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Review

Liquid-crystalline polymorphism of 4-alkyloxybenzylidene-4′-alkyloxyanilines and nonlinearity of their phase diagrams with different standards

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ABSTRACT

This article presents the summary of our investigations of liquid-crystalline polymorphism of asymmetrical 4-alkyloxybenzylidene-4′-alkyloxyanilines. The existing type of mesophases was confirmed by Sackmann–Demus miscibility method. In this paper the influence of the polarity and the structure of the mesophases standards on the topology of phase diagrams are broadly discussed. Additionally we present X-ray investigations of two derivatives.

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1. Introduction

Liquid-crystalline compounds show remarkably rich polymorphism, which often has unexpected type of ordering. Since the 1960s the unusual properties of liquid crystals have been extensively applied in the modern technology as the LCD, termochromic materials and many others. In spite of so long investigations the correlation between molecular structure and liquid-crystalline properties has not been completely understood. New LC compounds very often exhibit unknown types of mesophases. The presence of nematic phase is mainly associated with the anisotropy of shape but the presence of smectic mesophases depends on polarity, chirality, steric effect and many others.

Schiff bases are a popular type of liquid-crystalline compounds due to a not very complicated synthesis and rich polymorphism. This type of compounds is especially important, because many of them are acclaimed as the mesophase standards. Demus observed the presence of even six different mesophases in the 4-pentyloxybenzylide-4′-decylaniline (hexamorphism GBICAN type) [1].

In 2002 we published a preliminary article describing a group of 4-alkyloxybenzylidene-4′-alkyloxyanilines [2]. 11 homologous series of this kind of Schiff bases (121 derivatives)

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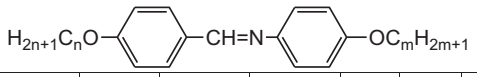
Table 1
Mesophase sequence of 4-alkyloxybenzylidene-4′-alkyloxyanilines.



n \ m	1	2	3	4	5	6	7	8	9	10	12
1	N	N	N	N	N	N	N	N	N	N	N
2	N	N	N	N	N	N	N	N	N	N	N
3	N	N	-	N	N	N	N	N	N	N	N
4	N	N	N	N	N	N	N	N	N	NC	NC
5	N	N	N	N	-	N	N	NC	NC	NC	NC
6	N	N	N	N	N	N	NC	NC	NC	NCI	NACI
7	N	N	N	NC	NC	NC	NC	NCI	NCI	NCI	NCI
8	N	N	N	NCI	NCIG	NCIG	NCI	NC	NC	NCI	CI
9	N	NACB	NACB	NACI	NCIG	NCIG	NCI	NCI	C	C	CI
10	N	NAB	NACB	NACB	NACIG	NACIG	CI	CI	CI	C	CI
12	N	NAB	NAB	NACB	ACB	ACB	CI	CI	CI	CI	C

were synthesized and investigated. Solely on the basis on the observation of texture an influence of the length of both alkyloxy chains on the temperatures of phase transitions and the type of mesophase were discussed. Recently we have published detailed investigations, with the special attention devoted to the proper recognition of the smectic phases, of the following series of Schiff bases: 4-dodecyloxybenzylidene- [3], 4-decyloxybenzylidene- [4], 4-nonyloxybenzylidene- [5], 4-octyloxybenzylidene- [6], 4-heptyloxybenzylidene- [7] and 4-hexyloxybenzylidene-4′-alkyloxyanilines [8].

A group of 4-alkyloxybenzylidene-4′-alkyloxyanilines showed rich liquid-crystalline polymorphism. The presence of observed mesophases was confirmed by the phase diagram technique (Sackmann–Demus miscibility method) [9]. Different standards of mesophases were used. During these studies interesting nonlinear properties were also observed, which are summarized in this publication.

In this paper we broadly discuss the influence of structure and polarity of the mesophases standards on the topology of phase diagrams. Additionally we present X-ray investigations of two derivatives this kind of Schiff bases, which confirm our earlier interpretations of mesophase sequence.

2. Experimental

2.1. Synthesis

The synthesis of 4-alkyloxybenzylidene-4′-alkyloxyanilines is outlined in our earlier papers [2–8]. All final products were purified by column chromatography, using silica gel (Fluka 60) and chloroform as eluent, followed by a few recrystallization from ethanol and heptane. The purity was recognized as sufficient for our investigations, when elemental analysis shows errors limit less than 0.3% and temperature range of biphasic area in isotropisations process, which is observed under the polarization microscopy, is less than 0.3 °C.

2.2. Equipment

Textures of mesophases were identified under OLYMPUS BX60 microscope equipped with a CCD JVC camera, connected with the PC computer through an ELSA graphic card and LINKAM HTM600 hot stage device with a TMS93 temperature regulator. Detailed description of the set-up and experimental procedures are published elsewhere [10].

In phase diagram investigations only mixtures of exact composition were prepared and studied. Very small samples were used (~10 mg). For this purpose very precise balance was used (Mettler AT20), with an accuracy 2×10^{-6} g.

Temperature evolution of smectic layer thickness was evaluated from X-ray diffraction measurements, performed with Bruker D8 Discover system (parallel beam of Cu Kα radiation, λ = 1.5418 Å, formed by Goebel mirror monochromator), equipped with Anton Paar DCS-350 heating stage. Measurements were conducted in a reflection mode and the sample was prepared as a thin film on the heated surface. For the high angle X-ray studies Bruker D8 GADDS was used in the reflection mode (Cu Kα line, Goebel mirror, point beam collimator, Vantec2000 area detector). Aligned samples were prepared as droplets with free surface on a heated plate.

3. Results and discussion

3.1. Liquid crystalline properties

The mesophase sequence of 4-alkyloxybenzylidene-4′-alkyloxyanilines is shown in Table 1. The influence of the alkyloxy chain length from the benzylidene site on the mesophase sequence appears to be greater than from aniline site. The number of existing mesophases increases with the lengthening of alkyloxy chain from the benzylidene site. Six types of mesophases have been recognized: nematic, smectic A, smectic C, smectic I, smectics B and G. Only derivatives with the longest alkyloxy chains show the presence of smectic mesophases. Most compounds have only one mesophase. As many as 62 derivatives have only nematic and 4 compounds have only smectic C. Two types of dimorphism are observed. First type is NC, which is present in 15 derivatives. 10 derivatives have smectics C and I. In this group of investigated compounds three types of trimorphism has been detected: NCI (in 10 derivatives), NAB (in 3 derivatives) and ACB (in 2 derivatives). Just a small number of cases of occurrence NAB and ACB sequences is associated with the fact that smectic A is an unexpected type of mesophase among the compounds with both alkyloxy chains. Four mesophases are detected in 11 derivatives. The following sequences are observed: NACI (in 2 compounds), NCIG (in 4 compounds) and NACB (in 5 compounds). Only 2 derivatives have five mesophases (NACIG). The sequences NCIG and NACIG are not described by Demus and Richter [1].

The analysis of the mesophase sequence of 4-alkyloxybenzylidene-4′-alkyloxyanilines shows that the most common phases are nematic and tilted smectics C and I. All investigated compounds with the shortest chains have nematic phase. This mesophase becomes unstable for derivatives, for which the total length of both alkyloxy chains is from 16 to 19 carbon atoms.