Researches Concerning the Synthesis, Physico-Chemical and Liquid Crystal Properties of New Azomonoetheramides

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The synthesis of some novel azomonoetheramides, five 4-(N-phenylacetamidoxy) azobenzenes and three 4-(N-phenylacetamidoxy)-4'-(phenylazo) biphenyls, was completed through condensation of some 4-(phenylazo) phenols or 4-hydroxy-4'-(phenylazo) biphenyls, 4-hydroxy-4'- (p-chloro-phenylazo) biphenyl, 4-hydroxy-4'-(p-methyl-phenylazo) biphenyl, in alkaline medium, with 4-ethoxy-N-chloroacetylaniline. The purification of compounds was achieved by recrystallization from toluene. The purity degree was checked by gas chromatography. The compounds were solid, with different colours, and with high melting points. Their structures were established both by elemental and spectral analysis (UV–Vis, FTIR, ¹H–NMR, GC–MS). The liquid crystal properties were studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

Keywords: azomonoetheramides, synthesis, physico-chemical characterization, liquid crystal properties

In the specialized papers, a method for the obtaining of azomonoetheramides is described. It supposes the condensation in alkaline medium, with different *N*-chloroacetylanilines [1–3], of some 4-(phenylazo) phenols and 4-hydroxy-4'-(phenylazo) biphenyls, respectively [4–10].

Azomonoetheramides were synthesized through a condensation reaction in alkaline medium, which took place between 4-(phenylazo) phenols and 4-hydroxy-4'-(phenylazo) biphenyls, respectively, with 4-ethoxy-N-chloroacetylaniline. Thus, eight compounds were obtained as follows: five 4-(*p*-ethoxy-N-phenylacetamidoxy) azobenzenes and three 4-(*p*-ethoxy-N-phenyl-acetamidoxy)-4'-(phenylazo) biphenyls.

The 4-(phenylazo) phenols and 4-hydroxy-4'-(phenylazo) biphenyls involved in the synthesis were the following: 4-(phenylazo) phenol, 4-(4'-nitro-phenylazo) phenol, 4-(4'-chloro-phenylazo) phenol, 4-(4'-methyl-phenylazo) phenol, 4-hydroxy-4'-(phenylazo) biphenyl, 4-hydroxy-4'-(*p*-chloro-phenylazo) biphenyl, and 4-hydroxy-4'-(*p*-methyl-phenylazo) biphenyl.

Synthesis reactions occurred according to a bimolecular nucleophil substitution mechanism (S_N2). This mechanism was given in figure 1.

Experimental part
Materials and methods
Synthesis was realized in an anhydrous medium due to the presence of azophenoxide that is very sensitive to the water traces. In this case, an azeotrop distillation was realized. The azeotrop mixture water-ethanol-benzene was removed, because the synthesis of azophenoxide took place in a benzene-ethanol (1:1, by volumes) mixture.

The synthesis ranged from 5 to 8 h, depending on the reaction products nature.

Solid compounds with different colours, from yellow to dark red, were obtained.

Recrystallization of 4-(N-phenylacetamidoxy) azo-benzenes and 4-(N-phenylacetamidoxy)-4'-(phenyl-azo) biphenyls, respectively, took place from toluene. The presence of a single chromatographic (GC) peak certified the purity of these compounds.
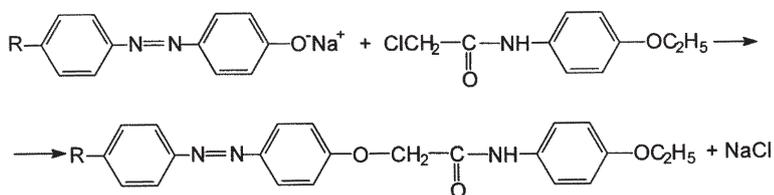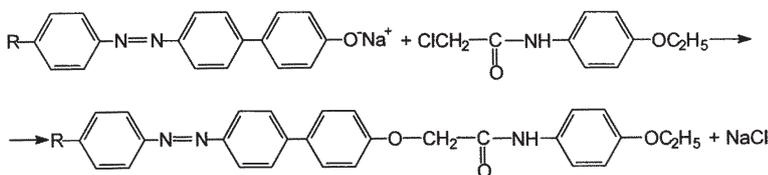
R = H, CH₃, NO₂, Cl.

Fig. 1. Synthesis reactions of the new compounds

R = H, CH₃, Cl.

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Synthesis of 4'-nitro-4-(p-ethoxy-N-phenylacetamidoxy) azobenzene

To a one-necked round-bottomed flask equipped with mechanical stirrer, thermometer and condenser, 1.22 g $(5 \times 10^{-3}$ M) of 4-(4'-nitro-phenylazo) phenol, 0.2 g $(5 \times 10^{-3}$ M) sodium hydroxide and 40 mL of ethanol–benzene mixture (1:1, by volumes) were added. The reaction mixture was stirred two hours at 70^0C, until the azophenol reacted with sodium hydroxide. The reaction water was removed by distillation of 15 mL from an ethanol–benzene–water azeotropic mixture. 1.0675 g $(5 \times 10^{-3}$ M) of 4-ethoxy-*N*-chloroacetylaniline were added to anhydrous azophenoxide and the reaction mixture was stirred for 5 hours at 50–55^{0}C. After cooling at room temperature, the solid product was filtered, then washed with water in order to remove the sodium chloride, and dried in a heating chamber, at 105^{0}C. Then, the reaction product was recrystallized from 70 mL toluene to obtain (yield 87.14%) 4'-nitro-4-(*p*-ethoxy-*N*-phenylacetamidoxy) azobenzene (m.p. 205–206^{0}C).

The synthesis was similar for all eight novel compounds.

Reagents

Aniline, *p*-toluidine, *p*-chloroaniline, *o*-chloroaniline, *p*-nitroaniline used for the preparation of diazonium salts were Fluka or Merck products. Phenol and 4-hydroxy-biphenyl used in the coupling reaction were also Fluka products. Chloro-acetyl chloride and *p*-ethoxyaniline used for the synthesis of 4-ethoxy-*N*-chloroacetylaniline were Fluka or Merck products.

Equipment

The melting points were established in capillaries (sulphuric acid bath) and with a Boetius apparatus.

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 $(4 \times 10^{-5}$ 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}.

^{1}H–NMR spectra were recorded with a Varian NMR-System 300 spectrometer, at 300 MHz, in CDCl$_3$ or DMSO–d$_6$. The chemical shifts referred to tetramethylsilane (TMS), as internal standard.

Phase sequences and phase transition temperatures were determined by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). First method was applied using an IOR MC–5A polarized light microscope with a heating table at a rate of 10^{0}C/min for both heating and cooling. The second method analyzed the compounds with a Perkin Elmer DSC–2 device, with the same heating–cooling rate (10^{0}C/min). Sometimes, lower speeds (5^{0}C/min, 2^{0}C/min) were used to separate the transition peaks. The device was set at a sensitivity of 5 mcal/s, in an inert atmosphere of argon.

Results and discussions

Those substituents from the para position as against the azo group influenced both melting point and reaction yield.

4-(N-phenylacetamidoxy) azobenzenes presented higher melting temperatures due to the presence of NO$_2$ and Cl groups, while the presence in para position of CH$_3$ and Cl groups for 4-(N-phenylacetamidoxy)-4'-(phenylazo) biphenyls determined a decrease in the melting points.

Reaction yields were usually high, but very dependent on the azomonoetheramides solubility into the solvent chosen for recrystallization (table 1).

UV–Vis spectra

Spectral analysis in UV-Vis highlighted absorption bands owed to the main component parts of these compounds. Thus, the presence of absorption bands of medium intensity at 252–290 nm, which were of E or B benzenoide type, intense bands of K type at 327–367 nm, and some bands of weak intensity of type R at 422–458 nm was observed.

The intense bands of K type were due to the conjugated Ar–N=N–Ar system, and those of medium intensity of E or B type appeared as consequence of d̄ electrons conjugation from benzene rings. Bands of weak intensity of R type from VIS were the result of the –N=N– chromophore existence in these compounds (table 2).

FTIR spectra

No.	Structural formulas	Molecular formulas	M	M.p. [°C]	η [%]
1.		$C_{22}H_{20}N_4O_5$	420	205–206	87.14
2.		$C_{22}H_{20}N_3O_3Cl$	409.5	197–198	84
3.		$C_{23}H_{23}N_3O_3$	389	202	84.31
4.		$C_{22}H_{21}N_3O_3$	375	159	95.46
5.		$C_{22}H_{20}N_3O_3Cl$	409.5	172–173	72.02
6.		$C_{28}H_{24}N_3O_3Cl$	485.5	177–178	81.56
7.		$C_{29}H_{27}N_3O_3$	465	147	92.04
8.		$C_{28}H_{25}N_3O_3$	451	143–144	93.12

M – Molecular mass; M.p. – Melting point; η – Yield.

Table 1
STRUCTURAL FORMULAE, MOLECULAR MASSES, MELTING POINTS AND YIELDS FOR THE EIGHT NOVEL SYNTHESIZED COMPOUNDS

No.	Name	λ_{max} [nm]	ε_{max} [1000 cm²] mol	Elemental analysis %C calcd. found	%C calcd. found	%C calcd. found
1.	4'-nitro-4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	254 367 458	17565 23525 9500	62.85 62.32	4.76 4.42	13.33 13.03
2.	4'-chloro-4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	252 350 448	23337 23112 1180	64.46 64.12	4.88 4.23	10.25 9.87
3.	4'-methyl-4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	250 348 443	18810 24305 975	70.95 70.64	59.12 58.94	10.79 10.43
4.	4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	252 343 444	17250 21535 882	70.40 70.12	5.60 5.27	11.20 11.01
5.	2'-chloro-4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	250 347 435	16775 85875 1622	64.46 64.12	4.88 4.29	10.25 10.06
6.	4-(p-ethoxy-N-phenylacetamidoxy)-4'-[p-chloro-phenylazo] biphenyl	251 288 327 422	21047 24457 84075 1320	69.20 68.89	4.94 4.67	8.65 8.34
7.	4-(p-ethoxy-N-phenylacetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	258 290 327 427	24317 27348 83925 1072	74.83 74.53	5.80 5.56	9.03 8.87
8.	4-(p-ethoxy-N-phenylacetamidoxy)-4'-[phenylazo] biphenyl	259 287 324 418	23720 26812 77225 1055	74.50 74.12	5.54 5.22	9.31 9.02

calcd. – Calculated.

Table 2
UV–Vis ABSORPTION BANDS AND ELEMENTAL ANALYSIS OF THE NOVEL COMPOUNDS

No.	Name	IR absorption bands, ν [cm^{-1}] –N=N–	–NH–	C_{Ar}–O–CH$_2$– antisymm.	symm.	–CO–NH– amide I / amide II
1.	4'-nitro-4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	1439.49 (s)	3365.49 (s)	1235.53 (vi)	1047.45 (i)	1676.91 (i) 1541.72 (vi)
2.	4'-chloro-4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	1418.96 (s)	3387.36 (s)	1236.80 (vi)	1056.19 (i)	1672.69(vi) 1534.82 (i)
3.	4'-methyl-4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	1447.62 (s)	3344.13 (s)	1249.77 (vi)	1046.27 (i)	1676.93(vi) 1522.62 (vi)
4.	4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	1438.44 (s)	3381.80 (s)	1249.94 (vi)	1063.34 (i)	1672.90 (i) 1540.18 (vi)
5.	2'-chloro-4-(p-ethoxy-N-phenylacetamidoxy) azobenzene	1432.16 (s)	3384.16 (s)	1241.19 (vi)	1058.72 (i)	1671.51 (i) 1542.06 (vi)
6.	4-(p-ethoxy-N-phenylacetamidoxy)-4'-[p-chloro-phenylazo] biphenyl	1454.03 (s)	3335.64 (s)	1236.39 (vi)	1060.02 (i)	1657.92(vi) 1515.14 (vi)
7.	4-(p-ethoxy-N-phenylacetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	1456.20 (s)	3334.12 (s)	1237.90 (vi)	1060.46 (i)	1659.12(vi) 1514.99 (vi)
8.	4-(p-ethoxy-N-phenylacetamidoxy)-4'-[phenylazo] biphenyl	1418.35 (s)	3330.75 (s)	1244.87 (vi)	1059.16 (i)	1659.59 (i) 1525.39 (vi)

FTIR absorption bands: *vi* – very intense; *i* – intense; *m* – moderate; *w* – weak; *antisymm.* – anti-symmetric; *symm.* – symmetric.

Table 3
IR ABSORPTION BANDS OF THE NOVEL COMPOUNDS

The structural formulae of the five 4-(N-phenyl-acetamidoxy) azobenzenes and the three 4-(N-phenylacetamidoxy)-4'-(phenylazo)biphenyls, respectively, were established by FTIR spectra, as well.

FTIR spectra for azomonoetheramides recording put into evidence the characteristic absorption bands, like –N=N– , –NH–, Ar–O–CH$_2$–, –CO–NH–, but also those bands due to benzene rings.

The vibration of valence $\nu_{N=N}$ should have been characteristic to these compounds, but absorptions occurred at small values of wave numbers, because this bond has a very weak polarity. Thus, the obtained bands had low intensities (1456–1417 cm^{-1}).

In the case of a ν_{NH} valence vibration for an amide group, the band appeared at high values of the wave number, due to the strong N-H bond. Band was sharp, and a large band accompanied it, at some spectra. As it was observed from spectra, wave numbers values differed little in function of the amide groups' association intensity (3387–3330 cm^{-1}). The presence of C–H bonds from the aromatic rings manifested by very weak bands at values ranging between 3110–3064 cm^{-1}.

These compounds, all presenting CH$_2$ and CH$_3$ groups, gave absorption bands in the aliphatic radicals region. Therefore, for ν_{CH3} antisymmetric there was a band at 2985–2974 cm^{-1}, and other bands appeared at 2927–2923 cm^{-1} due to ν_{CH2} antisymmetric vibrations. CH$_2$ and CH$_3$ groups gave symmetric valence vibrations that led to a weaker single band at 2867–2863 cm^{-1}.

An important band, which characterized spectra, was the one of the ν_{CO} valence vibration for the amide group, so called amide I, which was placed at very close values (1676–1657 cm^{-1}).

The band from 1542–1514 cm^{-1}, usually the most intense one from the spectrum, was considered amide II band.

A particular importance presented those bands due to ether vibrations, the compounds having an alkyl-O-aryl group. Very intense bands that appeared at 1249 –1235 cm^{-1} were attributed to antisymmetric valence vibrations, while weaker bands from 1063–1046 cm^{-1} were assigned to symmetric ether vibrations of valence (table 3).

No.	Aromatic protons	NH	CH₂ (–O–CH₂–)	CH₃ (CH₃–Ar)	CH₃ (–O–CH₂–CH₃)	CH₂ (–O–CH₂–CH₃)
1.	7.5 m	9.0 s	4.8 s	–	1.3 t	3.9 q
2.	7.5 m	9.0 s	4.6 s	–	1.4 t	3.9 q
3.	7.4 m	9.1 s	4.7 s	2.2 s	1.5 t	3.8 q
4.	7.4 m	8.9 s	4.8 s	–	1.3 t	3.9 q
5.	7.4 m	9.1 s	5.0 s	–	1.4 t	4.0 q
6.	7.4 m	8.9 s	4.9 m	–	1.4 t	3.8 q
7.	7.3 m	8.8 s	4.7 s	2.3 s	1.5 t	3.8 q
8.	7.5 m	8.9 s	4.8 s	–	1.3 t	3.9 q

s – singlet; *m* – multiplet; *t* – triplet, *q* – quartet.

¹H-NMR spectra

In ¹H-NMR spectra of 4'-methyl-4-(*p*-ethoxy-N-phenylacetamidoxy) azobenzene and 4-(*p*-ethoxy-N-phenylacetamidoxy)-4'-[*p*-methyl-phenylazo] biphenyl (compounds 3 and 7), six types of signals were identified. These were: a multiplet for aromatic protons, a singlet for the NH group proton, a singlet for CH_2 (–O–CH₂–) group protons, a singlet for CH_3 (CH₃–Ar) group protons, a triplet for CH_3 (–O–CH₂–CH₃) group protons, and a quartet for CH_2 (–O–CH₂–CH₃) group protons.

In contrast, ¹H-NMR spectra of the compounds 1, 2, 4, 5, 6 and 8 were characterized, at their turn, by five types of signals. Thus, there were: a multiplet for aromatic protons, a singlet for NH group proton, a singlet for CH_2 (–O–CH₂–) group protons, a triplet for CH_3 (–O–CH₂–CH₃) group protons, and a quartet for CH_2 (–O–CH₂–CH₃) group protons (table 4).

Investigation of liquid crystal properties

4'-Nitro-4-(*p*-ethoxy-N-phenylacetamidoxy)-azobenzene (compound 1) was an enantiotropic smectogen compound and presented polymorphism of solid phase at heating. From the DSC diagram (figure 2), a slightly pretransitional effect was observed at heating for the A smectic – isotropic transition.

Mesophases sequence was:
– at heating K 139.85 K₁ 207.35 S_A 220.65 I (K, K₁–crystalline phase, S_A–smectic phase, I–isotropic liquid);
– at cooling I 192.65 S_A 178.15 K (I–isotropic liquid, S_A–smectic phase, K–crystalline phase).

In figure 3 it was observed the appearance of paramorphotic texture for A smectic phase, when heating from the K₁ solid phase.

Compound 2 presented an enantiotropic A smectic phase, as the previous one.

Mesophases sequence, as it resulted from the DSC diagrams (fig. 4), was:
– at heating K 194.85 S_A 203.65 I;
– at cooling I 195.75 S_A 187.25 K.

Substance presented a pretransitional effect at heating and a sub-cooling of the isotropic liquid, in this case too.

Figure 5 gave the A smectic solid transition at heating.
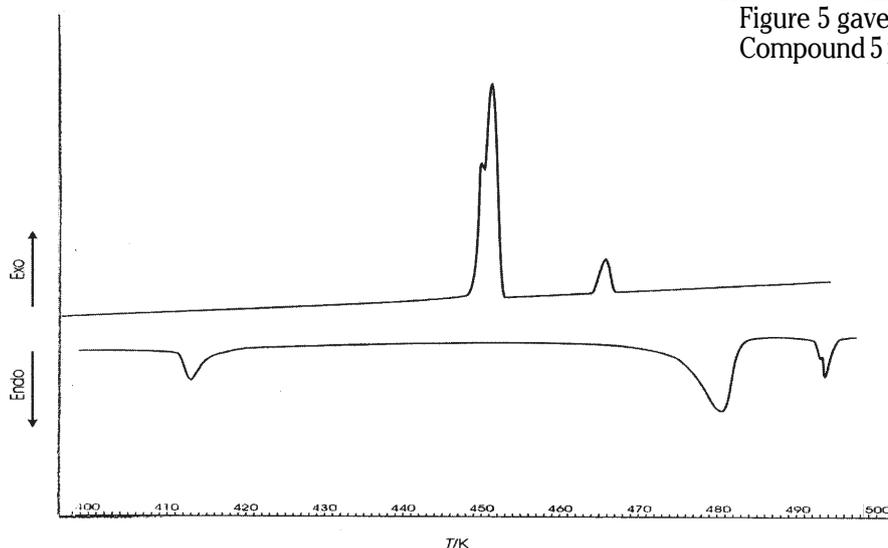
Compound 5 presented a sequence of solid and smectic

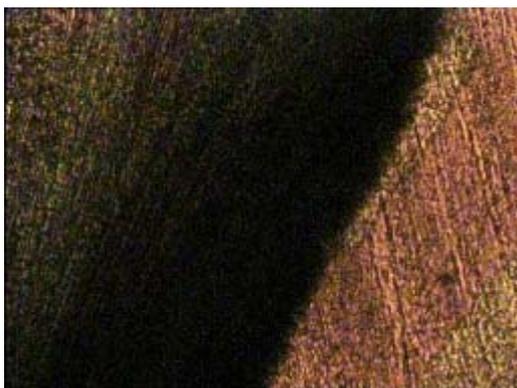Fig. 2. DSC diagram of 4'-nitro-4-(*p*-ethoxy-N-phenylacetamidoxy) azobenzene
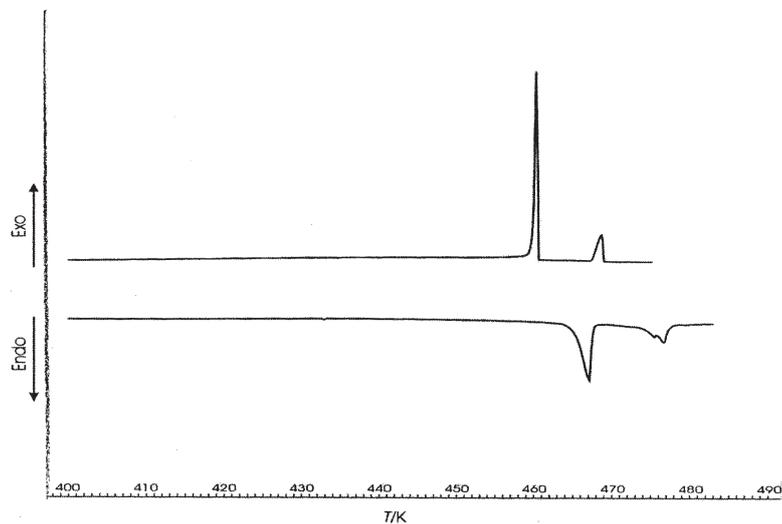

Fig. 3. Paramorphotic texture of A smectic phase

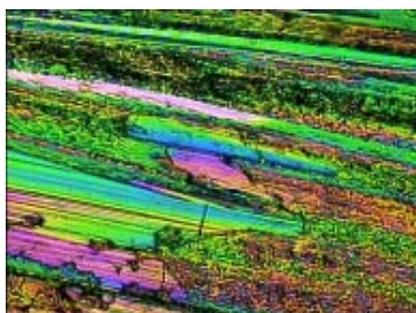Fig. 4. DSC diagram of 4'-chloro-4-(*p*-ethoxy-N-phenylacetamidoxy) azobenzene
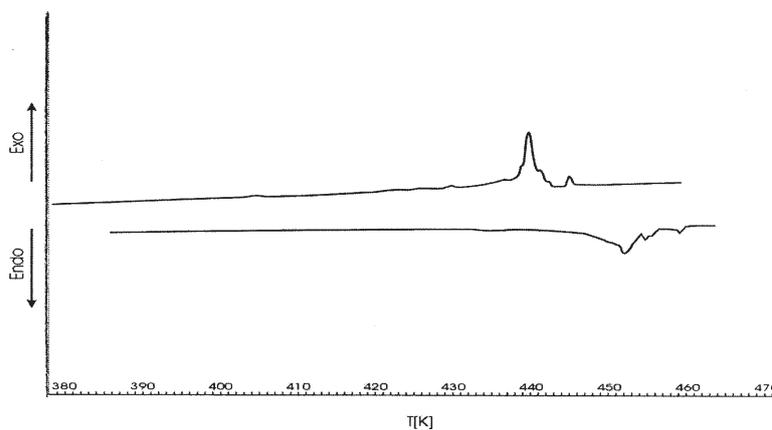

Fig. 5. A smectic solid transition at heating

Fig. 6. DSC diagram of 2'-chloro-4-(*p*-ethoxy-N-phenylacetamidoxy) azobenzene
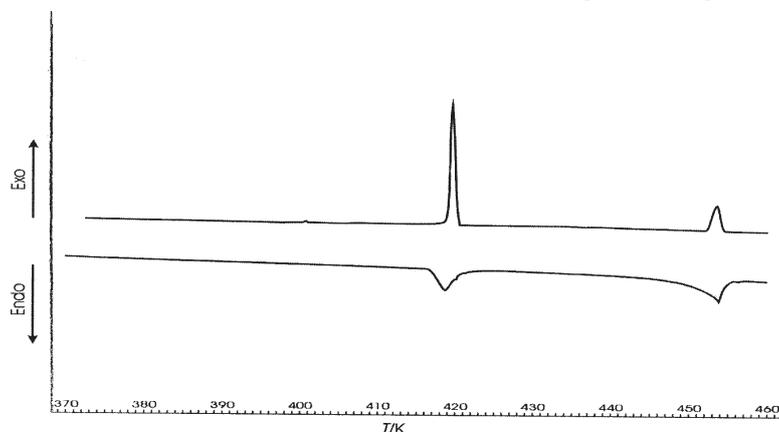

Fig. 7. DSC diagram of 4-(*p*-ethoxy-N-phenylacetamidoxy)-4'-[*p*-methyl-phenylazo] biphenyl

Fig. 8. Paramorphotic texture of K_I solid phase

Fig. 9. Focal conic texture of A smectic phase

rich phases, both at heating and at cooling. From the DSC diagrams (fig. 6), transition temperatures were:

– at heating K 160 K_I 179 S_X 181.65 S_A 186.05 I;
– at cooling I 171.85 S_A 169 S_X 166.75 K_2 157 K_I 131.65 K (where S_X represented the smectic phase, which was incompletely identified).

Compound 6 was an enantiotropic smectogen liquid crystal, with the following sequence of phases (DSC-figure 7):

– I 180.75 S_A 145.65 K_I 127.65 K.

In addition, this substance presented polymorphism of the solid phase.

Paramorphotic texture for the K_I solid phase was given in figure 8.

In figure 9, the focal conic texture for the A smectic phase was highlighted. This characterized the compound 8.

For the compound 8, a narrow field of existence temperatures for the monotropic A smectic phase was observed. At a very slow cooling, the broad peak of transition from the isotropic liquid phase, presented in DSC diagrams (fig. 10), was separated into two peaks. Thus, the transition temperature to smectic phase was highlighted.
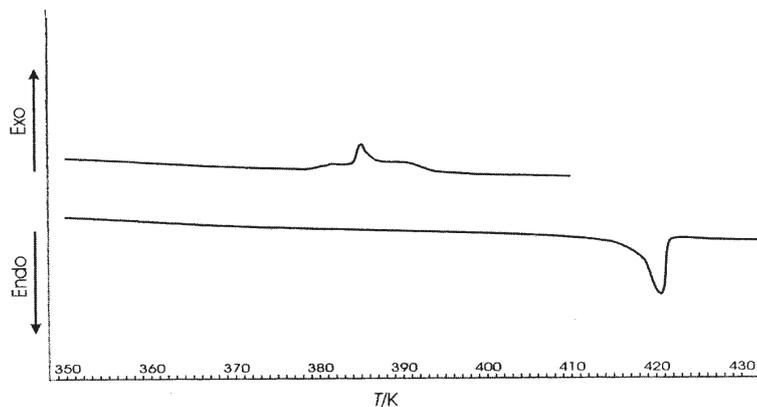
Fig. 10. DSC diagram of 4-(*p*-ethoxy-N-phenylacetamidoxy)-4'-[phenylazo] biphenyl

Phases sequence at cooling was:
– I 117.55 $\check{S}_A$ 112 K_I 108.45$\check{K}$.

Conclusions

The synthesis of the eight novel compounds, five 4-(*N*-phenylacetamidoxy) azobenzenes and three 4-(*N*-phenylacetamidoxy)-4'-(phenylazo) biphenyls, was achieved through the condensation of sodium azophenoxydes with 4-methoxy-*N*-chloroacetylaniline. Their structures were established by elemental and spectral analysis. The mesomorphic behaviour was studied by polarizing optical microscopy and differential scanning calorimetry. The obtained DSC diagrams and textures confirmed the liquid crystals properties of the novel azomonoetheramides.

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