

NOVEL AZODERIVATIVES AS LIQUID CRYSTALS

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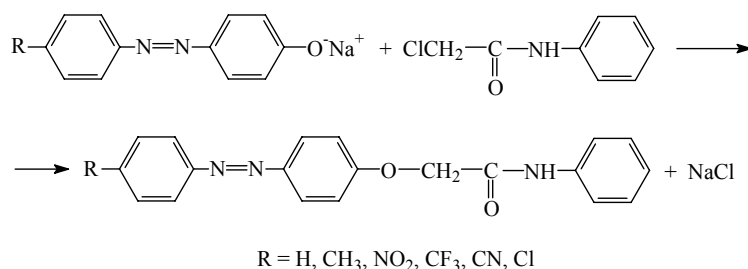
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In this paper the authors present novel azoderivatives obtained by the condensation of *N*-chloroacetylaniline with 4-(phenylazo)phenols or 4-hydroxy-4'-(phenylazo)biphenyls. The compounds have been characterised using UV-visible, IR, ¹H-RMN, and GC-MS methods. The liquid crystals properties of these novel azoderivatives were studied through calorimetric measurements and optical texture observations.

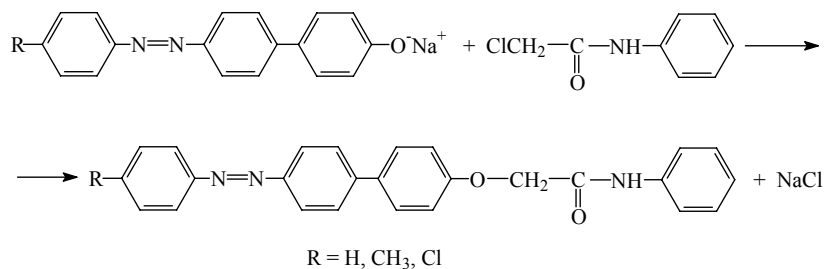
INTRODUCTION

The method used for the obtaining of azoderivatives was described in the speciality papers, through condensation of 4-(phenylazo)phenols, in alkaline medium, with different aromatic compounds mono- or bis(chloromethylated).¹⁻⁴ Then, the condensation of *N*-chloroacetylaniline for the obtaining of novel compounds with liquid crystal properties has been studied. For this purpose, the condensation of 4-(phenylazo)phenols, respectively

4-hydroxy-4'-(phenylazo)biphenyls, has been made in alkaline medium, with *N*-chloroacetylaniline. Through the SN₂ reaction, starting from 4-(phenylazo)phenols, 4-(*N*-phenylacetamidoxy) azobenzenes have been obtained (Scheme 1). Similarly, by the reaction of 4-hydroxy-4'-(phenylazo)biphenyls with *N*-chloroacetylaniline, 4-(*N*-phenylacetamidoxy)-4'-[phenylazo]biphenyls have been obtained (Scheme 2).



Scheme 1 – Synthesis of 4-(*N*-phenylacetamidoxy)azobenzenes.



Scheme 2 – Synthesis of 4-(*N*-phenylacetamidoxy)-4'-[phenylazo]biphenyls.

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The synthesis of these compounds supposes an anhydrous medium, for the prevention of alkaline phenoxides decomposition in the presence of water traces. The complete water elimination has been assured by azeotropic distillation, when separates the azeotropic water–ethanol–benzene, using a mixture of benzene–ethanol (1:1, in volumes). The synthesis has been made in 5–8 hours, depending on the reactivity of the compounds.

These novel azoderivatives are well-crystallised, having yellow to orange-red colour and high melting points. The purification of these compounds has been made through recrystallisation from toluene. The yields depend on the solubility of azoderivatives in the solvent chosen for recrystallisation. In the structure of these compounds, the presence of azo, ether and acetamido groups has been observed.

The physico-chemical properties of these novel azoderivatives are influenced by the substitutes in the *para* position with regard to the azo group.^{4,5}

RESULTS AND DISCUSSION

Tables 1–3 comprise the structural and molecular formulae of nine novel azoderivatives, the results of the elemental analysis (C, H, N), melting temperatures, yields, λ_{\max} and ϵ_{\max} from electronic spectra and the most important IR absorption bands.

The presence of some groups (NO_2 , F_3C , Cl, CN) in *para* position explains the melting points increase of 4-(N-phenylacetamidoxy)azobenzenes. But, for the 4-(N-phenylacetamidoxy)-4'-[phenylazo]biphenyls, the presence of CH_3 , Cl substituents in *para* position determines the decreasing of the melting points. The yields are generally high, depending on the raw material purity and the solubility in the solvent used for recrystallisation.

The UV–Vis spectra point out the absorption bands due to the main groups in the structure of these compounds. The presence of some absorption benzenoid-type E- or B-bands from middle intensity at 250–287 nm, intense absorption K-bands at 346–387 nm, and low intensity R-bands at 418–446 nm was observed. Intense absorption K-bands were associated with the conjugated system Ar-N=N-Ar . Middle intensity benzenoid-type E- or B-bands appear consequently to the $e\pi$ conjugation in the aromatic rings. Low intensity

R-bands from visible have been associated with $-\text{N=N}-$ chromophore (Table 2).

The electronic spectra of these novel azoderivatives exhibit absorptions like other similar compounds described in specialty papers.^{6,7}

The structures of 4-(N-phenylacetamidoxy)azobenzenes, respectively 4-(N-phenylacetamidoxy)-4'-(phenylazo)biphenyls were established using infrared spectra (Table 3). IR spectra acquisition for each compound show absorption bands characterising $-\text{N=N}-$, Ar-O-CH_2- , $-\text{CO-NH}-$, Ar-CH_3 , Ar-CN , Ar-NO_2 , and Ar-CF_3 groups, and also aromatic rings.

Comparative study of IR bands shows very similar values for the absorption frequencies. Valency vibration $\nu_{\text{N=N}}$ should be characteristic to these novel compounds. Because the bond polarity is very weak the absorptions appear at low values of the wavenumbers and with low intensities ($1444\text{--}1414\text{ cm}^{-1}$).

Valency vibration band of amide group (ν_{NH}) appears at high values of the wavenumber, because the N–H bond is strong. This band is usually sharp, but wide for some spectra.

The values of the wavenumber are different depending on the intensity of the amide groups association ($3388\text{--}3373\text{ cm}^{-1}$). Very weak bands between 3060 cm^{-1} and 3064 cm^{-1} show the presence of C–H bonds from the aromatic rings.

The most important in the spectra is the valency vibration ν_{CO} for the amide group, the so-called amide I band, which appears at much closed values ($1684\text{--}1676\text{ cm}^{-1}$). Amide II band is the most intense in the spectrum ($1545\text{--}1530\text{ cm}^{-1}$) for the majority of compounds.

Absorption bands in the aliphatic radicals' zone characterize $-\text{CH}_2-$ and $-\text{CH}_3$ groups. A single weak band at $2856\text{--}2852\text{ cm}^{-1}$ points out symmetrical valency vibrations for $-\text{CH}_2-$ and $-\text{CH}_3$ groups (compounds **3** and **9**). Absorption band for $-\text{CN}$ group, at 2231 cm^{-1} , characterizes the compound **6**.

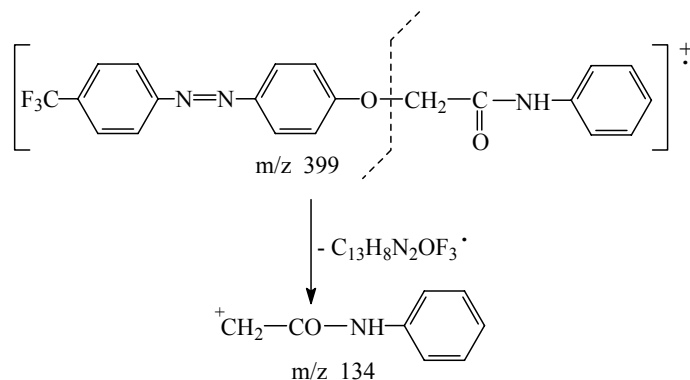
Vibration bands around 1600 cm^{-1} highlight the presence of benzene rings. Four bands due to the antisymmetrical (very intense, $1264\text{--}1241\text{ cm}^{-1}$) and symmetrical ($1070\text{--}1044\text{ cm}^{-1}$, much weak) etheric vibrations are much important and relevant (Table 3).

¹H–NMR spectra (Table 4) have confirmed the structure of the novel synthesized azoderivatives. Aromatic protons show a multiplet (m) at δ 7.23–

8.11, NH group proton a singlet (s) at δ 8.00–9.90, and CH₂ (O–CH₂) group protons appear as a singlet at δ 4.69–5.10. In addition, a singlet appears at δ 2.35 for the compound **9**, because of

CH₃ group protons.

Fragmentations of compound **4** characterizing the novel synthesized azoderivatives (Scheme 3).



Scheme 3 – The molecular ion obtained through the fragmentation of compound **4**

Table 1

Novel synthesized 4-(N-phenylacetamidoxy)azobenzenes and 4-(N-phenylacetamidoxy)-4'-[phenylazo]biphenyls

Compound	Structural formula	Molecular formula	M	Melting point [°C]	Yield [%]	%C	%H	%N
						calc. found	calc. found	calc. found
1		C ₂₀ H ₁₇ N ₃ O ₂	331	160–161	71.00	72.50 72.48	5.13 5.11	12.68 12.65
2		C ₂₀ H ₁₆ N ₄ O ₄	376	199	55.85	63.82 63.65	4.25 4.12	14.89 14.71
3		C ₂₁ H ₁₉ N ₃ O ₂	345	195	75.36	73.04 72.96	5.50 5.45	12.17 12.10
4		C ₂₁ H ₁₆ N ₃ O ₂ F ₃	399	180–181	50.12	63.15 62.87	4.01 3.91	10.52 10.34
5		C ₂₀ H ₁₆ N ₃ O ₂ Cl	365.5	220	64.29	65.66 65.43	4.37 4.22	11.49 11.39
6		C ₂₁ H ₁₆ N ₄ O ₂	356	198	84.26	70.78 70.67	4.49 4.34	15.73 15.66
7		C ₂₆ H ₂₁ N ₃ O ₂	407	161	73.72	76.65 76.43	5.15 4.92	10.31 10.11
8		C ₂₆ H ₂₀ N ₃ O ₂ Cl	441.5	156–157	78.14	70.66 70.42	4.53 4.31	9.51 9.23
9		C ₂₇ H ₂₃ N ₃ O ₂	421	158	54.63	76.95 76.90	5.46 5.21	9.97 9.73

Table 2

UV-visible spectra for the novel azoderivatives 1–9

Compound	Name	λ_{max} [nm]	ϵ_{max} [1000 cm ² /mol]
1	4-(N-phenylacetamidoxy)azobenzene	265	19395
		346	48860
		444	3385
2	4'-nitro-4-(N-phenylacetamidoxy)azobenzene	267	29865
		375	70992
		437	1075

Table 2 (continued)

3	4'-methyl-4-(N-phenylacetamidoxy)azobenzene	267	9865
		351	34750
		433	3385
4	4'-trifluoromethyl-4-(N-phenylacetamidoxy)azobenzene	266	18670
		353	47682
		428	600
5	4'-chloro-4-(N-phenylacetamidoxy)azobenzene	266	16290
		353	48065
		445	3645
6	4'-cyano-4-(N-phenylacetamidoxy)azobenzene	267	16400
		359	31777
		446	4427
7	4-(N-phenylacetamidoxy)-4'-[phenylazo]biphenyl	251	15110
		287	71870
		356	19485
		433	722
8	4-(N-phenylacetamidoxy)-4'-[p-chloro-phenylazo]biphenyl	250	51975
		285	31875
		370	76425
		428	725
9	4-(N-phenylacetamidoxy)-4'-[p-methyl-phenylazo]biphenyl	269	39772
		286	16667
		387	8595
		418	442

Table 3

Infrared spectra for the novel azoderivatives 1–9

Compound	IR absorption bands, ν [cm^{-1}]				
	–N=N–	–NH–	$\text{C}_{\text{Ar}}\text{--O--CH}_2\text{--}$		–CO–NH– amide I / amide II
			antisym.	sym.	
1	1437.22 (w)	3384.12 (w)	1252.64 (vi)	1061.49 (i)	1678.24 (vi) 1540.16 (i)
2	1437.00 (w)	3388.65 (w)	1254.23 (vi)	1061.31 (i)	1676.18 (i-vi) 1542.00 (vi)
3	1430.61 (w)	3378.46 (w)	1257.42 (vi)	1059.47 (i)	1679.41 (vi) 1539.48 (i)
4	1427.14 (w)	3374.29 (w)	1256.18 (vi)	1058.14 (i)	1678.92 (vi) 1540.63 (vi)
5	1432.47 (w)	3377.58 (w)	1248.29 (vi)	1060.72 (i)	1681.72 (vi) 1541.16 (vi)
6	1414.66 (w)	3386.71 (w)	1247.34 (vi)	1063.66 (i)	1681.79 (vi) 1530.19 (vi)
7	1444.82 (w–m)	3373.21 (w)	1240.84 (i-vi)	1059.27 (i)	1684.66 (vi) 1539.29 (vi)
8	1436.08 (w)	3375.62 (w)	1252.61 (vi)	1061.42 (i)	1677.24 (vi) 1545.19 (i)
9	1443.64 (w–m)	3379.29 (w)	1253.97 (i-vi)	1060.25 (i)	1679.89 (vi) 1535.80 (vi)

Table 4

Chemical shifts (δ) for the novel azoderivatives 1–9

Compound	δ [ppm]			
	Aromatic protons	NH	CH_2 (–O–CH ₂ –)	CH_3 (CH ₃ –Ar)
1	7.23–7.65 m	8.12 s	4.86 s	–
2	7.47–7.82 m	8.22 s	4.87 s	–
3	7.24–7.64 m	8.50 s	4.90 s	2.34 s
4	7.24–7.65 m	9.10 s	4.69 s	–
5	7.24–7.64 m	8.11 s	4.88 s	–

Table 2 (continued)

6	7.64–8.11 m	8.80 s	4.69 s	–
7	7.24–7.68 m	8.00 s	4.91 s	–
8	7.23–7.65 m	8.10 s	4.78 s	–
9	7.12–7.58 m	9.90 s	5.10 s	2.35 s

The compounds **5** and **6** have liquid crystal properties. The identification of the mesophases was realized by textures analysis, using a polarised light microscope. For the reason of a precise determination of the phase transition temperatures, capacitive method and thermodielectric effect have been utilised.^{8–14} Only by cooling the compound **4** has liquid crystal properties, respectively a high orderly smectic mesophase. The compound **6** has a high orderly smectic mesophase, and a nematic

mesophase the same at heating and cooling. The compound **5** has only a nematic mesophase.^{15,16} The compound **8** is a liquid crystal that shows high orderly smectic mesophase at the heating only, and nematic and smectic mesophase at the cooling only. Table 5 points out the polymorphism and the clarification temperatures for the compounds **4**, **5**, **6** and **8** only, depending on the substituents in *para* position (–CF₃, –Cl and –CN).

Table 5

Phase transition temperatures (obtained after scanning of the first cooling and second heating) for the novel azoderivatives

Compound	T/°C	
	Heating	Cooling
4	K 186.85 I	I 186.75 SmA 173 K
5	K 161 N 220 I	I 209 N 161 K
6	K 129 SmA 135 N 198 I	I 181 N 136 S 131 K
8	K 165.45 SmA 168.75 I	I 134 N 133 SmA 131.15 K ₁ 126.15 K

K, K₁ – crystalline phases, SmA – smectic A phase, N – nematic phase, I – isotropic liquid.

The liquid crystals properties of these compounds have been studied using calorimetric measurements and optical texture observations.^{17,18} Fig. 1 shows textures of solid, smectic and nematic phases obtained by heating of compounds.¹⁹ By

cooling, the nematic mesophase appears with the so-called droplets texture, and passed to the Schlieren texture at the decreasing of temperature (Fig. 2). Fig. 3 highlights the nematic–smectic phase transition, characterized by fan texture.¹⁹

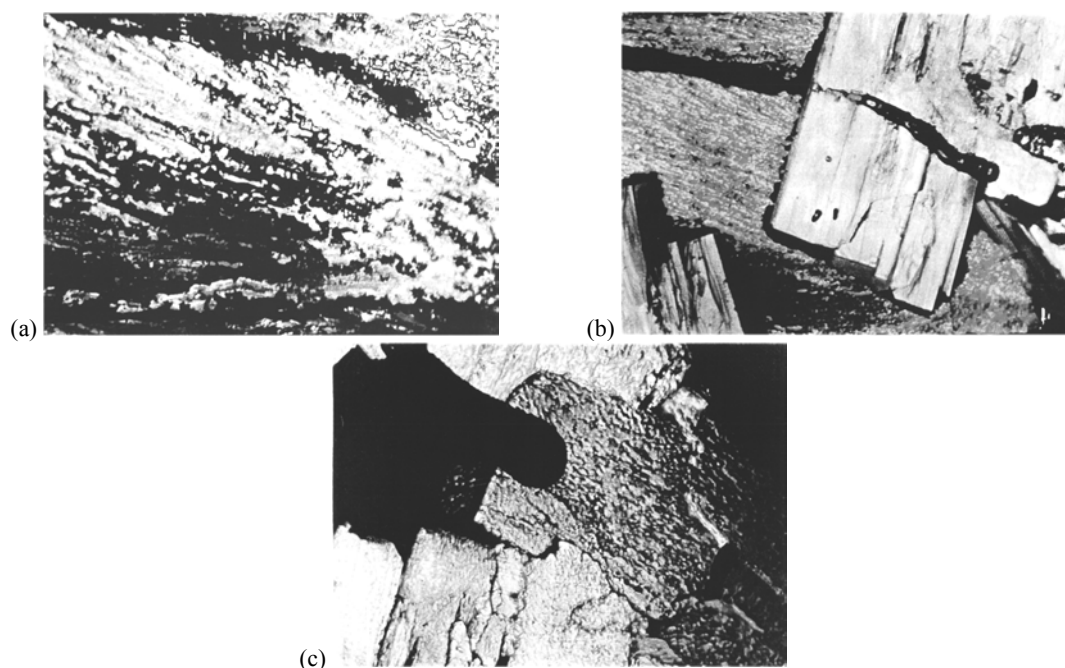


Fig. 1 – Textures of solid (a), smectic (b) and nematic (c) phases.

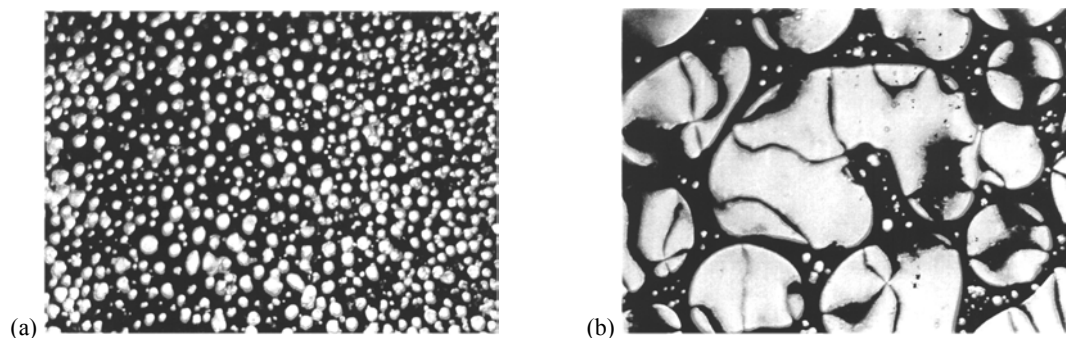


Fig. 2 – Nematic mesophase appearing with the so-called droplets texture (a), and passing to the Schlieren texture with the decreasing of temperature (b).

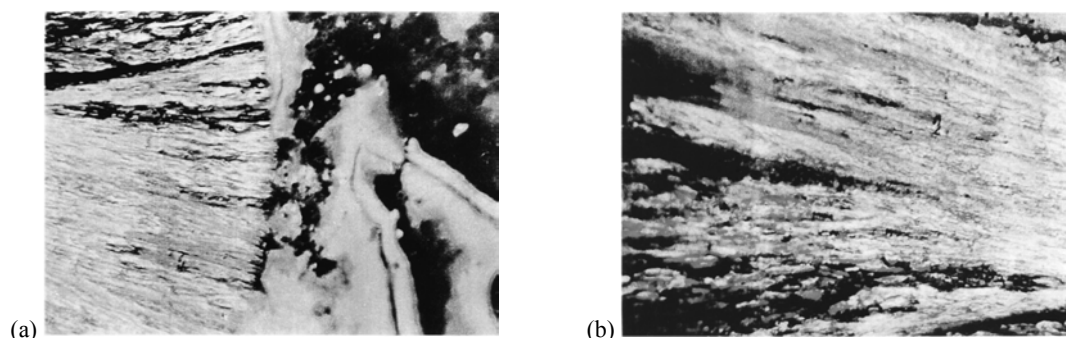


Fig. 3 – Nematic–smectic phase transition (a), characterized by fan texture (b).

EXPERIMENTAL

Materials

Novel azoderivatives have been synthesised starting from 4-(phenylazo)phenols or 4-hydroxy-4'-(phenylazo)biphenyls. As intermediates: 4-(phenylazo)phenol, 4-(4'-nitrophenylazo)phenol, 4-(4'-trifluoro-methyl-phenylazo)phenol, 4-(4'-cyano-phenylazo)phenol, 4-(4'-methyl-phenylazo)phenol, 4-(4'-chlorophenylazo)phenol, 4-hydroxy-4'-(phenylazo)biphenyl, 4-hydroxy 4'-(*p*-chlorophenylazo)biphenyl, and 4-hydroxy-4'-(*p*-methyl-phenylazo)biphenyl have been used. They have been obtained by the coupling of adequate diazonium salts with phenol or 4-hydroxybiphenyl. The aromatic amines and the phenols were Fluka products. 2-Ethoxy-*N*-chloroacetylaniline has been obtained by the chloroacetylation of aniline.

Techniques

The melting temperatures were established in capillaries and verified with a Gallenkamp Sanyo digital apparatus. Elemental analyses of carbon, hydrogen and nitrogen have been performed using a Vario EL analyser. The electronic spectra were carried out in dioxane, with a UV-Vis Jasco V-530 spectrophotometer, within 200–700 nm range. FTIR spectra were recorded on a Nicolet spectrophotometer in KBr pellets, within the range 3500–400 cm^{-1} (absorption bands intensity: *m* – middle, *i* – intense, *vi* – very intense, *vw* – very weak). $^1\text{H-NMR}$ spectra have been recorded on a Varian EM-360 spectrometer operating at 60 MHz in CDCl_3 or DMSO-d_6 , the chemical shifts referring to TMS as internal standard. Molecular weights have been obtained using a HPGC-MS 5890 MD 5971 spectrometer at 70 eV, with carrier gas He at 2 mL/min. The microstructural

analysis was performed using an IOR MC-5A polarised light microscope equipped with an electric heating stage connected to a KFKI-type NV 288/2 precision temperature controller. The compound was encapsulated by capillarity between In_2O_3 -glass electrodes, separated by 12 μm Mylar spacers. Simultaneously with the optical microscopy, the thermal stimulated depolarisation current was recorded as a function of the sample temperature (the so-called thermodielectric effect). The electric current was measured by a KEITHLEY C610 electrometer and the temperature by a copper-constantan thermocouple connected to a KEITHLEY 2000 multimeter, both instruments being coupled to a computer through a DAS 1201 data acquisition board and IEEE 488 interface, respectively.

4'-Cyano-4-(*N*-phenylacetamidoxy)-azobenzene (6)

To a one-necked round-bottomed flask equipped with a mechanical stirrer, thermometer and condenser 0.446 g (2 mmoles) of 4-(4'-cyanophenylazo)phenol, 0.08 g sodium hydroxide (2 mmoles), and 10 ml ethanol–benzene mixture (1:1, in volumes) were added. The reaction mixture was stirred 2 hours at 70°C, until the 4-(4'-cyanophenylazo)phenol reacted with sodium hydroxide. By the distillation of 3 mL azeotropic mixture ethanol–benzene–water, the reaction water was removed. 0.34 g (2 mmoles) of *N*-chloroacetylaniide was added to anhydrous azophenoxide and the reaction mixture was stirred five hours at 50–55°C. After cooling at the room temperature the solid product was filtered, washed with water to remove the sodium chloride, and dried in a heating chamber at 105°C. The reaction product was recrystallized from 40 cm^3 toluene to afford (yield 84%) of 4'-cyano-4-(*N*-phenylacetamidoxy) azobenzene (m.p. 198°C). The synthesis is similar for all the novel azoderivatives.

CONCLUSIONS

Nine novel azoderivatives were obtained and their structure was confirmed by elemental analysis, IR, UV–Vis, ¹H–NMR and mass spectra. The identification of mesophases was realized through analysis of textures, using a polarised light microscope. For a precisely determination of phase transition temperatures the capacitive method and thermodielectric effect was applied.

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