

SYNTHESIS AND THERMODYNAMIC CHARACTERIZATION OF 4-(P-ETHYL-N-PHENYL-ACETAMIDOXY)-4'-[P-METHYL-PHENYLAZO]BIPHENYL

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abstract: The new derivative with liquid crystals properties, characterized by IR and electronic spectra are prepared. Their mesomorphic behaviour have been determined by differential scanning calorimetry (DSC) and polarising optical microscopy (POM).

Introduction

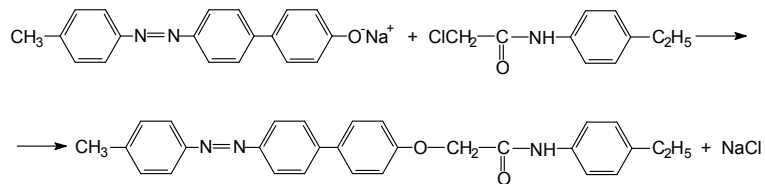
Liquid crystals have important applications in many advanced technologies like liquid crystal displays, optical filters, imaging systems, optical storage systems, radiation visualisation, temperature sensors and medical thermography.

In thermotropic liquid crystals, the changes between various possible mesomorphic phases, and from these phases to the crystalline or isotropic liquid phases, occur at well defined temperature, with well defined latent heats of transformation. These phase equilibria, called mesomorphic states, mesomorphic phases or mesophases, in their most stable form, could be classified into three fundamental types: nematic, cholesteric and smectic phases.

The smectic phases are more viscous therefore more organized, their molecules lay parallel one to each other in close – packed parallel planes.

In this paper we present synthesis and thermodynamic characterization of new compound with liquid crystal properties.

4-(p-ethyl-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo]biphenyl a new compound, was synthesized by the condensation of p-ethyl-N-chloroacethylaniline with sodium salts of 4'-(4-methylphenylazo)-4-hydroxy biphenyl:



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Experimental

Materials

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

p-Toluidine, p-phenetidine, chloroacetylchlorure were pure commercial products Merck or Fluka.

p-ethyl-N-chloroacetyl-aniline was prepared by p-phenetidine and chloroacetylchlorure.

Techniques

The analyses of carbon, hydrogen and nitrogen were performed with a Carlo Erba analyzer, model 1108.

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

Infrared spectra were recorded on a Nicolet spectrophotometer, in KBr pellets, within the range 4000-650 cm^{-1} .

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

The microstructural analysis of 4-(p-ethyl-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 substance was encapsulated by capillarity between In_2O_3 -glass electrodes, separated by 12 μm Mylar spacers.

In order to realize a complete physical-chemical characterization of new compound synthesized a thermodynamic study for thermal characteristic transition is necessary [1,2].

The transition path and thermodynamic function 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. Typically heating and cooling rates of 10 K/min were used.

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

To a solution of 1.44 g (5 mmoles) of 4-(p-ethyl-N-phenyl-acetamidoxy) - 4' - [p-methyl - phenylazo] biphenyl in 20 ml of benzene and 15 ml of ethanol is added 0,22 g (5 mmoles) of sodium hydroxide. The reaction mixture is stirred for 1.5 hours at 65-70 $^{\circ}\text{C}$, while the azophenol reacts with sodium hydroxide. The water resulted in reaction is isolated as an azeotropic mixture water-benzene-ethanol.

To anhydrous azophenoxide is added 0.9875 g (5 mmoles) of p-ethyl-N-chloroacetyl-aniline and the reaction mixture is stirred at 50-55 $^{\circ}\text{C}$ six hours. After cooling at room temperature, the solid product is filtered, washed with water for the removal of sodium chloride, then with two two 5 ml portion of ethanol.

The yellow-orange precipitate is dried in a heating chamber at 90°C. The solid is then recrystallized repeatedly from toluene to afford 1.97 g (5 mmoles) of 4-(p-ethyl-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl, m.p. 147°C, yield 87,75%.

Results and discussions

UV-VIS and infrared spectra

The molecular formula of new 4-(p-ethyl-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.

Molecular formula	%C	%H	%N	%O	Melting point °C	yield %	λ_{\max} [nm]	ϵ_{\max} [1000 cm ² /mol]
	calc.	calc.	calc.	calc.				
C ₂₉ H ₂₇ N ₃ O ₂	found	found	found	found	147	87.75	269	39772.5
	77.50	6.01	9.35	7.12				
	77.62	6.12	9.44	7.16				

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

The structure of these compounds has been investigated on the basis of IR and UV-VIS spectra.

The electronic spectra, recorded in dioxan, exhibit R-band due to azo-group at 387 nm, a high intensity K-band due to conjugated system Ar-N=N-Ar at 326 nm and a high intensity B-band due to the aromatic rings, at 269 nm.

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

Table 2. Results of IR spectra

Name of compound	IR (cm ⁻¹)				
	aromatic nuclei	-N=N-	C _{Ar} -O-CH ₂ - asim sim		-CO-NH-
4-(p-ethyl-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	3036.30 (m-s) 1663.96 – 1685.64 (m-s) 1654.85 (fs-s)	1577.83 (m-s) 1388.63 (i)	1237.00 (fi-i)	1021.00 (i)	1534.65- 1541.49 (s-m) 1718.80 (i)

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

As many as four absorptions are sometimes observed in the 1663.96-1685.64 cm^{-1} region because of complex molecular motions of the ring itself.

The compound 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 1400-1600 cm^{-1} available the bands due to the vibrations of azo group and those due to the stretching vibrations $\nu_{\text{C}=\text{C}}$ for the C-C linkages in aromatic nuclei. The absorptions bands due to the azo group appear in two regions, namely at 1400-1430 cm^{-1} and 1388.63 cm^{-1} .

The intensive bands of the first region are a result of conjugation of azo group with aromatic nuclei. The weak bands of region 1388.63 cm^{-1} are due to the vibration of azo group and agree with the data presented in literature.

The very intensive absorption at 1370-1380 cm^{-1} can be assigned to the $\delta_{\text{C-H}}$ and to ν_{CH_3} sym frequencies. These bands can be splitted in two or three peaks, with variable intensity.

4-(p-ethyl-N-phenyl-acetamidoxy)-4'-[p-methyl-phenylazo]biphenyl show two strong absorptions at 1237.00 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 strong absorption band at 1120-1150 cm^{-1} is characteristic to the vibration of the Ph-N band.

Mesomorphic properties

The mesomorphic properties of the material were investigated by Differential Scanning Calorimetry (DSC) and Polarising Optical Microscopy (POM).

Differential Scanning Calorimetry (DSC)

In a DSC curve, thermic flux (dH/dt , $\text{mcal}\cdot\text{s}^{-1}$) is function on temperature (T, K).

Typical DSC traces recorded on heating and cooling for new compound are shown in Fig. 1.

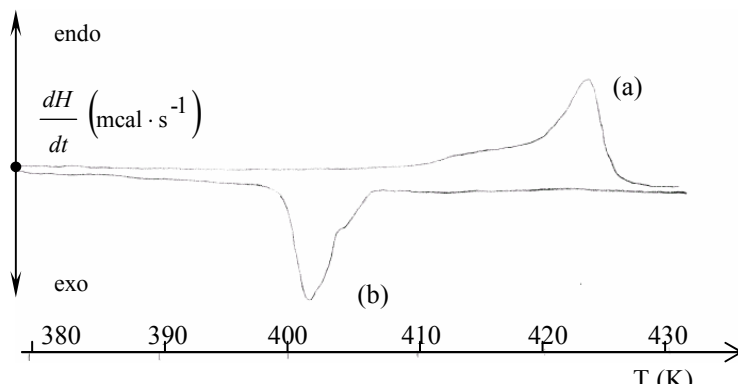


Fig. 1. The heating (a) and cooling (b) DSC curves.

Phase sequences and phase transition temperatures ($^{\circ}\text{C}$) by DSC:

- Heating: K 139.34 S_A 145.84 I
- Cooling: I 132.84 S_A 128.59 K

Polarising optical microscopy

In order to identify the types of mesophases presented by this compound, an IOR MC 5A polarized light microscope was used. The sample was encapsulated by capillarity between two glass plates using 12 μm thickness Mylar spacers and placed in a copper microscope hot stage. The temperature was measured with 0.01 $^{\circ}\text{C}$ precision using a T-type thermocouple and a KEITHLEY 2000 digital multimeter, a stability around 0.5 $^{\circ}\text{C}$ being obtained by a phase controlled device with a numerical PID algorithm [3]. The transitions temperatures were determined at 0.1 $^{\circ}\text{C}\text{s}^{-1}$. Microphotographs (Fig.2-4) were captured using a JVC camera while heating/cooling.



Fig. 2. Paramorphic mosaic texture of the smectic A phase, at heating from the solid state. Crossed polarizers, 136 $^{\circ}\text{C}$ ($\times 100$).



Fig. 3. Growth of the smectic A phase, from the isotropic phase, at 138 $^{\circ}\text{C}$. Crossed polarizers, ($\times 100$).

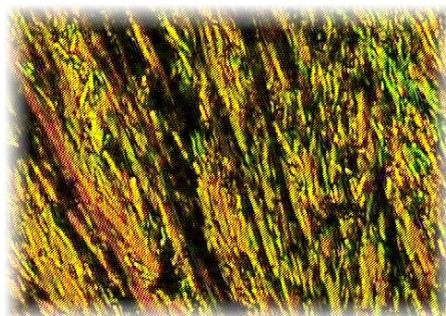


Fig. 4. Solid crystalline state at 129.5 $^{\circ}\text{C}$. Crossed polarizers, ($\times 100$).

The compound exhibits an enantiotropic transition between the liquid crystalline state and the isotropic liquid at 143 $^{\circ}\text{C}$ (clearing point). Additionally, it displays a crystal to mesophase transition at 135.5 $^{\circ}\text{C}$ on the first heating-cooling cycle. The texture appearance in crossed polarizers is typical for a smectic A phase [4] (Fig. 2). While cooling, a smectic

A phase slowly grows from the isotropic phase at 138°C (Fig. 3) and at 129.5°C the crystalline solid state appears (Fig. 4).

Phase sequences and phase transition temperatures (°C) by POM:

- Heating: K 135.5 S_A 143 I
- Cooling: I 138 S_A 129.5 K

Conclusions

The new compound synthesized present in the same molecule a specific structure for smectic phase observed by POM and DSC.

The differences between values were obtained because of working in different gaseous medium: inert for DSC (argon) and air for POM.

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