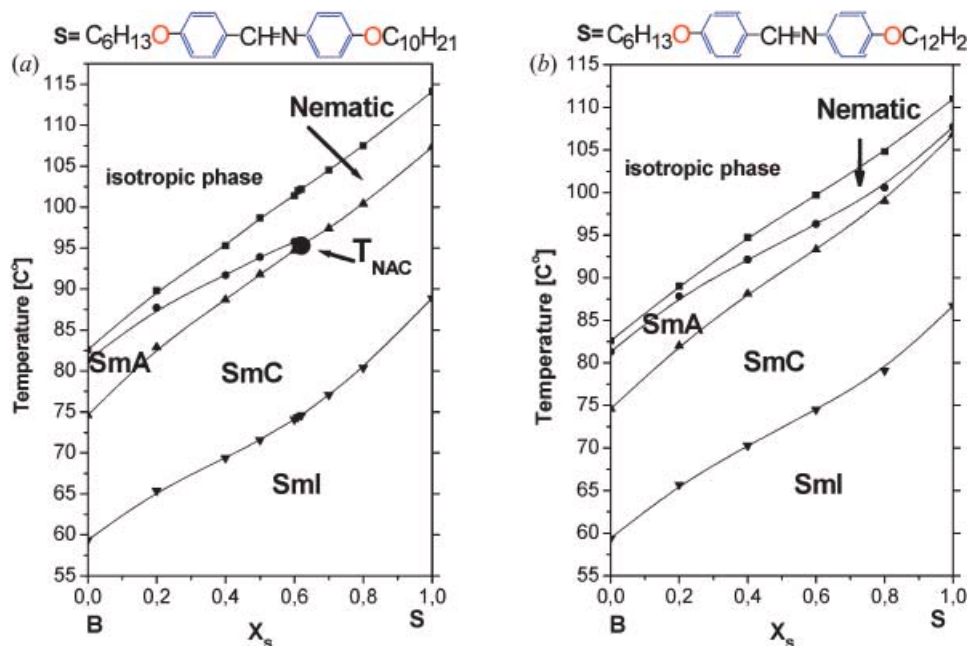
Figure 4.   Phase diagrams of 4-octyl-4′-decyloxyazobenzene (standard compound, B) and 4-hexyloxybenzylidene-4′-alkyloxya-nilines (S).

discussed in the literature [24, 25]. The presented phase diagrams show similar properties. The shift of this triple point with increase in the alkyl chain length for the higher value molar fractions is clearly visible, proving

Figure 5.   Phase diagram of 4-nonyloxybenzylidene-4′-buty-laniline (standard compound, C) and S′ mixture (for its composition, see figure 3c).

the stabilization of the SmA phase for compounds with longer alkyl chains. The phase diagram with the dodecyl derivative (figure 3e) has no NAC triple point because of the presence of a SmA mesophase in the pure compound.

As was mentioned above, a characteristic for these phase diagrams is the induction of a SmF phase, which is restricted by four triple points: CBF, CFI, BFG, FGI and four lines, which connect these points. SmB, SmF and SmI phases create one area for the full range of concentrations. This is connected with the similarity of the disorder of the three phases [26]. The temperature of the phase transition from SmB to tilted SmF does not depend on the concentration and has the following values of mole fractions, 0.17, 0.235, 0.33, 0.47, 0.685, in the sequence of increasing alkyl chain length.

This monotonic influence of the alkyl chain length on the stability of the orthogonal mesophase is the same as in the case of SmA. The phase transition line SmF–SmI depends on the temperature and on the alkyl chain length. This last influence is slower than for the phase transition line SmB–SmF, and as a result the range of stability of SmF decreases with alkyl chain increase. The disappearance of SmF is expected in diagrams with longer alkyl chains (possibly tetradecyl).

The phase diagram with the dodecyl derivative shows different properties (figure 3e). The triple point NAC disappears, due to presence of SmA in both components of mixtures, but the line of the phase transition SmA–
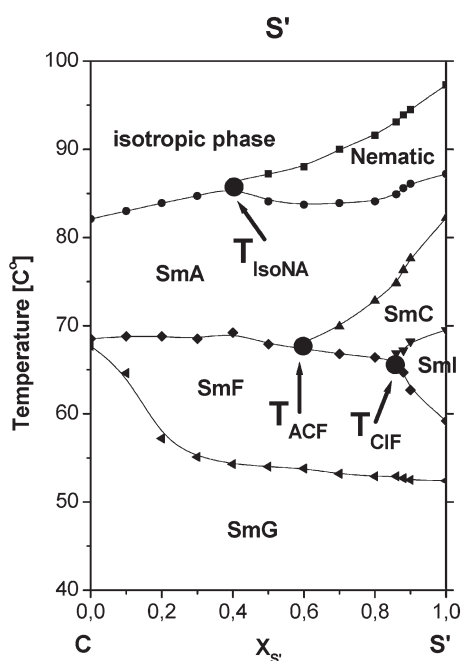
SmC crosses the phase transition line SmB–SmC, because of their different curvature. Two additional triple points are observed. Both are ACB type. As a result, six triple points are present.

5. Conclusions

1. Rich polymorphism in the 4-hexyloxybenzylidene-4′-alkyloxyaniline (6-*n*) series has been detected: tetramorphism in 6-12, trimorphism in 6-10, dimorphism in 6-7, 6-8 and 6-9 and monomorphism in the remaining derivatives.
2. The highest melting temperature is observed for the quasi-symmetric molecule 4-hexyloxybenzylidene-4′-hexyloxyaniline (6-6).
3. Mixtures with compounds with SmB and SmI mesophases induced the intermediate SmF phase.

References

[1] V. Bertleff. PhD thesis, Halle (1908).
[2] H. Haberland. *Berichte*, **58**, 2652 (1925).
[3] C. Weygand, R. Gabler. *J. Prakt. Chem. N.F.*, **151**, 215 (1938).
[4] C. Weygand, R. Gabler. *J. Prakt. Chem. N.F.*, **155**, 332 (1940).
[5] D. Vorlaender. *Berichte*, **70**, 1202 (1937).
[6] J.A. Castellano. *J. Org. Chem.*, **33**, 3501 (1968).
[7] H. Kelker, B. Scheurle. *Angew. Chem.*, **8**, 884 (1968).
[8] F. Hardouin, M.F. Achard, G. Sigaud, H. Gasparoux. *Mol. Cryst. liq. Cryst.*, **39**, 241 (1977).
[9] J.W. Goodby, G.W. Gray, A.J. Leadbetter, M.A. Mazid. In *Liquid Crystals of One- and Two-dimensional Order*, W. Helfrich, G. Heppke (Eds), p. 3, Springer Verlag, Berlin (1980).
[10] H. Sackmann, D. Demus. *Fortschr. Chem. Forsch.*, **349**, 12 (1969).
[11] M. Schadt, W. Helfrich. *Appl. Phys. Lett.*, **18**, 127 (1971).
[12] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe. *J. Mater. Chem.*, **6**, 1231 (1996).
[13] J.S. Dave, P.R. Patel. *Mol. Cryst.*, **2**, 103 (1967).
[14] G.W. Gray, B. Jones. *J. Chem. Soc.*, 1467 (1954).
[15] Z. Galewski, A. Hofmanska, K. Zielinska. *Pol. J. Chem.*, **73**, 1357 (1999).
[16] Z. Galewski, H.J. Coles. *J. Mol. Liq.*, **79**, 77 (1999).
[17] G.W. Gray, K. Harrison. *Symp. Faraday Soc.*, **5**, 54 (1971).
[18] G.W. Gray. In *The Molecular Physics of Liquid Crystals*, G.R. Luckhurst, G.W. Gray (Eds), Academic Press (1980).
[19] R. Berardi, L. Muccioli, C. Zannoni. *ChemPhysChem*, **5**, 104 (2004).
[20] M. Baron. *Pure Appl.Chem.*, **73**, 845 (2001).
[21] J. Zienkiewicz, Z. Galewski. paper presented at the European Conference on Liquid Crystals 99, Hersonissos, Crete, Greece, 25–30 March (1999).
[22] G. Pelzl, N.K. Sharma, L. Richter, A. Wiegeleben, G. Schröder, S. Diele, D. Demus. *Z. Phys. Chem.*, **262**, 815 (1981).
[23] D. Demus, J.W. Goodby, G.W. Gray, H. Sackmann. In *Liquid Crystals of One- and Two-dimensional Order*, W. Helfrich, G. Heppke (Eds), p. 31, Springer Verlag, Berlin (1980).
[24] R. DeHoff, R. Biggers, D. Brisbin, R. Mahmood, C. Gooden, D.L. Johnson. *Phys. Rev. Lett.*, **47**, 664 (1981).
[25] R. Shashidhar, B.R. Ratna, S. Krishna Prasad. *Phys. Rev. Lett.*, **53**, 2141 (1984).
[26] A. Adamczyk. *Mol. Cryst. liq. Cryst.*, **249**, 1 (1994).