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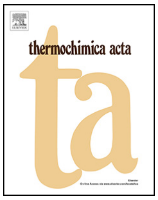

Monotropic or enantiotropic mesophases? Liquid-crystalline and solid state polymorphism 4-Chloro-1,3-phenylene bis-[4-(4-alkyloxyphenylazo)benzoates

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ABSTRACT

This article presents a homologous series of bent-core molecules consisting of a 4-chlororesorcinol as a central unit and 4-[(4-alkyloxyphenyl)diazenyl]benzoic acids as wings. With the use of polarizing optical microscopy (POM), thermal analysis (TOA) and differential scanning calorimetry (DSC) the mesogenic properties were detected. Furthermore, the X-ray diffraction (XRD) measurements were also performed for selected samples. Compounds of the above mentioned series form nematic, B_6, and smectic C mesophases. An interesting phenomenon in the solid phase polymorphism was observed in some cases. In our experiment one crystalline form (CrI) melts to nematic phase while the second form (CrII) melts at higher temperature directly to isotropic phase. The solid state modification determines whether a monotropic and an enantiotropic mesophase is observed.

1. Introduction

Azo compounds constitute a large branch of the liquid crystals sciences. In addition to a variety of possible applications, azo dyes have very interesting physical, chemical, and liquid-crystalline properties, which were investigated for many years, [1,2] also at our university [3–9]. Further studies and the ability to control isomerization process make this group a very interesting research object [10]. The sensitivity to light allows azo compounds to be used as components of advanced polymers that form a broad group of photo-sensitive smart materials [11,12]; as well as they can be applied as a holographic grid in modern optoelectronics [13,14]. Furthermore, the above described compounds can also provide a good linking unit in novel bent-core molecules.

The first banana-shaped compounds were synthesized in 1929 [15,16]. However, the real development of research on bent-core liquid crystals occurred only in 1997 after Niori and his co-workers pioneered publication on the polar properties of such type molecules [17,18]. Interesting features and possible applications [19,20] allowed banana-shaped compounds to be synthesized and studied extensively in many research centers.

New bent-core molecules are created in order to achieve a rich liquid-crystalline polymorphism as well as interesting optical and physicochemical properties. As the central unit of banana-shaped mesogens many substances were applied including resorcinol and its mono- and polysubstituted derivatives [21]. Schematic structure composed of a core and wings allows the synthesis of a large number of compounds using a variety of linking and lateral groups. The most common linking group is an ester linkage [22–24]. Moreover, commonly used are also Schiff bases [25–28] and in recent years azobenzenes [29,30]. Also the effects of substituent in the aromatic rings of the wins were also extensively researched [31,32].

The goal of our study, was the synthesis and investigation of mesogenic properties of five ring bent-core compounds based on the 4-chlororesorcinol and the azo group included in the 4-[(4-alkyloxyphenyl)diazenyl]benzoic acids. In addition, we wanted to determine the influence of the length of alkyloxy chain on the liquid-crystalline properties of our substances. Five members of this series (Res-8, Res-10, Res-12, Res-14 and Res-16) were recently described by Tschierske's group [33].

2. Experimental

2.1. Measurements setup

Chemical structure of synthesized compounds was checked by two methods: elemental analysis (EA) and nuclear magnetic resonance spectroscopy (NMR). EA measurements were carried out

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with the Vario EL III elemental analyzer. All NMR spectra were measured with the Bruker Avance III 500 MHz high resolution spectrometer with the use of deuterated chloroform ($CDCl_3$) as the solvent.

For mesogenic properties investigation we used polarized optical microscopy (POM), thermo-optical analysis (TOA) [34] and differential scanning microscopy (DSC). All calorimetric measurements were made using the Perkin Elmer 8500 calorimeter in nitrogen atmosphere. Scan rate amounted to 10 K min $^{-1}$.

Textures and liquid-crystalline phase transitions were observed by the Olympus polarized light microscope BX61-P (TRF). Additional elements of the thermo-optical analysis (TOA) are: the Linkam heating stage and the Motic digital camera. For selected samples XRD studies were conducted in reflection mode. XRD wide angle measurements of the samples, which were prepared as drops on heating plate, were performed with the Bruker D8 GADDS system with an additional LINKAM heating stage.

2.2. Synthesis

Main root of synthesis of 4-Chloro-1,3-phenylene bis-[4-(4-alkyloxyphenylazo)benzoates] is shown in Fig. 1. The most important of the above mentioned synthesis is diazotization reaction, which we also performed, this reaction is quite popular and frequently used to create a double chemical bond between the two nitrogen atoms [33–41]. Ethyl 4-aminobenzoate, 4-chlororesorcinol and other inorganic substrates were obtained from commercial sources and used as obtained. Progress of the reaction was checked using thin layer chromatography (TLC) with aluminum plates covered with silica gel and dichloromethane as the eluent.

2.2.1. Synthesis of ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate **(2)**:

Ethyl 4-aminobenzoate **(1)** (50 g, 0.303 mol) was dissolved in 1 M aqueous HCl and kept in the ice bath at 0–5 °C. $NaNO_2$ (20.9 g,

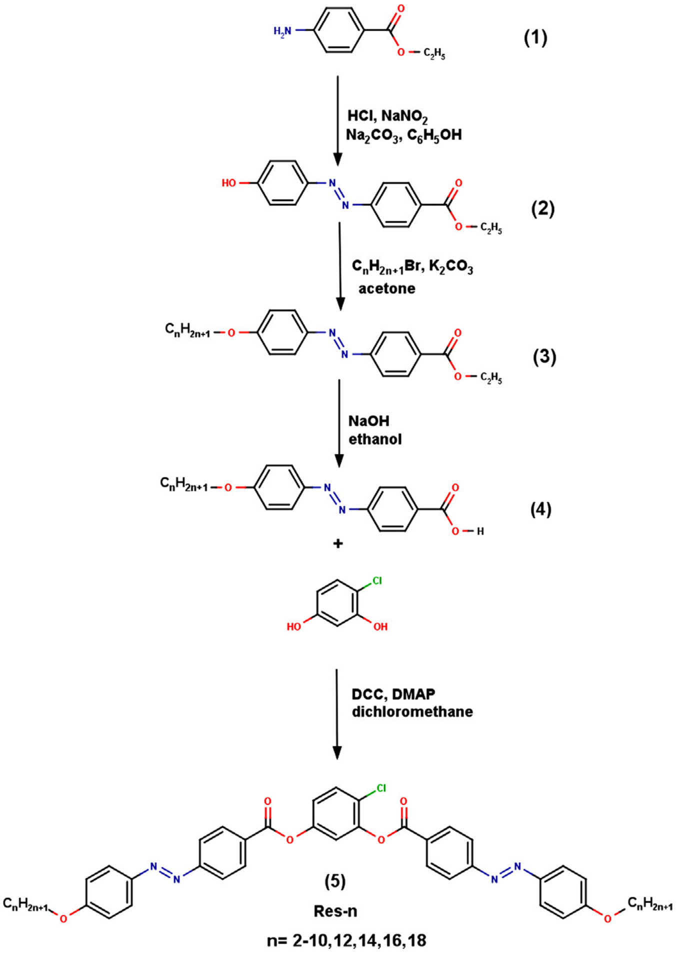

Fig. 1. Main root of synthesis 4-Chloro-1,3-phenylene bis-[4-(4-alkyloxyphenylazo)benzoate].

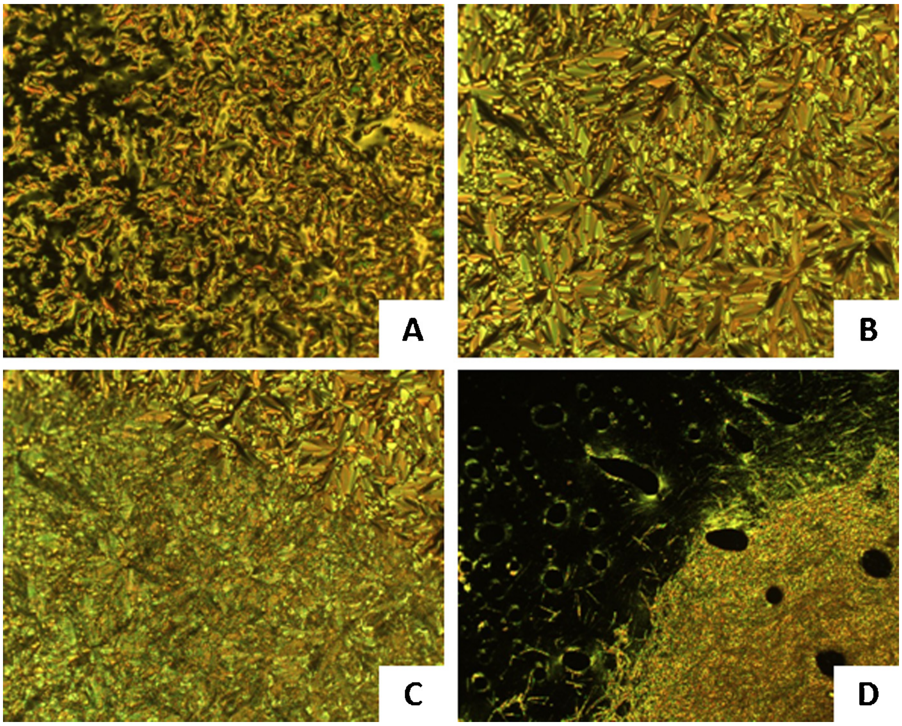

Fig. 2. Textures of Res-2 seen by polarizing microscopy. (A) Nematic texture. (B) B_6 mesophase texture. (C) Crystallization of CrI from B_6 phase during cooling. (D) Crystallization process of CrII from nematic phase during heating.

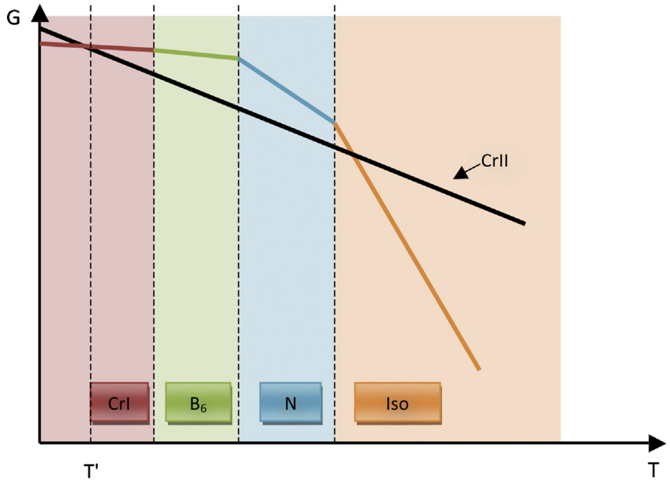

Fig. 3. Schematic diagram of G(T) for Res-2.

0.303 mol), dissolved in a minimum amount of water, which was added dropwise to the ethyl 4-aminobenzoate and HCl mixture to produce a diazonium salt solution. Sodium carbonate (53.0 g 0.500 mol) and phenol (28.5 g 0.303 mol) were dissolved in 200 ml water cooled to less than 5 °C and then earlier prepared, cooled diazonium salt solution was added dropwise. Resulting mixture was stirred for 3 h at 0–5 °C and next neutralized with diluted HCl resulting with yellow crude product. Then it was filtered off and air-dried. Yield: 70.9 g (88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, 2H), 7.93 (d, 4H), 7.00 (d, 2H), 4.45 (q, 2H), 1.45 (t, 3H).

*2.2.2. Synthesis of ethyl 4-[(4-ethoxyphenyl)diazenyl]benzoate **(3)***

Compound **(2)** (10 g, 0.037 mol), ethyl bromide (16.2 g, 0.09 mol), K_2CO_3 (2.5 g) were all dissolved in 200 ml of acetone. The mixture was refluxed for 24 h. After evaporation of acetone the achieved mixture was dissolved in dichloromethane. Potassium carbonate was filtered off and dichloromethane was evaporated. The crude product was purified using flash chromatography (silica gel Fluka 60 mash and dichloromethane) and recrystallized from hexane. Yield: 54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.95 (d, *J* = 8.9 Hz, 4H), 7.04 (d, *J* = 9.0 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* 7.1 Hz, 6H). Other 4-[(4-alkyloxyphenyl)diazenyl]benzoates were synthesized according to procedure described above.

*2.2.3. Synthesis of 4-[(4-ethoxyphenyl)diazenyl]benzoic acid **(4)***

Compound **(3)** was dissolved in EtOH and NaOH (1 g, 0.025 mol) was added. Mixture was refluxed for 24 h and after cooling to room temperature was acidified with diluted HCl. After vacuum filtration the crude product was twice recrystallized from acetic acid. Yield: 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.97 (d, *J* =8.9 Hz, 4H), 7.04 (d, *J* = 9.0 Hz, 2H), 4.17 (q, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 7.0 Hz, 3H). Other 4-[(4-alkyloxyphenyl)diazenyl]benzoic acids were synthesized according to procedure described above.

*2.2.4. Synthesis of 4-Chloro-1,3-phenylene bis-[4-(4-alkyloxyphenylazo)benzoates] **(5)***

The 4-chlororesorcinol (0.08 g, 0.59 mmol), appropriate 4-[(4-alkyloxyphenyl)diazenyl]benzoic acid **(4)** (1.18 mmol), N,N′-Dicyclohexylcarbodiimide (DCC) (0.24 g, 1.18 mmol) and, a pinch of 4-Dimethylaminopyridine (DMAP) were dissolved in dichloromethane and stirred at room temperature for about 24 h. After evaporation of solvent the orange precipitate was purified with the use of gel column chromatography with dichloromethane as the eluent. Solvent was removed using evaporator and recrystallized from hexane. Yield: 27%–91%. Res-2: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.7 Hz, 2H), 8.33 (d, *J* = 8.7 Hz, 2H), 8.03–7.97 (m, 8H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.04 (dd, *J* = 9.0, 1.2 Hz, 4H), 4.16 (q, *J* = 7.0 Hz, 4H), 1.48 (dt, *J* = 6.9, 3.4 Hz, 6H). Elemental analysis: calc.: N 8.63%, C 66.61%, H 4.50%, Cl 5.46%, O 14.79%. Found: N 8.52% (Δ 0.11), C 66.44% (Δ 0.17), H 4.48% (Δ 0.02).

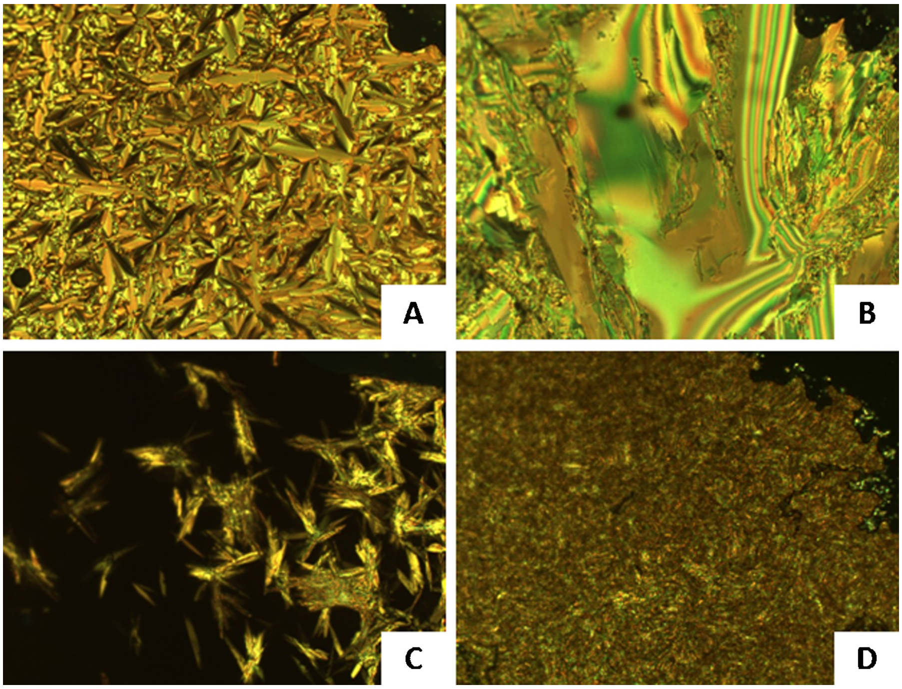

Fig. 4. Textures of 4-Chloro-1,3-phenylene bis-[4-(4-propyloxyphenylazo)benzoate]. (A) Texture of B_6 mesophase. (B) Crystals CrI. (C) Crystallization of CrII from isotropic phase seen under polarizing microscope during heating. (D) Crystals of CrII.

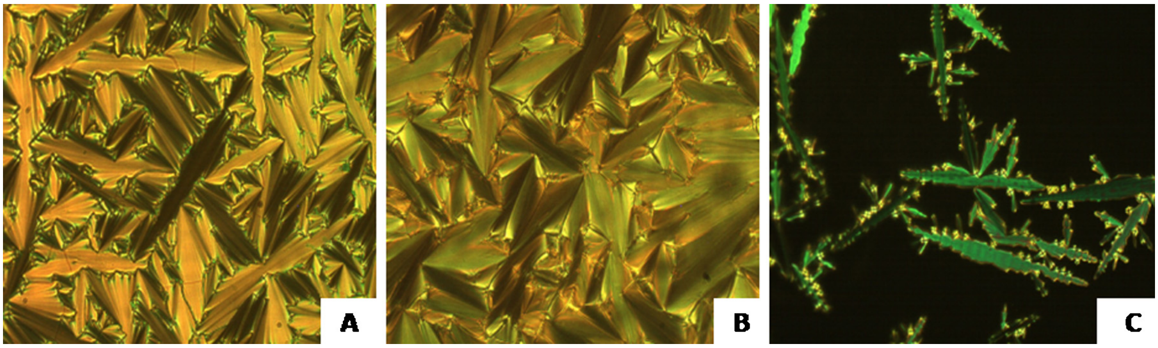

Fig. 5. Various textures of banana mesophase B$_6$ observed in 4-chlororesorcinol derivatives. (A) Focal-conic fan shaped texture of Res-2. (B) Fan shaped texture of Res-4. (C) The appearing of battones and coalescales from the isotropic of compound Res-8.

All NMR and elemental analysis data of other Res-n compounds are included in the supplementary data.

3. Results and discussion

The 4-Chloro-1,3-phenylene bis-[4-(4-alkyloxyphenylazo)benzoates] have very interesting liquid-crystalline properties. During our investigation of these compounds we found 4 mesophases: nematic, smectic C, banana mesophase B$_6$ and unknown phase X.

Even the shortest homologue of this series, Res-2, is mesomorphic. Despite the relatively high melting point (179.5 °C) we observed both enantiotropic nematic (Fig. 2A) and monotropic B$_6$ phase, which forms characteristic focal-conic fan-shaped texture. In the cooling mode we observed under a polarizing microscope phase transition from the isotropic phase to a nematic, and then to the banana phase and then crystallization results. This phenomenon is a very complex process.

Obtained crystalline form (Fig. 2C) named CrI was formed during cooling with scan rate of 10 K min^{-1}. This sample was next heated at the same rate. Then we saw the sample melt to the nematic phase and next changed to the isotropic phase. While keeping the system for some time in temperature range of a nematic phase we observed crystallization process of other crystalline form, CrII (Fig. 2B), which is characterized by higher melting point (193.5 °C) than temperature of Iso-N phase transition. As a consequence, CrII during heating does not show liquid-crystalline properties. We also have cooled our sample using scan rate of 5 K min^{-1}. Then we noticed nematic and B$_6$ mesophases, crystallization of CrI form and then slow growing of crystals CrII. To this behaviour we can give thermodynamic explanation proposed by Gibbs' function depending upon the temperature (shown in Fig. 3). Supercooling of the system during the measurements at low speed causes that form CrII is thermodynamically more stable above a certain temperature T'. Slow cooling of the sample favors the formation of crystals CrII (above T'). In fast cooling mode we can cool the sample below T' temperature without the transformation to CrII. So CrI in this temperature range is more stable. It means that the chemical potential of CrI (μ_{CrI}) is less than the chemical potential of CrII (μ_{CrII}) $\mu_{\mathrm{CrI}} < \mu_{\mathrm{CrII}}$

Next homolog, 4-Chloro-1,3-phenylene bis-[4-(4-propyloxyphenylazo)benzoate], has only monotropic B$_6$ phase and significantly lower melting point in relation to the Res-2. Despite the absence of a nematic phase as in the previous case, we observed a polymorphism of the solid phase. For this compound we can use the same explanation as for the Res-2. Quick cooling (50 K min^{-1}) promotes the formation of a form CrI having a lower clearing point, possessing texture as shown in Fig. 4A. Slow rate of cooling allows creation of the second crystalline form CrII (Fig. 4B) from B$_6$. In addition, this form (CrII) crystallizes from the isotropic phase during fast heating (Fig. 4C).

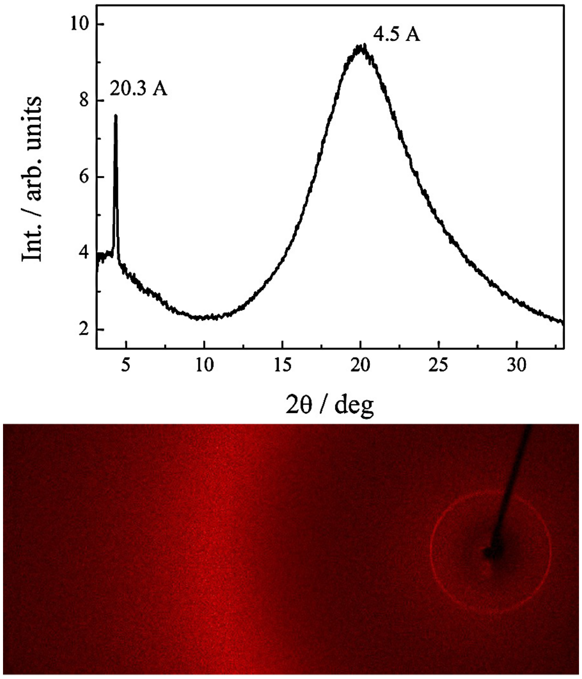

Fig. 6. The XRD measurements of Res-6.

Compounds with an average alkyloxy chain length (from $n = 4$ to $n = 8$) manifest the liquid-crystalline properties in form of one monotropic banana type B$_6$ phase. This mesophase can form both focal-conic (as for $n = 2$, Fig. 5A) as well as fan-shaped texture (for $n = 4$, Fig. 5B), which appears from isotropic as battones and coalescales (as for $n = 8$, Fig. 5C). To confirm phase assignment XRD

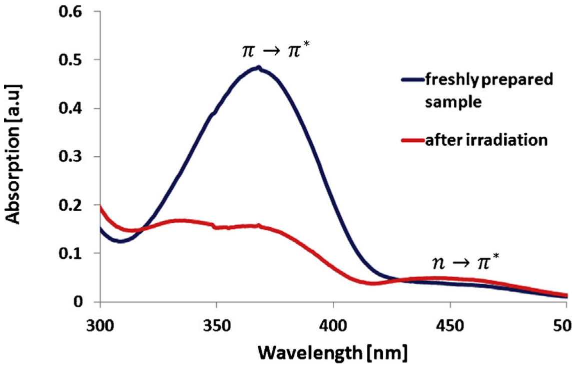

Fig. 7. The UV–Vis spectra obtained for Res-5 for freshly prepared sample and after irradiation.

Table 1
Temperatures of phase transitions of 4-Chloro-1,3-phenylene bis-[4-(4-alkyloxyphenylazo)benzoate] obtained during cooling mode.

n	Melting CrI	Melting CrII	Crystallization (to CrI)	B_6		X		SmC		N		Iso
2	179.5[c]	193.5[c]	142.4 [34.32]	•	(167.5) [3.54]					•	186.7 [0.56]	•
3	159.2[c]	162.9[c]	131.1 [36.00]	•	(158.7) [8.40]							•
4	163.3 [45.21]	–	131.5 [31.55]	•	(156.5) [8.94]							•
5	143.1 [42.14]	–	91.6 [24.74]	•	(137.5) [9.79]							•
6	137.2 [47.65]	–	85.5 [17.90]	•	(130.5) [10.95]							•
7	125.3[b]	–	75.6[b]	•	(115.6) [10.76]							•
8	115.0 [53.22]	–	84.5 [14.24]	•	(105.8) [9.56]							•
9	104.4[c]	110.0[c]	82.1 [21.66]	•	(91.3) [6.97]					•	95.3 [0.64]	•
10	96.8[c]	105.0[c]	78.0 [32.80][a]	•	(79.6) [32.80][a]					•	96.2 [0.22]	•
12	89.1[c]	102.7[c]	79.8 [32.80]							•	96.9 [0.63]	•
14	93.1[c]	104.0[c]	82.9 [42.85]							•	96.2 [0.83]	•
16	96.0[c]	103.8[c]	87.2 [47.25]			•	89.4 [0.50]			•	100.6 [1.18]	•
18	97.9[c]	104.0[c]	89.0 [49.71][a]			•	92.9 [49.71][a]	•	(98.4) [4.35][a]	•	101.3 [4.35][a]	•

[a] Enthalpy is given together for two phase transitions due to overlapping of peaks.
[b] Enthalpy could not be measured because of slow crystallization process.
[c] Quantitative calorimetric measurements are not possible because of the presence of both crystalline form at the same time.

studies were performed for the selected compound (*n* = 6, 4-Chloro-1,3-phenylene bis-[4-(4-hexyloxyphenylazo)benzoates]). In B_6 mesophase single sharp diffraction peak was observed at low angle region and a broad diffused signal in high angle range (Fig. 6). The smectic layer thickness, 20.3 Å, evaluated from low angle signal corresponds to half of the molecular length (43 Å) evidencing strong intercalation typical for B_6 phase. Res-8 has also been recently investigated by Halle's group (Germany). Our phase transitions temperatures for this compound presented in Table 1 which are fully consistent with Halle's [33]. For 4-Chloro-1,3-phenylene bis-[4-(4-pentyloxyphenylazo)benzoate] we also measured UV–Vis spectrum. We prepared a 10^{-5} M solution of Res-5 in dichloromethane. First, we measured the spectrum of a freshly prepared solution, which was then exposed for 20 min irradiation ($\lambda = 365$ nm). Then we measured spectrum directly after irradiation. Collected spectra (shown in Fig. 7) demonstrate that the light

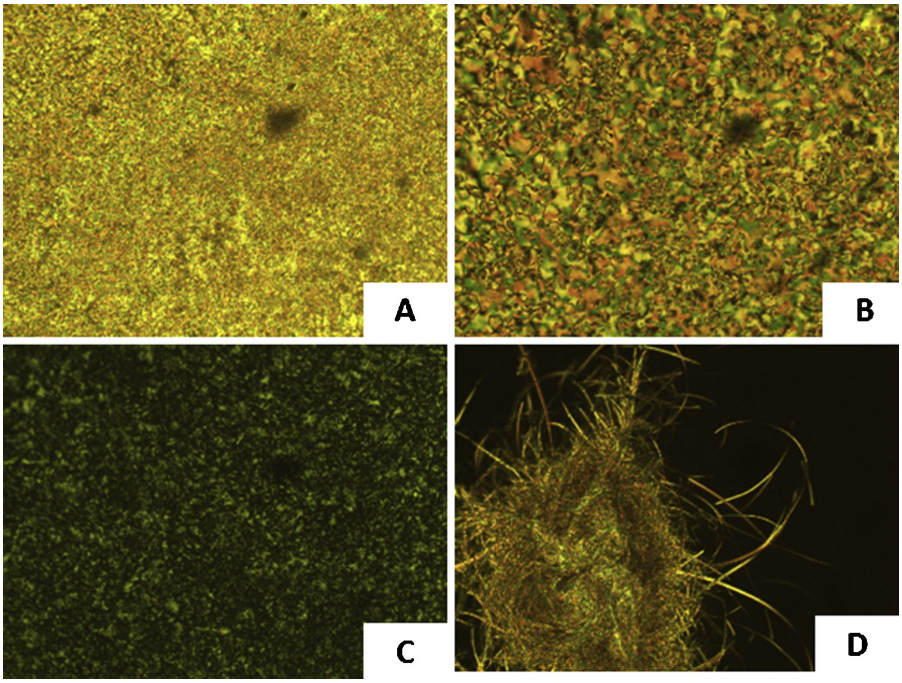

Fig. 8. Polarizing microscopy textures of Res-16. (A) Mesophase X. (B) Nematic texture. (C) Texture of CrI. (D) Crystals of CrII.

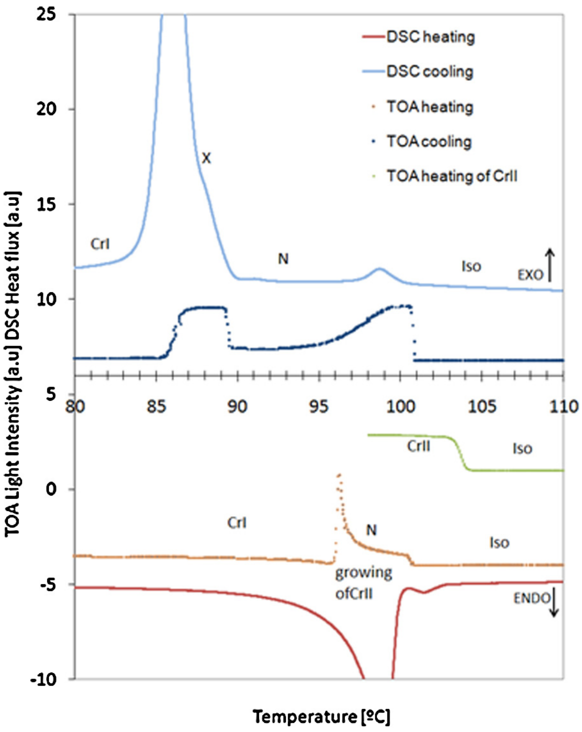

Fig. 9. The DSC and the TOA diagram of Res-16.

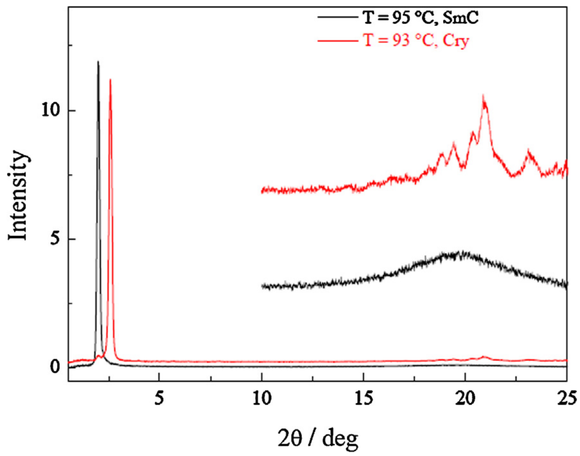

Fig. 10. The XRD measurements of Res-18, which confirm SmC mesophase.

influences on azo-bond isomerization (from trans to cis form). This process is confirmed by the appearance of a broad band at about 480 nm corresponding to the n–π^* transition. There is also a visible change in the band intensity at 370 nm, which corresponds to the transition π–π^*. As in [33], we left overnight the irradiated sample in the dark. Obtained spectrum was the same as before irradiation. Sample returned to a more stable trans isomer. Comparing the spectrum of the Res-5 with Res-16 [33], we may conclude that the alkyl chain length does not affect the position of the bands.

Chain elongation favors the formation of the nematic phase and but it has negative effect on more ordered smectic B_6 phase. For nonyl and decyl derivatives TOA and DSC studies showed the presence of both mesophases: nematic and B_6. However, for Res-10 banana-type phase temperature range is very narrow, (1.6 °C). This homolog is a compound with the longest alkyloxy chain, within the B_6 mesophase is present. It is also worth mentioning that the appearance of the nematic phase from the Res-9 induces solid-state polymorphism, as in the case of Res-2. Also in the case of Res-10 we obtained the phase transition temperatures comparable with the results of Alasaar et al. [33].

In the next two homologous series of 4- chlororesorcinol Res-12 and Res-14 nematic phase and solid phase polymorphisms were observed. As in the previous compounds Res-2 and Res-10 the liquid-crystalline phase is relative, enantiotropic or monotropic. For this series of compounds the nature of the nematic mesophase depends on the crystalline type. For CrI we observe the characteristic nematic texture during both heating and cooling processes. However, for the form CrII mesophase is a monotropic, therefore it is only observed at cooling. Phase transition temperatures of Res-12, Res-14 and Res-16, that we present (Table 1) are consistent with those given by Alasaar et al. [33] and are within the experimental error.

Also the investigation of mesogenic properties of homologues with the longest chain ($n = 16$, $n = 18$) showed some interesting phenomena. Firstly, the solid phase polymorphism is observed. Secondly, for Res-16 and Res-18 there is visible under the polarizing microscope a very narrow phase X (Fig. 8A). This mesophase occurs during cooling just prior to crystallization. Most likely it is a crystalline or smectic phase. However, after the texture analysis we were not able to identify phase X. XRD measurements were unsuccessful because of crystallization process. In addition, a nematic phase (Fig. 8B) and two crystalline forms (Fig. 8C and D) are present. Microscopic observations are also consistent with the TOA and the DSC measurements (Fig. 9). In the cooling mode both methods used (DSC and TOA) detected three phase transitions. The first is the Iso-N. The TOA scan shows increase of the signal which next decreases because of the homeotropisation. Next nearly at 89.5 °C an anomaly is observed and it corresponds with smectic A phase appearance. The DSC scan presents it as a complex crystallization process. In the heating mode both methods used identified melting to the nematic phase and five 5 °C above isotropisation process. The part C of Fig. 9 shows the TOA curve after creation of CrII in the heating mode. No mesophase was observed.

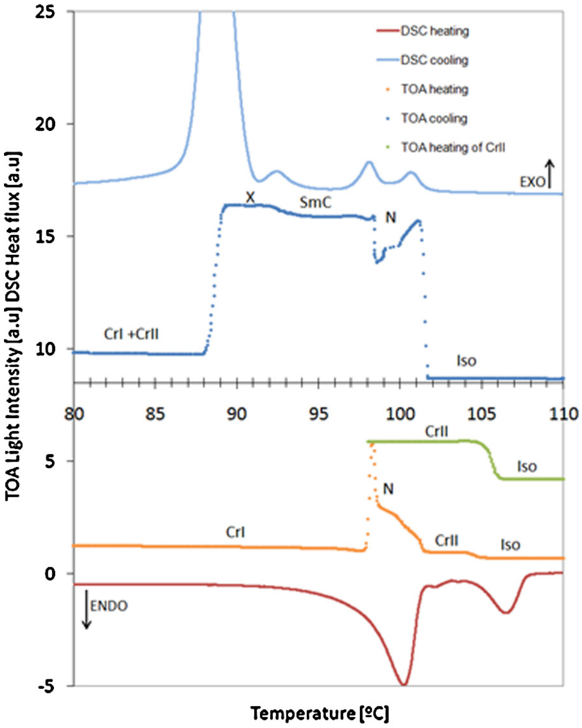

Fig. 11. The TOA and the DSC measurements of 4-Chloro-1,3-phenylene bis-[4-(4-octadecyloxyphenylazo)benzoate].

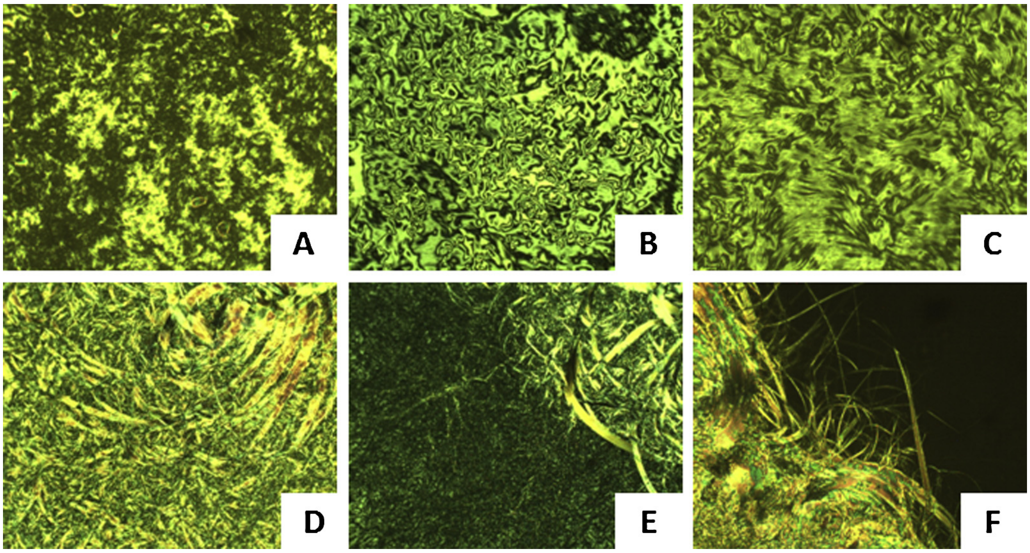

Fig. 12. Textures of Res-18. (A) Nematic phase, (B) SmC mesophase, (C) texture of CrI, (D) crystals of CrII, (E) CrII and nematic form, which was formed from CrI, (F) crystals of CrII and isotropic phase (from CrI).

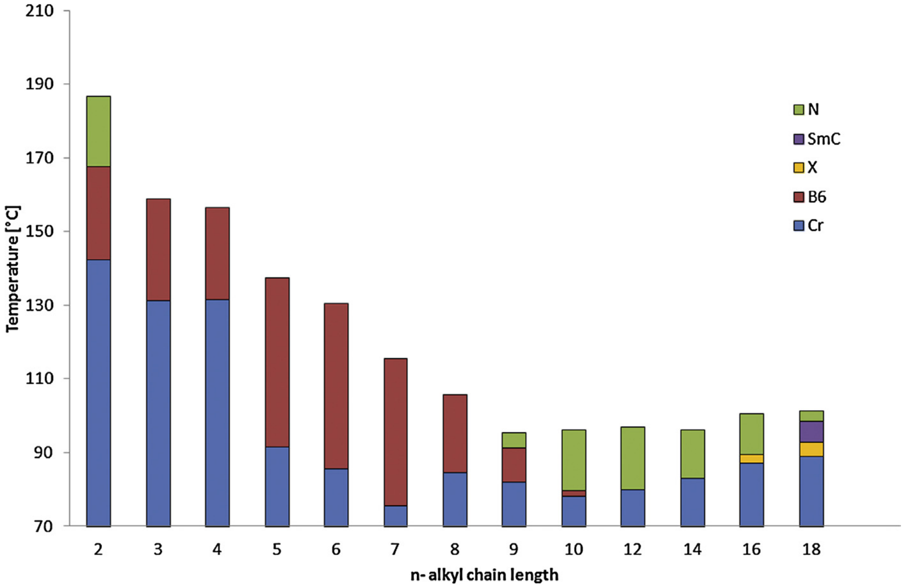

Fig. 13. Phase behaviour of 4-Chloro-1,3-phenylene bis-[4-(4-octadecyloxyphenylazo)benzoates].

More interesting liquid-crystalline polymorphism is shown in Res-18 possessing the longest alkyloxy chain in this experiment. According to the DSC and the TOA measurements Res-18 forms nematic (Fig. 12A) and smectic C phases (Fig. 12B). Smectic C phase was confirmed by XRD studies (Fig. 10). Also very narrow phase X is visible during the DSC and the TOA measurements as well as crystallization process (Fig. 11). As in the previous homologues solid state polymorphism exists. Both crystalline forms are characterized by different melting temperatures and textures, which are shown in Fig. 12C and D. In addition, their liquid-crystalline properties are diverse. CrI form melts at a lower temperature and has enantiotropic nematic phase (Fig. 12E), while the CrII crystals shown in Fig. 12F melt to isotropic phase. This behaviour is shown in Fig. 11. In the cooling mode both methods used identified four phase transitions and three types of mesophases: nematic, smectic C and X mesophase. The last phase is rather soft phase because small value of the enthalpy smectic C- X, compared to the crystallization process. In the heating mode the melting from CrI to nematic was observed by both methods used. However, extraordinary phase transition CrI–CrII and melting CrII–Iso is observed. Because of the presence of both crystalline forms in the sample quantitative calorimetric measurements are not possible. The presence of SmC is confirmed with XRD method (Fig. 10). Narrow low angle peak identifies lamellar character of the mesophase, and diffused wide angle ring is typical for smectic C mesophase.

4. Conclusions

To conclude, we synthesized 13 bent-core compounds, which form a homologous series of 4-chlororesorcinol derivatives. Also mesogenic studies have been performed with use of POM (and TOA), DSC and XRD. We found liquid-crystalline mesophases in each investigated substance (Fig. 13). Also solid-state polymorphism which can change character of the presented mesophases has been noted. Moreover we observed a very rare phenomenon of the gap without nematic phase among derivatives with middle alkyl chain length.

In the group of 4-Chloro-1,3-phenylene bis-[4-(4-alkyloxyphenylazo)benzoate] only five homologues have been recently described [33]. Therefore it was very interesting to note in our data the polymorphism of the solid states. Depending on the type of the crystal modification monotropic or enantiotropic mesophase can be obtained.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tca.2014.04.024.

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