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Liquid-Crystalline Polymorphism of Symmetrical Azobananas: bis(4-(4-alkylphenyl)azophenyl) 2-nitroisophtalates

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In this paper we present a series of novel compounds, bis(4-(4-alkylphenyl)azophenyl) 2-nitroisophtalates, which exhibit nematic and banana-type liquid-crystalline phases. The alkyl chain length varies from 1 to 18 carbons. The first ten members of this series exhibit nematic phase. The last eleven compounds exhibit banana-type liquid crystalline phases. The propyl and pentyl derivatives have extra second type of banana mesophase.

Keywords: 2-isophtalic acid; antiferroelectric switching; banana mesophases; bent-core; liquid crystals; nematic

INTRODUCTION

Since the time of their discovery liquid crystals have been very extensively investigated. The exploration of liquid crystals included molecules with different shapes (rod-like, disc-like, sanidic). Also there are different possibilities of substitution and combination of linking units in designing new molecular structures. From 1997 [1] much attention was dedicated to bent-core molecules because of their unusual properties. Built of achiral modules these compounds show properties typical for chiral molecules having tilted smectic phases with ferroic features. The banana-type mesophases for bent-core molecules have been denoted as B_x[2], where the subscript 'x' describes the

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specific type of mesophase. Up till now eight type of banana phases were identified [2–6]. Ferroic properties are described in the second type notation as the SmCP, where “P” means that the mesophases has ferroic properties.

Most common bent-core liquid crystals are resorcine esters, because of simplicity of their synthesis. Molecules with reversed linking groups at the central phenyl ring, namely isophthalic acid derivatives, are often ignored. Nguyen et al in their review paper [7] described 20 types of structures with the isophthalic acid units. So small amount of published papers about these types of molecules was results from their high phase transition temperatures [7]. Decreasing of these temperatures is possible by introducing a substituent in the central benzene ring.

The aim of this paper is the description of the new series of bent-type compounds, bis(4-alkylphenyl-4'-hydroxyazophenyl) 2-nitroisophthalates, and detection of all present mesophases with special attention to the switching banana-type mesophases.

2. EXPERIMENTAL

The main root of synthesis is shown on Scheme 1.

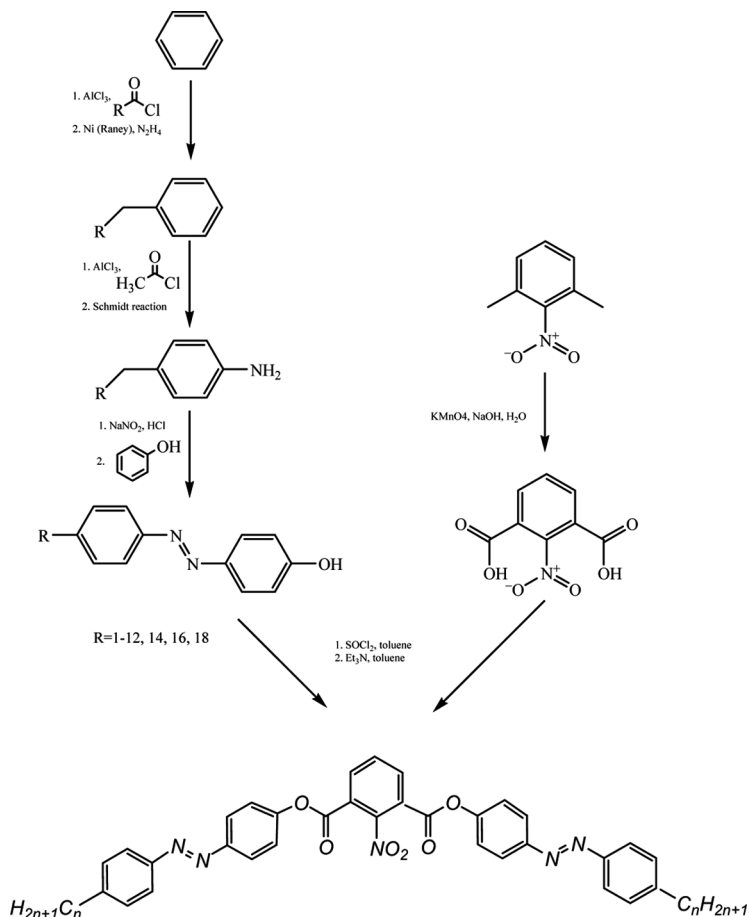
2.1. General Information

All the solvents (DCM, toluene, ethanol) were used without purification. For the diazotation reaction distilled water was used. 2,6-dimethylnitrobenzene was obtained from Aldrich. NMR spectra were recorded using a Bruker Avance 500 spectrometer with TMS as internal standard. Purity of all compounds was confirmed by thin layer chromatography and elemental analysis, Perkin-Elmer 2400 CHN. Microphotographs of mesophases textures were taken using BX-60 Olympus microscope with Motic M2000 digital camera attached. Transition temperatures and enthalpies were determined using Perkin-Elmer DSC7 calorimeter at a rate 10°C/min and with the indium as the standard of caloric effects.

2.2. Synthesis

4-Alkylanilines

were synthesized in a classical manner by acylation of benzene, reduction of thus formed keton with hydrazine and subsequent acylation with acetyl chloride. 4-Alkylphenylmethyl ketons were transformed



SCHEME 1 Scheme of synthesis of bis(4-(4-alkylphenyl)azophenyl) 2-nitroisophthalates.

into anilines in Schmidt reaction. All the compounds were purified by vacuum distillation.

4-Alkylphenyl-4'-Hydroxyazobenzenes

—0.5 mole of 4-alkylaniline was dissolved in 200 cm³ of 12% solution of hydrochloric acid. Solution was cooled to 0°C in an ice bath. Then 0.52 mole of sodium nitrite(III) in 80 cm³ of distilled water was added within 30 minutes. Solution of diazoted amine was put into the refrigerator. 0.5 mole of phenol was dissolved in 10% solution of sodium carbonate. Resulting mixture was cooled and placed in the ice bath.

After cooling it to 0°C the solution of diazo compound was added dropwise into it, with mechanical stirring. After 60 minutes yellow precipitate was filtered off on a Buechner funnel and dried on air.

2-Nitroisophtalic Acid [8]

–15.8 g (0.104 mol) of 2,6-dimethylnitrobenzene was placed in a flask containing 800 cm³ of distilled water and 6.4 g (0.16 mole) of sodium hydroxide. The mixture was heated to 90–95°C and 66 g (0.42 mol) of kalium permanganate was added within 90 minutes. It was left overnight with stirring. Next it was cooled to room temperature and brown precipitate was filtered off. The clear solution was cooled below 5°C and then it was acidified with concentrated solution of hydrochloric acid. White precipitate was filtered off and dried on air. It was used in next step without further purification. Analysis: Calc. –45.51 C%, 2.39 H%, N 6.63%; Found – 45.39 C%, 2.10 H%, 6.62 N%.

Bis(4-(4-dodecylphenyl)azophenyl) 2-nitroisophtalate

–0.144 g (0.95 mmol) of 2-nitroisophtalic acid was placed in the 100 cm³ round-bottom flask together with 0.4 cm³ of thionyl chloride and 50 cm³ of toluene was added. The mixture was heated for three hours. Then the toluene was removed on the rotatory evaporator. Oily remaining was dissolved in fresh portion (20 cm³) of dry toluene. 0.5 g of 4-dodecyl-4'-hydroxyazophenyl was placed in a 250 cm³ round-bottom flask and dissolved in 150 cm³ of toluene. The flask with azophenol was placed in an ice bath. The solution of acid chloride was poured into flask with phenol while stirring. The mixture was cooled below 3°C. To this was added slowly a solution of triethylamine in 10 cm³ of toluene from pipette. The reaction mixture was left overnight. Next it was heated till boiling for 2 hours and filtered hot. Toluene was removed on the rotator evaporator. Light orange solid was dissolved in DCM and chromatographed on silica gel (mesh 60) with DCM as eluent. Only the first fraction was collected. DCM was evaporated. The solid was recrystallized from 1:1 mixture of absolute ethanol and acetone, filtered off and dried on air. Analysis: Calc. –; 74.06 C%, 7.66 H%, 7.71 N% Found –74.28 C%, 7.80 H%, 7.80 N%. The rest of compounds was synthesized in a similar way.

3. RESULTS AND DISCUSSION

All the synthesized compounds exhibit mesomorphic behavior. Compounds with 1–2 carbons in alkyl chain show only nematic phase. The elongating of chain up to 8 carbon atoms leads to dimorphic compounds – nematic and B_x phases appear. Only one derivative,

the pentyl one, is trimorphic with nematic and two banana type mesophases. The nematic phase vanishes in the derivative with 8 carbons in the alkyl chain. Further elongating it from 9 carbons to 18 gives only monomorphic derivatives. The dependence of transitions temperatures against alkyl chain length is shown on Figure 1. Transition temperatures have been confirmed by differential calorimetry studies presented in Table 1.

The nematic phase was denoted as such after careful observations. On isotropic-nematic phase transition very discrete formation of homeotropic texture was observed, with almost indistinguishable difference from liquid phase. The nematic was confirmed by flashing, when subjected to a shearing stress (Fig. 2a). Other confirmation was given by microscopic observations on oriented sample. The typical observed textures of the presented mesophases are shown in Figure 2. As the sample was chosen bis(4-(4-pentylphenyl)azophenyl) 2-nitroisophtalate (5-2N).

This derivative (5-2N) has extraordinary properties. Only this one has three types of mesophases. Typical thermo-optical scan is shown in Figure 3. In both scans, in the heating and cooling modes, there are three mesophases distinguishable. As was shown in Figure 2 each mesophase has characteristic texture and with the change of texture

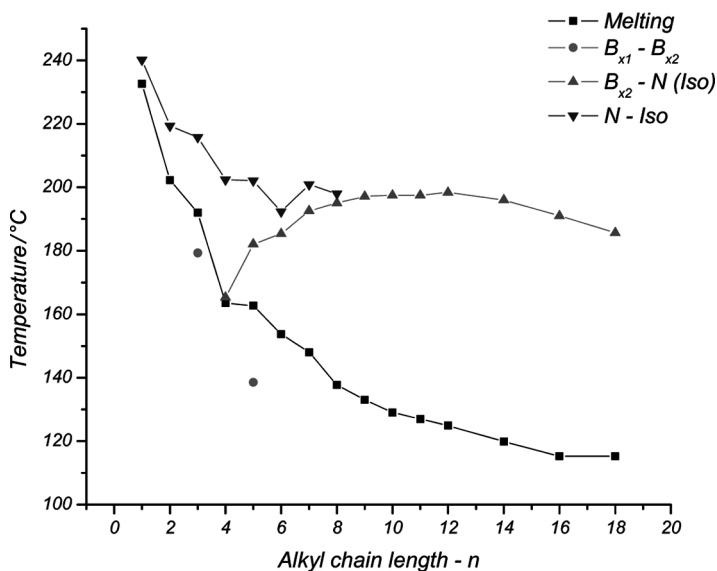


FIGURE 1 Dependence of transition temperatures against alkyl chain length.

TABLE 1 Transition Temperatures (in °C) and Enthalpies (in kJ/mol) in Rectangular Brackets

n	Cr	B _{x2}		B _{x1}		N	Is
1	•	232.6				•	240.2
		[55.25]					[0.20]
2	•	202.2				•	219.3
		[49.02]					[0.45]
3	•	192.0	•	(179.3)		•	215.67
		[28.77]		[0.24]			[0.33]
4	•	163.5			•	165,3	•
		[26.09]				[6.08]	[0.35]
5	•	162.7	•	(138.5)	•	182.1	•
		[24.53]		[1.33]		[7.18]	[0.47]
6	•	153.7			•	185.3	•
		[24.75]				[9.17]	[0.43]
7	•	148.0			•	192.5	•
		[25.86]				[13.07]	[0.12]
8	•	137.7			•	195.0	•
		[23.64]				[15.49]	[0.32]
9	•	133.0			•	197.2	•
		[21.66]				[14.07]	
10	•	129.0			•	197.5	•
		[22.27]				[15.33]	
11	•	126.9			•	197.5	•
		[21.84]				[14.94]	
12	•	124.9			•	198.4	•
		[21.51]				[10.67]	
14	•	119.8			•	196.0	•
		[22.65]				[14.91]	
16	•	115.2			•	191.0	•
		[29.5]				[15.82]	
18	•	115.2			•	185.7	•
		[27.95]				[11.47]	

the change of the light intensity coming through the microscope is observed. We have detected four phase transitions. The same were observed in calorimetric measurements (DSC). Figure 4 shows four peaks of caloric anomalies, which are connected with the phase transitions. The temperatures read at DSC scan are the same as in the thermo-optic measurements.

Particularly interesting are enthalpies of the phase transitions. The melting process has almost 4 times higher enthalpy than the phase transition B_{x1}-N. It is typical for the mesophases with some translational disorder. The small value of the phase transition B_{x1}-B_{x2} shows significant similarity of both banana-mesophases.

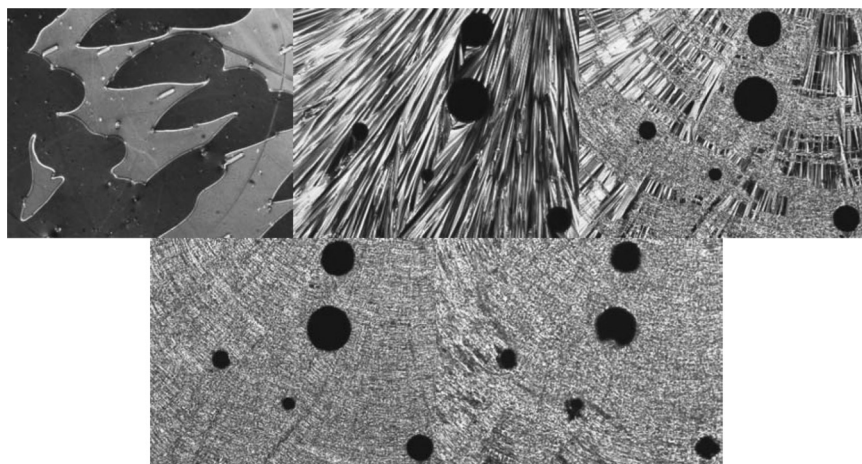


FIGURE 2 Microphotographs of the textures of bis(4-(4-pentylphenyl)azophenyl) 2-nitroisophthalate. A) nematic phase, b) B_{X1} mesophase, c) phase transition B_{X1} - B_{X2} , d) B_{X2} mesophase, e) recrystallization process.

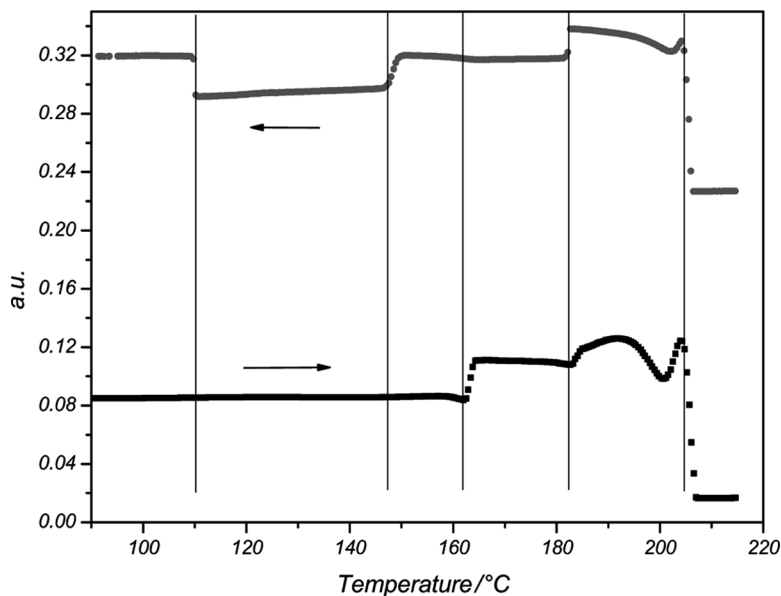


FIGURE 3 Thermo-optical analysis of bis(4-(4-pentylphenyl)azophenyl) 2-nitroisophthalate (5-2N), heating and cooling $10^{\circ}\text{C}/\text{min}$.

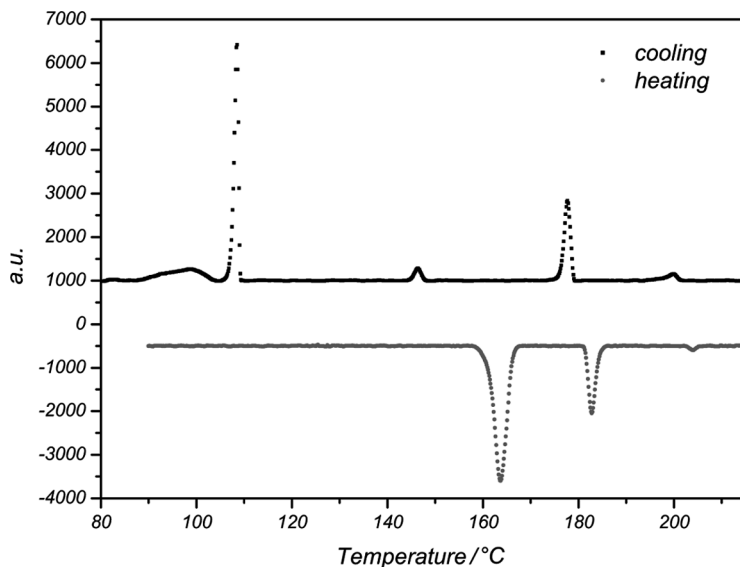


FIGURE 4 DSC traces of bis(4-(4-pentylphenyl)azophenyl) 2-nitroisophthalate (5-2N), heating and cooling 10°C/min.

Unexpectedly low value of B_{X-N} phase transition enthalpy was observed in the propyl derivative. It suggests that this banana mesophase is rather B_{x2} than B_{x1} . The proper identification will be done on the base of X-ray experiment.

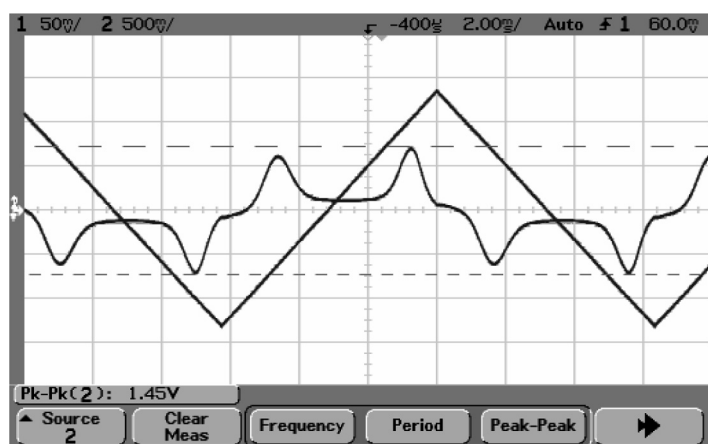


FIGURE 5 Ferroic switching of tetradecyl derivative.

In this group of compounds we have tried to observe the switching effects. Our preliminary investigations show that for banana mesophases in the hexyl and tetradecyl derivatives such effect was observed. An example of ferroelectric switching is shown in Figure 5 (tetradecyl derivative).

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