4-(p-ETHYL-N-PHENYLCETAMIDOXO)-4’-[p-PHENYLALO] BIPHENYLS WITH LIQUID CRYSTALS PROPERTIES

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4-(p-ethyl-N-phenylacetamidoxo)-4’-[p-phenylazo] biphenyls were synthesized. They were in their solid state, being characterized by elevated melting points and high reaction yields. The new compounds purity was verified by a gas chromatograph coupled with a gas spectrometer and it was confirmed by the appearance of a single peak. Elemental analysis and spectral analysis (UV-Vis, FTIR and 1H-NMR) confirmed the structural formulas deduced from those equations of the synthesis chemical reactions. The compounds presented properties of liquid crystals, fact demonstrated by the presence of a solid phase polymorphism during the heating process, and of a nematic phase during cooling, followed by a smectic A phase.

INTRODUCTION

Liquid crystals, intermediates between the liquid state and the solid state, are of two main types: smectic, soap like or grease like, and nematic, thread like.1-5 Liquid crystals have their utilization in many areas, like science, device technology, engineering, and also medicine and pharmaceuticals.6-9

In medicine, liquid crystals are used for evaluating pains, associated with arthritis, soft tissues injuries, back pains, for diagnosis and monitoring different diseases, like cancer, tumour, inflammatory states, evolution of skin tests and forensic medicine.10-12 DNA, cholesterol, many proteins and biological membranes are naturally occurring liquid crystals. Due to their very low toxicity and high biocompatibility, all liquid crystals with pharmaceutical properties are relatively secure to be used as drugs.13,14

Synthesis of 4-(p-ethyl-N-phenylacetamidoxo)-4’-[p-phenylazo] biphenyls consisted in the condensation in an alkaline medium of some 4-hydroxy-4’-(phenylazo) biphenyls,15 namely: 4-hydroxy-4’-(phenylazo) biphenyl, 4-hydroxy-4’-(p-ethyl-phenylazo) biphenyl, 4-hydroxy-4’-(p-trifluoromethyl-phenylazo) biphenyl, 4-hydroxy-4’-(p-chloro-phenylazo) biphenyl, 4-hydroxy-4’-(p-nitrophenylazo) biphenyl, 4-hydroxy-4’-(p-cyano phenylazo) biphenyl with 4-ethyl-N-chloroacetylaniline (Fig. 1).

Fig. 1 – Reaction scheme for 4-(p-ethyl-N-phenylacetamidoxo)-4’-[p-phenylazo] biphenyls synthesis.*
RESULTS

Reaction yields were high and dependent on the reaction products solubility in the chosen solvent. The elevated melting points were due to the presence of different substituents from the para position. Based on the recorded temperature interval, these compounds demonstrated their liquid crystals properties (Table 1).

Elemental analysis. The elemental analysis for C, H, N, F and Cl gave the following results: (1) calculated, %: C 77.24, H 5.74, N 9.65, found, %: C 76.91, H 5.61, N 9.12; (2) calculated, %: C 77.50, H 6.01, N 9.35, found, %: C 77.61, H 6.12, N 9.19; (3) calculated, %: C 69.18, H 4.77, N 8.34, F 3.77, found, %: C 69.35, H 4.81, N 8.41, F 3.84; (4) calculated, %: C 71.56, H 5.11, N 8.94, Cl 7.56, found, %: C 71.61, H 5.26, N 8.41, Cl 7.72; (5) calculated, %: C 70.00, H 5.00, N 11.66, found, %: C 70.21, H 5.26, N 11.53; (6) calculated, %: C 75.65, H 5.21, N 12.24.

UV–Vis spectra. The bands of E or B benzene type were due to the π electrons conjugation from the benzene rings. They gave absorption bands of medium intensity at 249–289 nm. The bands of K type, due to the conjugated Ar–N=N–Ar system, presented intense absorption bands at 348–379 nm, while the R type bands, characteristic to the –N=N– chromophoric group, gave absorption bands of weak intensity, of R type at 432–450 nm.

FTIR spectra. An important band from spectrum was the one of the νCO valence vibration of the amide group, so-called amide I, which appeared at 1685–1680 cm⁻¹. The usually most intense band from the spectrum, which was recorded at 1549–1530 cm⁻¹, was considered the amide II band. The band due to νN=N valence vibration should have been characteristic, but the absorptions were produced at small values of the wavelengths and the bands had low intensities (1445–1439 cm⁻¹), due to the very weak bond polarity.

Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Structural formulas</th>
<th>Molecular formulas</th>
<th>M [g/mol]</th>
<th>M.p. [°C]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4-(p-ethyl-N-phenylacetamidoxy)-4’-(p-phenylazo) biphenyl</td>
<td>C₂₈H₂₅N₃O₂</td>
<td>435</td>
<td>158–159</td>
<td>70</td>
</tr>
<tr>
<td>2.</td>
<td>4-(p-ethyl-N-phenylacetamidoxy)-4’-(p-ethyl-phenylazo) biphenyl</td>
<td>C₃₀H₂₉N₃O₂</td>
<td>463</td>
<td>193–194</td>
<td>76</td>
</tr>
<tr>
<td>3.</td>
<td>4-(p-ethyl-N-phenylacetamidoxy)-4’-(p-trifluoromethyl-phenylazo) biphenyl</td>
<td>C₂₉H₂₄N₃O₂F₃</td>
<td>503</td>
<td>164–165</td>
<td>81</td>
</tr>
<tr>
<td>4.</td>
<td>4-(p-ethyl-N-phenylacetamidoxy)-4’-(p-chloro-phenylazo) biphenyl</td>
<td>C₂₉H₂₄N₃O₂Cl</td>
<td>469.5</td>
<td>176–177</td>
<td>69</td>
</tr>
<tr>
<td>5.</td>
<td>4-(p-ethyl-N-phenylacetamidoxy)-4’-(p-nitro-phenylazo) biphenyl</td>
<td>C₂₈H₂₄N₄O₄</td>
<td>480</td>
<td>187–188</td>
<td>65</td>
</tr>
<tr>
<td>6.</td>
<td>4-(p-ethyl-N-phenylacetamidoxy)-4’-(p-cyano-phenylazo) biphenyl</td>
<td>C₂₉H₂₄N₄O₂</td>
<td>460</td>
<td>198–199</td>
<td>73</td>
</tr>
</tbody>
</table>
In the ¹H-NMR spectra of the compounds, five signals appeared, from which a multiplet characteristic to aromatic protons at \( \delta(\text{ppm}) = 7.6-7.8 \), two un-split signals, singlet, given by the protons from the NH (\( \delta(\text{ppm}) = 8.3-8.4 \)) and CH\(_2\) (–O–CH\(_2–\), \( \delta(\text{ppm}) = 4.7-4.9 \)) groups, two split signals: a quartet signal given by the protons from the CH\(_2\) group (–CH\(_2–\text{CH}_3\), \( \delta(\text{ppm}) = 2.5-2.7 \)) and a triplet signal given by the protons from the CH\(_3\) group (–CH\(_2–\text{CH}_3\), \( \delta(\text{ppm}) = 1.2-1.4 \)).

**DISCUSSION**

4-(p-ethyl-N-phenylacetamidoxy)-4’-[p-phenylazo]biphenyls as new organic materials for nonlinear optics

As shown from the DSC diagram (figure 2), 4-(p-ethyl-N-phenylacetamidoxy)-4’-[p-phenylazo]biphenyl (1) presented a smectic A phase at heating and a nematic-smectic A sequence on cooling. The transition temperatures and the mesophase type at heating and cooling, respectively, were:

- K158 (31.2) S\(_A\)168.75 (4.2) I;
- I168.75 (4.1) N163 (37.5) S\(_A\)161.15 (51.25) K1158 (2.5) K.

where: K,K\(_1\)- crystalline phase, N-nematic phase, S\(_A\)-smectic phase, I-isotropic liquid, (enthalpy of transition, \( \Delta H/\text{kJ mol}^{-1} \)).

4-(p-ethyl-N-phenylacetamidoxy)-4’-[p-ethylphenylazo]biphenyl (2) showed a nematic phase at heating and a nematic-smectic A polymorphic solid phase sequence on cooling. The sequence of phases (Fig. 3), resulted from the polarized light microscopy method and confirmed by the differential scanning calorimetry method on heating and cooling, respectively, was:

- K193.5 (33.2) K203.6 (21.8) N211.65 (3.9) I;
- I211.65 (3.9) N208.25 (20.7) S\(_A\)203.6 (37.75) K193.5 (4.5) K.

According to the DSC diagram (Fig. 4), 4-(p-ethyl-N-phenylacetamidoxy)-4’-[p-trifluoromethylphenylazo]biphenyl (3) gave the following phases sequence on cooling:

- I135.65 (4.1) N132.65 (21.8) S\(_A\)129.75 (26.7) K.

![DSC diagram of 4-(p-ethyl-N-phenylacetamidoxy)-4’-[p-phenylazo]biphenyl (1).](image-url)
Fig. 3 – DSC diagram of 4-(p-ethyl-N-phenylacetamidoxy)-4'-[p-ethyl-phenylazo] biphenyl (2).

Fig. 4 – DSC diagram of 4'-trifluoromethyl-4-(p-ethyl-N-phenylacetamidoxy) azobenzene (3).
For the 4-(p-ethyl-N-phenylacetamidoxy)-4'-[p-chloro-phenylazo] biphenyl (4) it was observed a narrowed range of temperatures of existence for the monotropic smectic A phase. During the very slow cooling process from the isotropic liquid phase, the large transition peak from the DSC diagram (Fig. 5) was separated into two peaks, thus highlighting the transition temperature at smectic phase:

\[
\text{– I} 117.55 \ (4.2) \ \text{S} \ \text{A} 112 \ (21.75) \ \text{K} 1108.45 \ (7.5) \ \text{K}.
\]

The compound 4-(p-ethyl-N-phenylacetamidoxy)-4'-[p-nitro-phenylazo] biphenyl (5) showed a nematic phase during heating and a nematic-smectic A sequence on cooling. It was characterized by a mottled texture of the nematic phase on cooling, immediately before the transition to the smectic A phase. From the DSC diagram (Fig. 6) it was observed that the nematic phase appeared from the isotropic liquid phase, subcooled only at a very low cooling rate (2°C/min):

\[
\text{– I} 133.65 \ (4) \ \text{N} 131.65 \ (33.2) \ \text{S} \ \text{A} 129.75 \ (42.2) \ \text{K}.
\]

The 4-(p-ethyl-N-phenylacetamidoxy)-4'-[p-cyano-phenylazo] biphenyl (6) was an enantiotropic smectogen liquid crystal, having a polymorphism of the solid phase. It presented the following sequence of phases (Fig. 7):

\[
\text{– I} 180.75 \ (4) \ \text{S} \ \text{A} 145.65 \ (32) \ \text{K} 1127.65 \ (7.5) \ \text{K}.
\]
Textures of 4-\((p\)-ethyl-N-phenylacetamidoxyl\)-4'-\([p\)-phenylazo\] biphenyls recorded on cooling between the crossed polars, with a cooling rate of 6°C/min, were presented in Fig. 8 a. b. c. and d.

EXPERIMENTAL

Materials and methods. The presence of azophenoxide, which is very sensitive to water traces, was responsible for these compounds synthesis to occur in an anhydrous medium. For this reason, an azotropic distillation took place, in which the water-ethanol-benzene azotropic mixture was removed because the azophenoxide synthesis was realized into a benzene-ethanol mixture (1:1 in volumes). The synthesis of the novel compounds took between 5 and 6 hours. The products were solids, with different colours, from yellow to dark red. Recrystallization was realized from toluene, and the presence of a single chromatographic peak confirmed the purity of the reaction products.

Synthesis of 4-\((p\)-ethyl-N-phenylacetamidoxyl\)-4'-\([p\)-trifluoromethyl-phenylazo\] biphenyl. The synthesis was realized in a reflux installation formed by a round-bottom flask and a reflux condenser in which 1.006 g (2 mmol) 4-hydroxy-4'-\([p\)-trifluoromethyl-phenylazo\] biphenyl, 0.08 g (2 mmol) NaOH and 10 mL ethanol-benzene mixture (1:1 in volume) were introduced, under stirring. The obtained mixture was maintained under reflux for 2 hours, in order to assure the complete reaction of azophenol with sodium hydroxide. The reaction mixture was then refluxed for 3 hours, at 50–55°C, by the help of the same electrical jacket. After cooling, vacuum filtration took place. The precipitate was washed well with water directly on the filter in order to remove the sodium chloride and then it was dried in the oven at 105°C. The reaction product was subjected to recrystallization from 100 cm³ toluene. The melting point: 164–165°C. Yield: 81%. The synthesis was similar for all novel 4-\((p\)-ethyl-N-phenylacetamidoxyl\)-4'-\([p\)-phenylazo\] biphens.

Reagents. All substances necessary for the synthesis of the new 4-\((p\)-ethyl-N-phenylacetamidoxyl\)-4'-\([p\)-phenylazo\] biphens were Fluka or Merck commercially available products.

Equipment. The melting points were established with both Boetius and Sanyo devices. Elemental analysis was made on CHNOS Vario EL analyzer. Electronic spectra were recorded with a UV–Vis Jasco V–530 spectrophotometer, within 200–700 nm range. Dioxane solutions (4×10⁻⁵ M) were prepared one day before recording spectra and kept in a dark place. FTIR spectra were recorded in potassium bromide pellets (KBr, Merck), with a Bio–Rad FTS 135 spectrophotometer, within the range 3500–400 cm⁻¹. The ¹H–NMR spectra were recorded with a Varian NMR-System 300 spectrometer, at 300 MHz, in DMSO-d₆. The chemical shifts referred to tetramethylsilane (TMS) as the internal standard.
Phase sequences and phase transition temperatures were determined by polarizing optical microscopy (POM) – it was applied using an IOR MC–5A polarized light microscope with a heating table at 10°C/min rate for both heating and cooling, and differential scanning calorimetry (DSC) – it analyzed the compounds with a Perkin Elmer DSC–2 device with the same heating–cooling rate (10°C/min.). Sometimes, to separate the transition peaks, the study was carried out at lower rates (5°C/min, 2°C/min). The device was set at a sensitivity of 5 mcal/s in an inert atmosphere of argon.

**CONCLUSIONS**

The new synthesized 4-(p-ethyl-N-phenylacetamidoxy)-4’-[p-phenylazo] biphenyls were purified and characterized by physico-chemical methods. The research activity concerning the nematic and smectic liquid crystals properties have revealed that the size, position and polarity of the terminal group have a strong influence on both the mesophase type presented by each new synthesized compound and the transition temperatures.

**REFERENCES**