

THE EFFECT OF PARA SUBSTITUTION OF NEW AZODERIVATIVES ON THEIR LIQUID CRYSTAL BEHAVIOUR

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abstract: In this paper, we present the synthesis and the thermodynamic characterization of new azoderivative compounds in order to emphasize the role of the terminal group on the liquid crystal behaviour. The methoxy radical substituted in *para* position at the aromatic core induces the appearance of liquid crystal mesophases on cooling, for the new compound. The melting points of the substituted and the original compounds it was found to have very close values.

Introduction

In the last decades, researches in the field of liquid crystal (LC) azoderivatives have been strongly encouraged due to their potential uses in various photonic applications such as optical switching, optical image storage, optical display, and optical computing [1].

A large number of azoderivatives compounds with liquid crystal properties was synthesised in order to elucidate the correlation between their structures and the mesomorphic behaviour [2,3].

The type of mesophases formed by a liquid crystal and the transition temperatures strongly depend on its molecular shape. In some cases, the presence of two terminal aliphatic chains can induce liquid crystal behaviour for a compound initially with only one aliphatic chain.

For systems that have two terminal aliphatic chains with different lengths, typically, nematic and orthogonal smectic phases can occur.

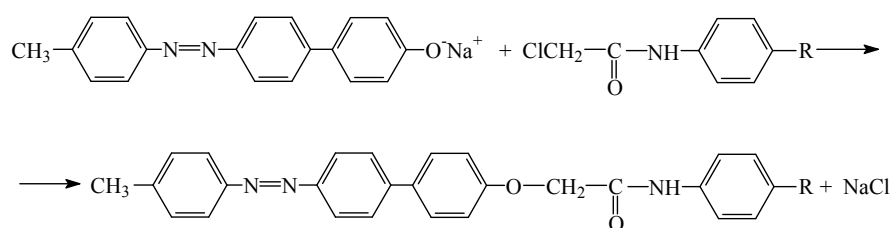
The aim of this work is to emphasize that the simple substitution in *para* position of the aromatic core of a new azoderivative compound with the methoxy radical, leads to a new liquid crystal compound.

The new mesomorphic compound was thermodynamically characterised for further applications.

The method used for obtaining of the new azoderivatives was described in the specialized papers [4-6].

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The compounds 4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl and 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl, were synthesized by the condensation of N-chloroacethylaniline or p-methoxy-N-chloroacethylaniline with sodium salts of 4-hydroxy-4'-(p-methylphenylazo)-biphenyl, following the subsequent scheme:



R =H, OCH₃.

Experimental

Materials

4-hydroxy-4'-(p-methylphenylazo)-biphenyl was synthesized by coupling of corresponding diazonium salt with phenol.

p-Toluidine, p-anisidine, chloroacetylchlorure and phenol were pure commercial products Merck or Fluka.

N-chloroacethylaniline and p-methoxy-N-chloroacethylaniline were prepared by p-phenetidine and chloroacetylchlorure.

Techniques

The analyses of carbon, hydrogen and nitrogen were performed with a CHNOS Vario El analyzer.

The electronic spectra were carried out in dioxane with a UV-VIS Jasco V-530 spectrophotometer within the range 200-700 nm.

FTIR spectra were recorded using a Bio-Rad FTS 135 spectrophotometer, in KBr pellets, within the range of 3500-400 cm⁻¹.

¹H-NMR spectra were recorded on a Varian EM-360 spectrometer operating at 60 MHz in CDCl₃. The chemical shifts were referred to TMS as internal standard.

Molecular weight was obtained with a HPGC-MS 5890 MD 5971 spectrometer at 70eV, carrier gas He at 2ml/min.

The melting temperatures were established in capillaries and verified with a Boetius apparatus.

The microstructural analysis of 4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl and 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl was performed using an IOR MC-5A polarized light microscope equipped with an electric hot stage connected to a KFKI-type NV 288/2 precision temperature controller.

The substances were encapsulated by capillarity between In_2O_3 -glass electrodes, separated by 12 μm Mylar spacers.

The temperatures were recorded with 0.01°C precision using a T-type thermocouple and a KEITHLEY 2000 digital multimeter. We obtain a stability around 0.5°C using a phase-controlled device with a numerical PID algorithm [7].

Microphotographs were captured using a JVC camera while heating/cooling

The transition paths and thermodynamic functions were measured by differential scanning calorimetry (DSC).

The calorimetric measurements were made with a Perkin-Elmer DSC 2 calorimeter in a highly purified argon atmosphere. The weight of samples lay in the range of 1-3 mg. The heating and cooling rates were 10 K/min.

Synthesis of 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl:

Into a solution of 1.44 g (5 mmoles) of 4-hydroxy-4'-(p-methylphenylazo)-biphenyl in 15 ml of benzene and 15 ml of ethanol was added 0.22 g (5 mmoles) of sodium hydroxide. The reaction mixture is stirred for 1.5 hours at 65-70°C, while the azophenol reacts with sodium hydroxide. The water resulted in reaction is isolated as an azeotropic mixture water-benzene-ethanol.

Into anhydrous azophenoxide is added 0.9875 g (5 mmoles) of p-methoxy-N-chloroacethylaniline and the reaction mixture is stirred at 50-55°C five hours.

After cooling at room temperature, the solid product is filtered, washed with water for the removal of sodium chloride, then with two 5 ml portion of ethanol.

The yellow-orange precipitate was dried in a heating chamber at 90°C. Then, the solid was recrystallized repeatedly from toluene to afford 1.28 g (5 mmoles) of 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl, m.p. 161°C, and yield 82.17%.

Results and discussions

UV-VIS and FTIR spectra

The structural and molecular formula of new 4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl and 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl and the semi-microanalytical results of carbon, hydrogen and nitrogen, the melting temperatures, the yields and the values of λ_{max} and ϵ_{max} established from electronic spectra are given in Table 1.

Table 1. Results of electronic spectra.

No	Molecular formula	%C	%H	%N	Melting point °C	yield %	λ_{\max} [nm]	ϵ_{\max} [1000 cm ² /mol]
		calc. found	calc. found	calc. found				
1	C ₂₇ H ₂₃ N ₃ O ₂	76.95	5.46	9.97	159-160	54.63	269	39772
		76.90	5.21	9.73			286	7745
							387	8595
							418	442
							249	17305
2	C ₂₈ H ₂₅ N ₃ O ₃	74.50	5.54	9.31	160-161	82.17	287	10295
		74.35	5.48	9.02			344	24902
							439	1237

Analytical results of C, H, N presented in Table 1 confirmed the purity and the molecular formulae of new synthesised 4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl and 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl.

The structures of these compounds have been investigated on the basis of FTIR and UV-visible spectra.

The electronic spectra, recorded in dioxan, exhibit R-band due to azo-group at 418-439 nm, a high intensity K-band due to conjugated system Ar-N=N-Ar at 344-387 nm and a high intensity B-band due to the aromatic rings, at 249-287 nm.

FTIR spectra confirm the presence of azo, ether, amide and methyl groups in the structure of compounds as mentioned in Table 2.

Table 2. Results of FTIR spectra.

No	Name of compound	FTIR, ν (cm ⁻¹)				
		-N=N-	-NH-	C _{Ar} -O-CH ₂ - asim.	sim.	-CO-NH- amide I/ amide II
1	4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	1443.64 (w-m)	3379.29 (w)	1253.97 (vi)	1060.25 (i)	1679.89 (vi) 1535.80 (vi)
2	4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	1437.00 (w)	3434.96 (w)	1243.64 (vi)	1032.92 (i)	1654.94 (vi) 1543.62 (i)

w-weak, m-medium, i-intense, vi-very intense.

Aromatic rings show a characteristic series of peaks in the 1663.96 – 1685.64 cm⁻¹ range of the infrared spectra.

The new synthesised compounds show strong absorptions in the 700-800 cm⁻¹ range due to C-H out-of-plane bending.

The exact position of absorptions is diagnostic of the substitution pattern of the aromatic ring.

In the region 1437-1600 cm⁻¹ arise the bands due to the vibrations of azo group and those due to the stretching vibrations $\nu_{C=C}$ of the C-C linkages in aromatic nuclei.

4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl and 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl show two strong absorptions at 1243.64-1253.97 cm⁻¹ due to the antisymmetrical valency vibration of the C-O-C group and at 1021.00 cm⁻¹ due to the symmetrical valency vibration of the same group.

The intensive bands for -CO-NH- groups were identified at 1535.80-1543.62 cm^{-1} , but it was observed a very intensive band at 1654.94-1679.89 cm^{-1} .

^1H NMR spectra recorded at 60 MHz in the CDCl_3 solution support the structure formulas assigned to these compounds, deduced from the equation of the synthesis reaction.

Table 3 gives the m/e values (%) of the base peak in the mass spectra of the new 4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl and 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl.

Table 3. The base peaks in the mass spectra

No	Name	Molecular mass		Base peak m/e 100%
		Calc.	Exp. (SM)	
1	4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	421.49	421	92
2	4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	451.52	451	106

Table 4. Phase transition temperatures and corresponding enthalpy values (obtained from the first cooling scan and the second heating scan) for the studied compounds.

No	Compound	$T/^\circ\text{C}$ ($\Delta H/\text{kcal mol}^{-1}$)	
		Heating	Cooling
1	4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	K 160(6.6) I	I 111.2(2.8) K ₃ 108 K ₂ 106.2 K ₁ 104.7 K
2	4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	K 161(6.05) I	I 135,6(0.3) N 132,6(0.2) S _A 129,7(2.15) K ₁ 128(2) K

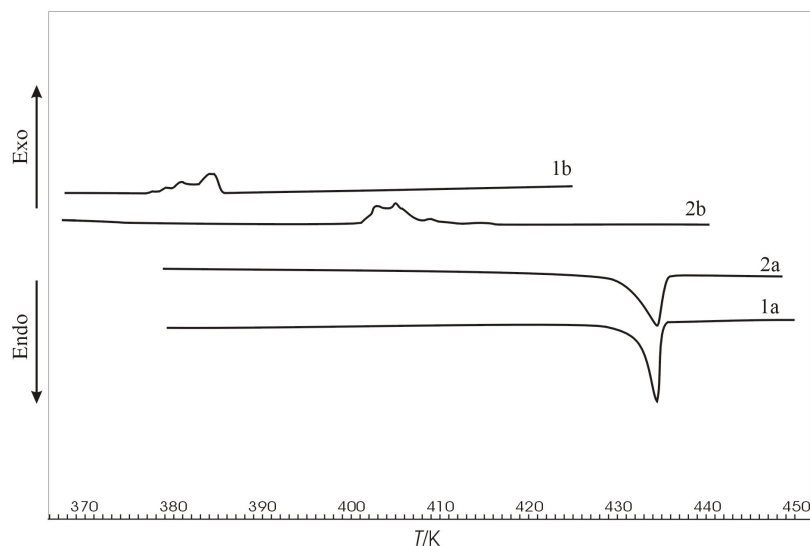


Fig. 1: DSC thermodiagrams obtained for compounds 4-(*N*-phenyl-acetamidoxy)-4'-[*p*-methyl-phenylazo] biphenyl (1) and 4-(*p*-methoxy-*N*-phenyl-acetamidoxy)-4'-[*p*-methyl-phenylazo] biphenyl (2), at heating (a) and cooling (b), respectively.

Mesomorphic properties

Liquid crystalline behaviours and phase transition temperatures of the new compounds were investigated by Polarising Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC).

The phase transition temperatures, corresponding enthalpy values and mesophase types of compounds were listed in Table 4. The DSC thermodiagrams are shown in Fig. 1.

The compound 4-(*N*-phenyl-acetamidoxy)-4'-[*p*-methyl-phenylazo] biphenyl exhibits no liquid crystalline phases on repeated heating/cooling cycles.

Nevertheless, a strong polymorphism of the solid state was observed on the first and second heating/cooling cycles. Fig. 2 and Fig. 3 show the solid state K and of the polymorphic solid state K₂ on cooling from the isotropic liquid.

The compound 4-(*p*-methoxy-*N*-phenyl-acetamidoxy)-4'-[*p*-methyl-phenylazo] biphenyl becomes mesomorphic after substitution in para position with the methoxy radical. It exhibits a monotropic phase transition on cooling from the isotropic phase, as shown in Table 4.

The type of mesophases was identified after examination of the textures under cross polarizers, at different temperatures [8].

At heating, the compound 4-(*p*-methoxy-*N*-phenyl-acetamidoxy)-4'-[*p*-methyl-phenylazo] biphenyl became isotropic liquid directly from the solid state, at about the same temperature as the previous compound (161°C). Any mesophases were observed on heating.

The DSC thermodiagram (Fig. 1) confirm this transition since the corresponding enthalpy has an appropriate value ($6.05 \text{ kcal mol}^{-1}$).

While cooling, the nematic phase grows from the isotropic liquid at 135.6°C (Fig. 4), followed by the smectic A phase at the transition temperature 132.6°C (Fig. 5). Each mesophase has a narrow temperature range of about 3°C . Fig. 6 shows the texture of the smectic A phase at 130°C .

It is interesting to note that the temperature ranges of the mesophases of compound 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl are very similar of the temperature ranges of polymorphic solid states of compound 4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl. It is like the methoxy substitute in the first compound slips the phase transition over higher temperatures, in the liquid region.

On further cooling the compound 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl exhibits a smectic A to solid phase transition followed by a transition between to solid states (Fig. 7).

Conclusions

Two azoderivatives compounds were synthesised and thermodynamically characterised. The compound substituted with methoxy radical in para position at the aromatic core was found to show liquid crystal properties, after POM and DSC investigations.

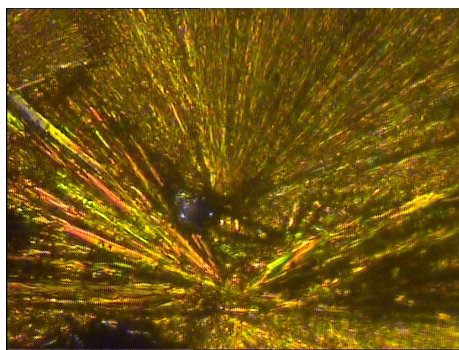


Fig. 2: Solid crystalline state of 4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl at room temperature. Crossed polarizers ($\times 100$)

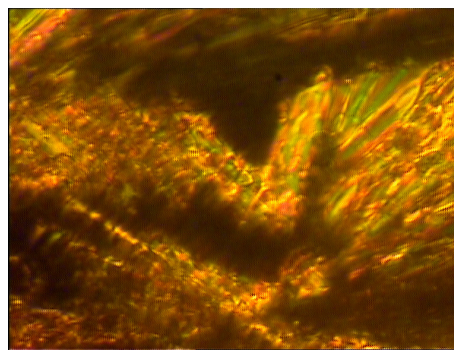


Fig. 3: Solid state K_2 of 4-(N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl on cooling, at 107°C . Crossed polarizers ($\times 100$)

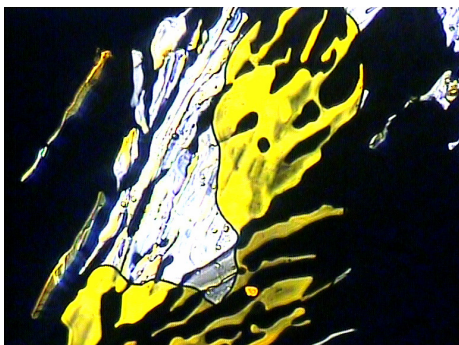


Fig. 4: Growth of the nematic phase of 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] on cooling from the isotropic state, at 135.5 °C. Crossed polarizers ($\times 100$)



Fig. 5: Nematic - smectic A transition on cooling, at 132.5 °C, for 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo]. Crossed polarizers ($\times 100$)

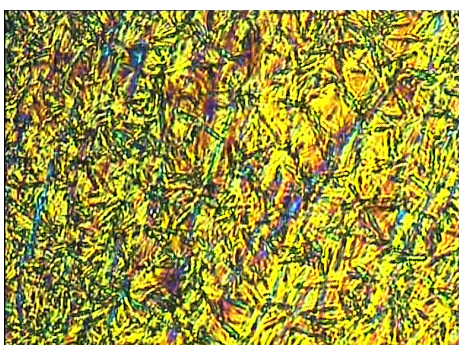


Fig. 6: Smectic A phase of 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo], at 130 °C. Crossed polarizers ($\times 100$)

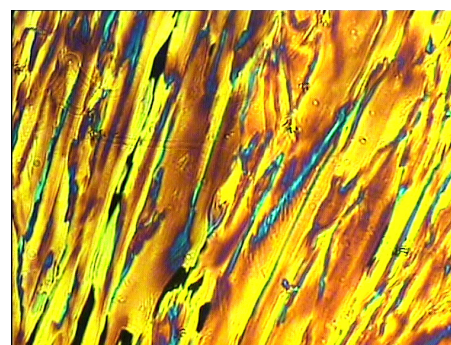


Fig. 7: Solid state K of 4-(p-methoxy-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] at room temperature. Crossed polarizers ($\times 100$)

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