Transition Bars and Related Honeycomb and Fingerprint Textures Exhibited by 12OBAC, 16OBAC and a Binary Mixture of Them

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ABSTRACT. By means of the polarized light microscopy, at the transitions between the smectic and nematic phase and between the smectic and the isotropic phase of some liquid crystals, we can observe the rising of transition bars and the presence of undulations in them. We can also see "honeycomb" and "fingerprint" textures as the evolution of the transition bars. Here, we will show some of these textures exhibited by compounds of the 4,n-alkyloxybenzoic (nOBAC) acid series. The compounds are 12OBAC, 16OBAC and a binary mixture of them. The binary mixture originates remarkable textures, which seem those of a modern art painting.

Introduction. The thermotropic liquid crystals are materials displaying one or more mesophases between the isotropic liquid and the solid phase. The mesophase sequence is observed when the temperature of the liquid crystal changes, that is, the mesophases are appearing according to a sequential ordering of molecular arrangements, mainly constrained by the molecular shape. For instance, in the case of rod-like molecules in it, the material can achieve a mesophase characterised by an orientational order of the long axes of molecules, passing in this manner from the isotopic to the nematic phase by decreasing the temperature. A further decrease of temperature can produce a smectic phase. In this mesophase, the order increases: besides the orientational order, the molecules are arranged in layered structures, in some cases with tilt (smectic C), or positional order within the layers, as observed in smectic B for instance [1-4].

Since the liquid crystal materials are strongly anisotropic, they possess optical birefringence. For this reason, these materials can be studied by means of a polarized light microscope, inserting the liquid crystal by capillarity in a cell made by two glass slides, with a gap between them ranging from 10 to 100 microns. The cell is placed in a thermostage, where the temperature drives the phase transitions of the material. The transitions are accompanied by beautiful phenomena, with sudden changes of colours and textures and a very rich formation of different patterns.

In this paper we show the appearance of transition bars and undulated textures during the observation of two 4,n-alkyloxybenzoic acids (12OBAC, 16OBAC) and a binary mixture of them. These acids are members of the family of compounds, some of which we investigated in [5-11]. The undulated textures, which are different from the well-known transition bars [4], appear at the isotropic-smectic phase transition of 16OBAC and at the nematic-smectic phase transitions of 12OBAC and of the binary mixture. As discussed in [11], these undulated textures look like those observed in the smectic C phase near a smectic C - smectic A transition, by Johnson and Saupe [12]. Similar undulations have also been found in the smectic A phase [13,14]. In this paper we will point out that, in the case of 12OBAC, the transition bars can also evolve in "fingerprint" and "honeycomb" textures, where the focal conic domains seem arranged in a honeycomb structure. For the binary mixture 12OBAC-

16OBAC, the transition bars rapidly evolve in fingerprints dressed by stripes. Honeycomb textures are also observed.

The binary mixture originates remarkable textures, which seem those of a modern art painting.

Alkyloxybenzoic compounds. The 4,n-alkyloxybenzoic acid (nOBAC) compounds have mesophases because their molecules are able to form hydrogen-bonded dimers, rigid and long enough to provide mesogenic conditions. The molecular structures of the closed and open dimers have been investigated in the framework of ab-initio calculations in Ref.15.

The monomeric units of the 4,n-alkyloxybenzoic acid (nOBAC) compounds are composed of two sterically distinct molecular parts, the oxybenzoic acid residue and the aliphatic chain (n is the number of carbon atoms in the aliphatic tail). The compounds with number n ranging from 3 to 6 have a nematic mesophase but not a smectic phase. From 7 to 18 carbon atoms in the alkyl tails, the smectic phase appears [16].

Some of the 4,n-alkyloxybenzoic acids possess the texture transition in the nematic phase [6-8,17]. Optical investigations in compounds with homologous index n ranging from 6 to 9, show a nematic phase subdivided in two sub-phases, characterized by different textures. The transition from one of the nematic sub-phases into the other, that is the texture transition, is considered as originated by the growth of cybotactic clusters in the nematic phase (the cybotactic clusters are groups of dimers possessing a short-range smectic order [18]).

Binary mixtures, approximately 1:1 in weight of 6OBAC with other members of the homologous series (7-, 8-, 9-, 12- and 16OBAC), have also the texture transition in the nematic phase [6]. It is remarkable to note that these binary mixtures exhibit an increase in the temperature ranges of the smectic and nematic phases. In these mixtures, the mesogenic units are dimers of the same acid (homodimers) but also hydrogen bonded pairs of two different acids (heterodimers) [18-21]. In spite of the microscopic disorder introduced by mixing two components, the polarized light microscope analysis of the liquid crystal cells reveals the texture transition [6]. This means a persistence of cybotactic clusters, also in the case of mixed dimers.

For the investigation of the transition bars and related textures, here we are using 12OBAC, 16OBAC and a binary mixture of them, approximately 1:1 in weight (52:48). In the Table I we report the characteristic features of these materials. 16OBAC compound does not possess a nematic phase. 12OBAC compound does not possess a texture transition in the nematic phase. In fact, the temperature range of nematic phase is quite narrow and at rather high temperature. The smectic-like nematic phase is suppressed, included in a wide smectic phase. This happens because the compound has rather long dimers. The binary mixture has a narrow temperature range for the nematic phase but a wide smectic range.

Table 1. Transition temperatures (in °C) of the two alkyloxybenzoic acid compounds and of their mixture, on heating and on cooling. 12OBAC does not show a texture transition in the nematic phase. 16OBAC exhibits just a smectic phase. The mixture does not exhibit the texture transition.

Compound	Transition temperatures (°C)
12OBAC	Cr – 65 – Cr – 91 – Sm – 131 – N – 138 – I I – 137 – N – 130 – Sm – 88 – Cr
16OCAC	Cr – 93 – Sm – 133 – I I – 132 – Sm – 88 – Cr
12OBAC-16OBAC	Cr – 71 – Sm – 132 – N – 138 – I I – 136 – N – 130 – Sm – 66 – Cr

All the compounds were inserted in the cell when the material was in the isotropic phase. The untreated glass surfaces of the cell walls were rubbed with cotton-wool, to favor a planar alignment. As previously told, the liquid crystal cells were heated and cooled in a thermostage and textures observed with a polarized light microscope.

16OBAC. This compound has so long molecules and so high transition temperatures that a nematic phase is not allowed. If we use this material we see a direct transition between isotropic and smectic phases. On cooling, the transition appears as a branched figure growing from the black field of crossed polarizers, as we can see in the Figure 1. In a slow cooling from the isotropic liquid phase, if the temperature is immediately fixed at the instant when the smectic phase starts its formation, undulated textures dressing the Schlieren texture can be observed near defects (Figures 1 and 2).

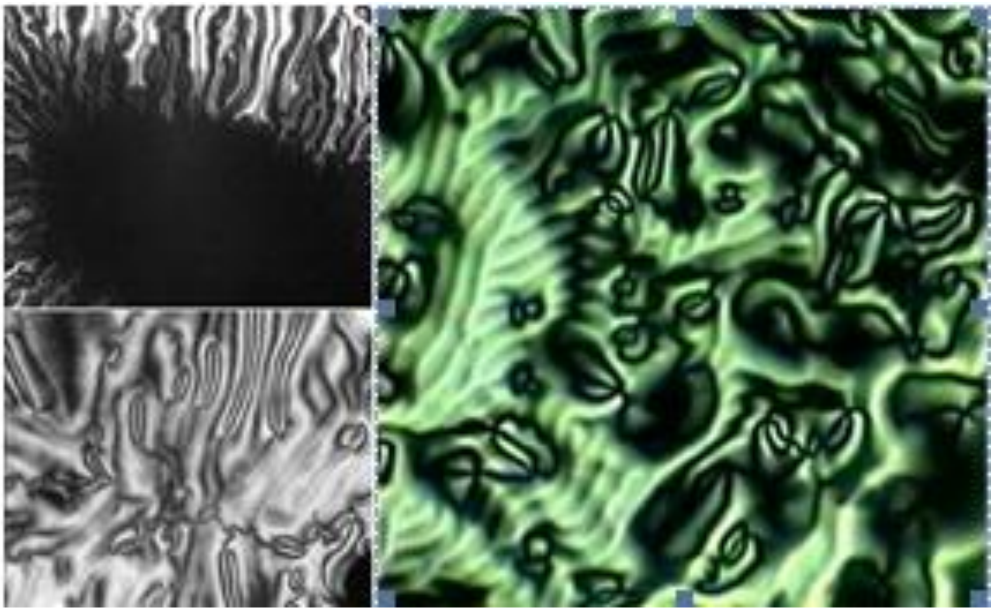

Fig. 1. 16OBAC compound has a transition directly from the isotropic phase in the smectic C phase. On the left, we can see the transition bars, which evolve in a Schlieren texture (the width of the images on the left is 1 mm). On the right, we are showing the periodic undulation appearing near the defects of 16OBAC smectic phase. The undulation is due to some stresses on the smectic planes (image on the right is 0.25 mm width).

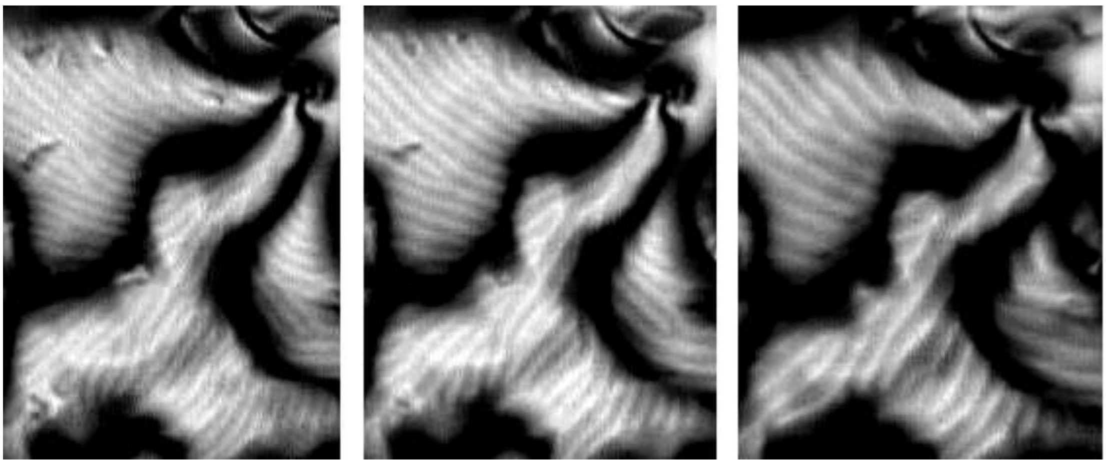

Fig. 2. The sequence shows an evolution of the decorative undulation near defects (16OBAC). From left to right, the temperature is lowered of one degree. The stripes are removed by a further decrease of the temperature.

Johnson and Saupe have observed undulation instabilities for the first time, when studying the transition from smectic C to smectic A [5]. As for those observed by Johnson and Saupe, the undulations are dressing the texture of the smectic phase. The undulations are considered as smectic layer undulated deformations, which appear due to the thermal stresses. In the smectic C of 16OBAC, we have observed that undulations are metastable, when the sample is kept at the same temperature for enough time [11]. We can see that they disappear due to the motion of dislocations. The image sequence in the Fig.2 shows the evolution of undulated texture when the temperature is lowered with a rate of 0.5 degree per minute. The period grows, and, when the temperature is further lowered of about two degrees, the undulated texture disappears.

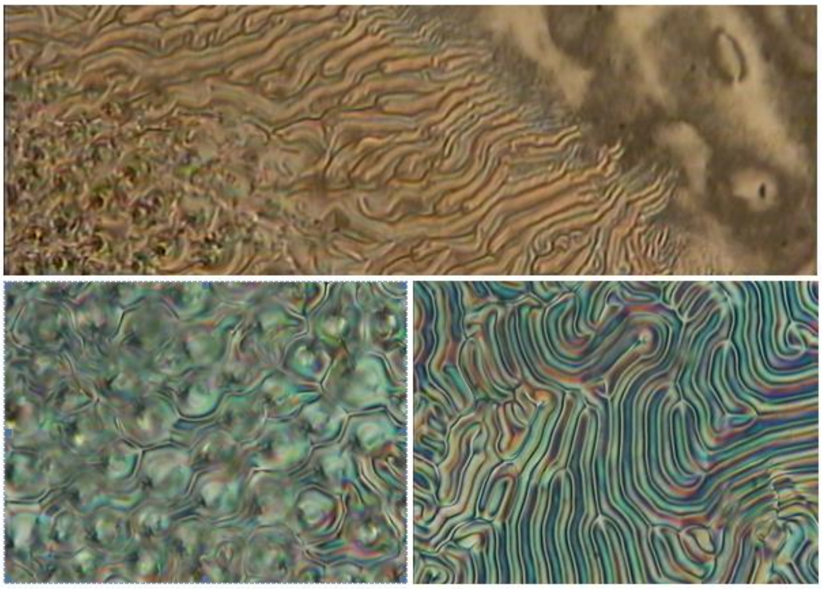

Fig. 3. In the upper panel we can see the transition bars exhibited by 12OBAC, which appear on cooling from the nematic phase. Image width is 1 mm. In the lower two panels, a "honeycomb" texture (on the left) and a "fingerprint" texture (on the right) are shown. These textures are observed in the sample, when the temperature is maintained constant as soon as the transition bars are observed.

12OBAC. In this material, dimers are long enough to maintain the smectic order until a high temperature is reached.

On cooling, the nematic phase appears at 137°C. Then we can see the coloured nematic bubbles display themselves in the black field of the microscope. Under a further lowering of temperature, the smectic phase appears at 130°C. Of the undulations in the smectic texture, we have discussed in [11]. Here we concentrate on the transition bars at the nematic-smectic transition. We can see a beautiful example of transition bars growing in the nematic phase in the upper panel of the Figure 3.

Actually, on cooling the sample, if the temperature is fixed just 0.5-1 degree below the nematic-smectic transition, the transition bars are observable. We can also observe their evolution into "honeycomb" and "fingerprint" textures. These textures are given in the lower panels of the Figure 3. One of the textures is defined "honeycomb", because it seems that the boundaries among domains have hexagonal patterns. Two other examples of "honeycomb" textures are given in the Figures 4 and 5.

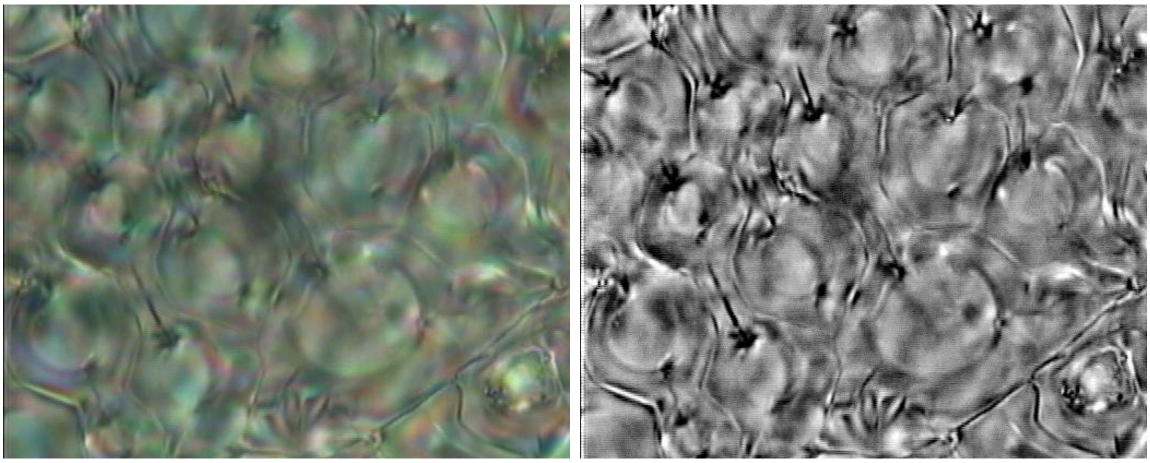

Fig. 4. Honeycomb texture. In the left panel, the original image. In the right panel, the same image in grey tones, enhanced by means of the GIMP Retinex filter.

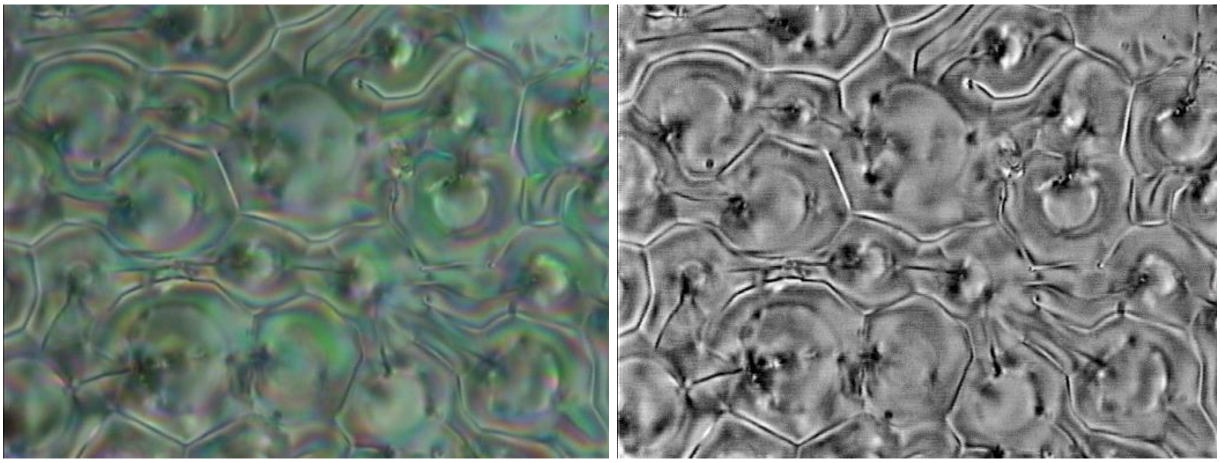

Fig. 5. Another example of the honeycomb texture. In the lower panel, the image in grey tones has been enhanced by means of the GIMP Retinex filter.

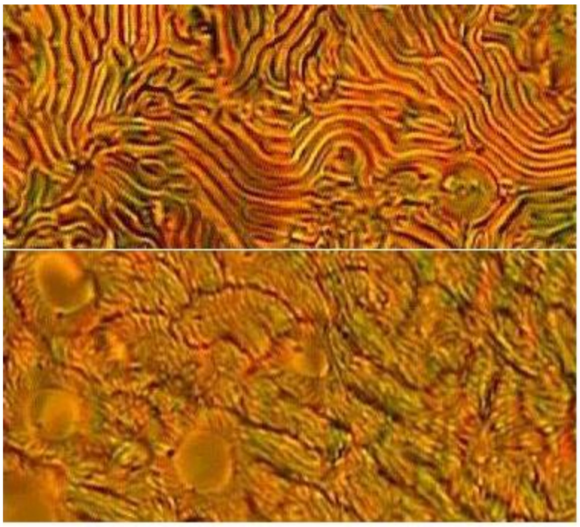

Fig. 6. In the upper panel we can see the fingerprint texture at the transition from the nematic to the smectic phase of the binary mixture 12OBAC-16OBAC. Stopping the decrease of the temperature as soon as we see the passage of fingerprints, we can observe the texture in the lower panel (image 0.5 mm width).

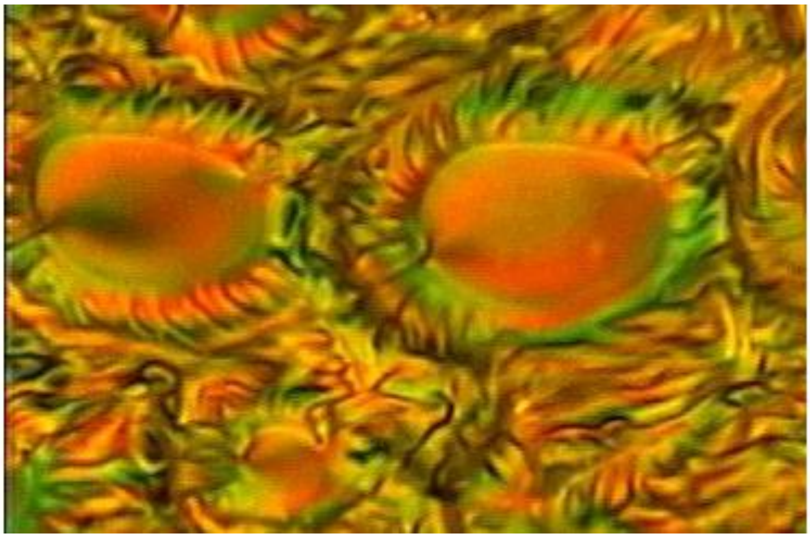

Fig. 7. In another part of the same sample shown in Figure 6, we can see some focal conic domains surrounded by the transition bars.

Binary mixture. The mixture 1:1 in weight of 12OBAC and 16OBAC has a clearing point at 138°C and a transition from smectic to nematic at 132°C. The smectic range, as shown by Table I, is wider, twenty degrees more than that of the single compounds. As previously told, the increase of smectic range in the case of binary mixtures of alkyloxybenzoic acids is an interesting phenomenon, observed for mixtures of 6OBAC with 7-,8-,9-,12- and 16OBAC [13].

Transition bars are very beautiful and with a rapid evolution in a fingerprint patter. If the temperature is stopped when the fingerprint appears, we can observe that periodic instabilities are decorating the texture and the domains (see Figure 6). The behaviour of these instabilities is the same as that of 12OBAC instabilities [11].

We can also observe some focal conic domains surrounded by the transition bars, in the manner shown in the Figure 7.

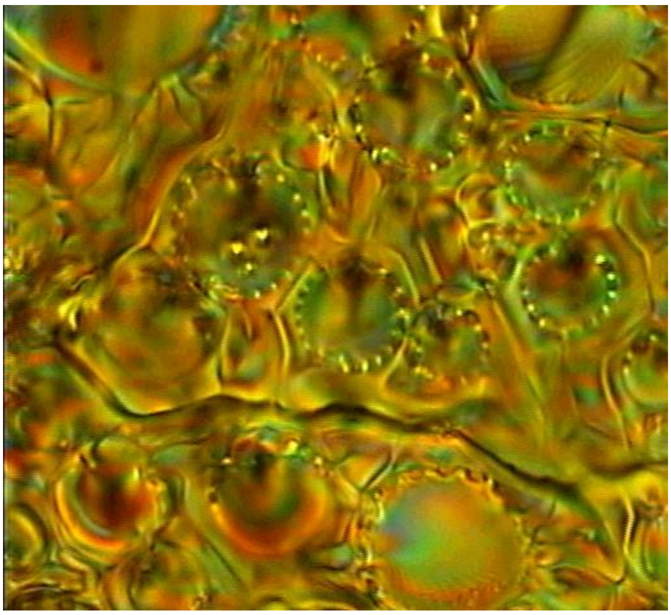

Fig. 8. It is possible to observe some “honeycomb” domains also in the binary mixture.

Let us note that, as shown by the Figure 8, it is also possible to observe some "honeycomb" domains. As in the case of 12OBAC, the smectic phase can have focal conic domains. For the binary mixture, these domains are surrounded by period patterns, merged in the fingerprints, as given in the image of Fig.7. The decrease of temperature destroys the periodic pattern and the fingerprints. In the Figure 9, we give two other examples of focal conic domains merged in fingerprints in the smectic phase of the binary mixture. The binary mixture originates remarkable textures, which seem those of a modern art painting.

The Figure 10 is also showing a remarkable similarity between 12OBAC and the binary mixture 12OBAC/16OBAC. Both materials have focal conic domains arranged in hexagonal distribution.

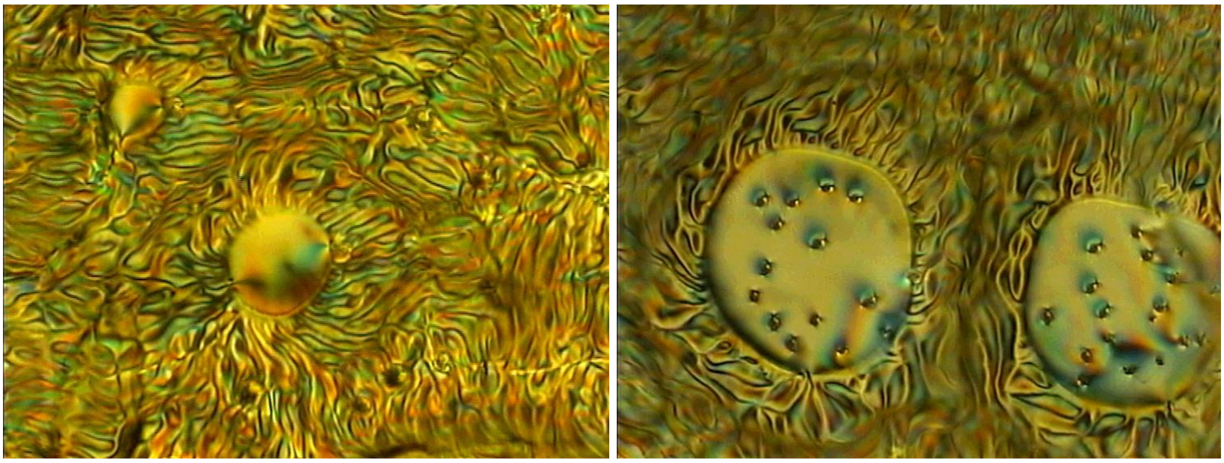

Fig. 9. Focal conic domains in the smectic phase of binary mixture 12OBAC-16OBAC, merged in the fingerprints. The width of images is 1 mm. Sometimes we can see defects looking like "eyes" in the domains.

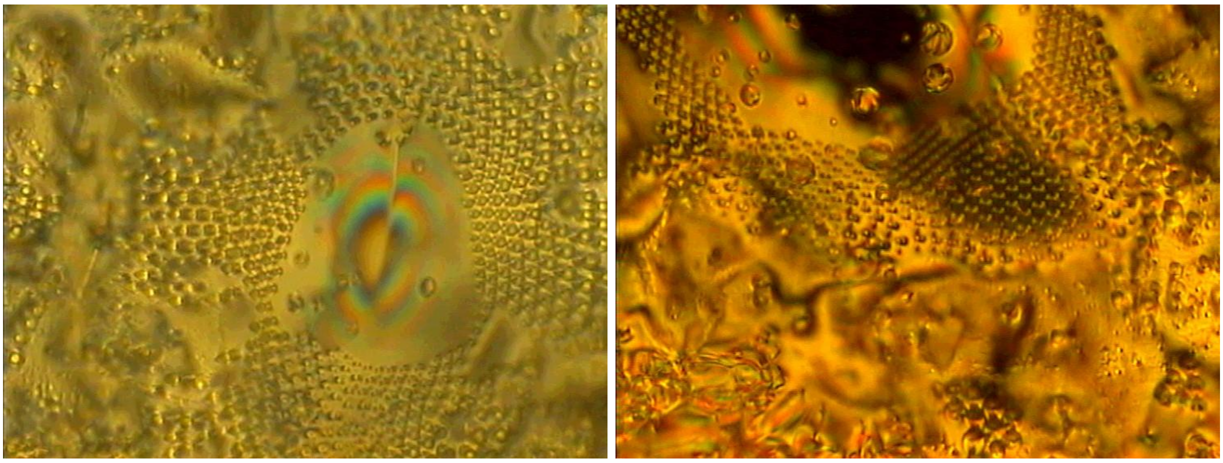

Fig. 10. Focal conic domains with hexagonal arrangement in the smectic phase of 12OBAC (left panel) and of the binary mixture 12OBAC-16OBAC (right panel).

Summary. The alkyloxybenzoic compounds that we have here considered have a similar behaviour, that is, they show the appearance of an undulated texture, dressing the smectic texture. The binary mixture has undulations too, decorating a fingerprint texture.

In the binary mixture, the fingerprints are substituting the usual transition bar. Let us remember that in this material the molecular disorder is increased, as shown by the wider smectic range given in the Table I. Actually, the melt of the nematic phase is composed of monomers, and open and closed homo- and heterodimers. After the transition in the smectic phase, the presence of homo- and heterodimers, with rather different lengths, persists. This intrinsic disorder increases the smectic range. The fact that a cholesteric-like texture (the fingerprint) is observed near the nematic-smectic transition could be due to a chiral-like behaviour of heterodimers, probably of the open ones.

The chiral-like behaviour is suppressed by a further decrease of temperature, because open dimers turn into closed dimers.

References

[1] de Gennes, P. G., & Prost, J. (1993). The Physics of Liquid Crystals. Clarendon Press, Oxford. ISBN-13: 978-0198517856

[2] Chandrasekhar, S. (1992). Liquid Crystals. Cambridge University Press. DOI 10.1017/CBO9780511622496

[3] Gray, G., & Goodby, J. (1984). Smectic Liquid Crystals. Leonard Hill, Glasgow and London. ISBN-10: 0863440258, ISBN-13: 978-0863440250

[4] Demus, D., & Richter, L. (1978). Texture of Liquid Crystals, VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig.

[5] Sparavigna, A., Mello, A., & Montrucchio, B. (2006). Texture transitions in the liquid crystalline alkyloxybenzoic acid 6OBAC. Phase Transitions, 79(4-5), 293-303. DOI 10.1080/01411590600748132

[6] Sparavigna, A., Mello, A., & Montrucchio, B. (2007). Texture transitions in binary mixtures of 6OBAC with compounds of its homologous series. Phase Transitions, 80(3), 191-201. DOI 10.1080/01411590601007603

[7] Frunza, L., Frunza, S., Petrov, M., & Sparavigna, A. C. (1996). Dielectric and DSC investigations of 4-n-substituted benzoic and cyclohexane carboxylic acids. 1. Textural changes in homologous 4-n-alkoxybenzoic acids. Molecular Crystals and Liquid Crystals, 6(3), 215-223.

[8] Montrucchio, B., Sparavigna, A., & Strigazzi, A. (1998). A new image processing method for enhancing the detection sensitivity of smooth transitions in liquid crystals. Liquid crystals, 24(6), 841-852. DOI 10.1080/026782998206669

[9] Strigazzi, A., Sparavigna, A. C., Torgova, S. I., Montrucchio, B., & Sanna, A. (1998). Chiral mesoscopic structure of the nonchiral liquid crystal OOBA. National Conference on Physics of Matter – INFMeeting, Rimini, 25-30 Giugno, 1998

[10] Torgova, S.I., Sparavigna, A., & Strigazzi, A. (2000). Chiral Textures Formed by Achiral p-Substituted Biphenylcarboxylic and Benzoic Acids, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 352:1, 111-118, DOI 10.1080/10587250008023167

[11] Sparavigna, A., Mello, A., & Massa, G. (2009). Undulation textures at the phase transitions of some alkyloxybenzoic acids. Phase Transitions, 82(5), 398-408. DOI 10.1080/01411590902898874

[12] Johnson, D., & Saupe, A. (1977). Undulation instabilities in smectic C phases. Physical Review A, 15(5), 2079. DOI 10.1103/physreva.15.2079

[13] Delaye, M., Ribotta, R., & Durand, G. (1973). Buckling instability of the layers in a smectic-A liquid crystal. Physics Letters A, 44(2), 139-140. DOI 10.1016/0375-9601(73)90822-0

[14] Clark, N. A., & Meyer, R. B. (1973). Strain-induced instability of monodomain smectic A and cholesteric liquid crystals. Applied Physics Letters, 22(10), 493-494. DOI 10.1063/1.1654481

[15] Bobadova-Parvanova, P., Parvanov, V., Petrov, M., & Tsonev, L. (2000). Molecular structure of the nematic liquid crystals made by hydrogen bonded in dimers molecules. Crystal Research and

Technology, 35(11-12), 1321-1330. DOI: 10.1002/1521-4079(200011)35:11/12%3C1321::aid-crat1321%3E3.3.co;2-3

[16] Bryan, R. F., Hartley, P., Miller, R. W., & Shen, M. S. (1980). An X-Ray Study of the p-n-Alkoxybenzoic Acids. Part VI. Isotypic Crystal Structures of Four Smectogenic Acids Having Seven, Eight, Nine, and Ten Alkyl Chain Carbon Atoms. Molecular Crystals and Liquid Crystals, 62(3-4), 281-309. DOI 10.1080/00268948008084027

[17] Petrov, M., Braslau, A., Levelut, A. M., & Durand, G. (1992). Surface induced transitions in the nematic phase of 4-n octyloxybenzoic acid. Journal de Physique II, 2(5), 1159-1193. DOI 10.1051/jp2:1992194

[18] De Vries, A. (1970). X-ray photographic studies of liquid crystals I. A cybotactic nematic phase. Molecular Crystals and Liquid Crystals, 10(1-2), 219-236. DOI 10.1080/15421407008083495

[19] Dhar, R., Pandey, R. S., & Agrawal, V. K. (2002). Optical and thermodynamic studies of binary mixtures of nematic liquid crystals from homologous members of alkyloxybenzoic acid. Indian journal of pure & applied physics, 40(12), 901-907.

[20] Kang, S. K., & Samulski, E. T. (2000). Liquid crystals comprising hydrogen-bonded organic acids I. Mixtures of non-mesogenic acids. Liquid Crystals, 27(3), 371-376. DOI 10.1080/026782900202822

[21] Herbert, A. J. (1967). Transition temperatures and transition energies of the p-n-alkoxy benzoic acids, from n-propyl to n-octadecyl. Transactions of the Faraday Society, 63, 555-560. DOI 10.1039/tf9676300555