



SYNTHESIS, LIQUID CRYSTALLINE PROPERTIES AND THERMAL STABILITY OF 4-(4-ALKYLOXYPHENYLAZO) BENZOIC ACIDS

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abstract: The paper details the synthesis, liquid crystalline properties and thermal stabilities of some mesogenic groups with the general formula $\text{HOOC-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{-OC}_n\text{H}_{2n+1}$, $n = 6 \div 10, 18$. Their mesomorphic properties were investigated by differential scanning calorimetry and polarized optical microscopy. All the synthesized compounds presented liquid crystalline properties of nematic or smectic type. The thermal stability was established by using thermogravimetric analysis. The synthesized compounds may be further used in the synthesis of new classes of bent core liquid crystals by reaction with different dihydroxy cores.

key words: mesogenic compounds; azo groups; thermal behavior; liquid crystals.

received: November 5, 2010

accepted: November 16, 2010

1. Introduction

In liquid crystalline materials, mesomorphic properties appear in different temperature intervals. There are many types of mesophases which may be identified by their individual textures when investigated by polarized optical microscopy (POM) or by differential scanning calorimetry (DSC), which clearly evidence the transition temperatures and the values of enthalpy transitions [1].

In the case of liquid crystals, alongside optical birefringence and fluidity, compounds must be thermally stable in the mesophases domain. For such compounds, thermal stability is critical especially when clearing points are near the decomposition temperature. More, in designing new liquid crystals, it is of primary importance to attach mesogenic units which are thermally stable even at elevated temperatures [2-4].

The present paper presents the synthesis, liquid crystalline properties and thermal stability of some 4-(4-alkyloxyphenylazo) benzoic acids (compounds 3a÷3f) (Scheme 1) which may be used in the synthesis of new banana shaped liquid crystalline compounds. These compounds have been studied in terms of thermostability, differential scanning calorimetry and polarized optical microscopy.

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2. Experimental

2.1. Materials

All starting materials were purchased from Aldrich and Merck and were used as received. Silica gel 60 (Merck) were used for column chromatography (CC). Thin-layer chromatography (TLC) was performed on silica gel plates (Merck, silica gel F₂₅₄).

2.2. Techniques

Structures of all intermediate and final products were confirmed using ¹H and ¹³C-NMR spectroscopy. The spectra were collected with a Bruker Avance DRX 400 MHz spectrometer with tetramethylsilane as internal standard, and the infrared spectra were collected using a Nicolet Magna 550 spectrometer (NaCl crystal window). Mass spectra were recorded on a quadrupole-time of flight mass spectrometer equipped with an electro spray ion source (Agilent 6520 Accurate Mass Q-ToF LC/MS). Transition temperatures were determined using a Linkam heating stage and Linksys 32 temperature control unit in conjunction with a Axioscop 40 Zeiss polarizing optical microscope and Qimaging/Retiga-1000R camera for image capture, the transitions being confirmed by DSC analysis (Mettler Toledo DSC1). Heating and cooling cycles were run at rates of 10⁰C/min under nitrogen atmosphere, with sample measured in closed lid aluminum pans.

All the thermal analysis were performed on 2.5 - 4.5 mg samples on a Mettler-Toledo[®] TGA SDTA851[°] derivatograph in N₂ atmosphere, with a flow rate of 20 ml/min, with a heating rate of 10 K/min from 25 to 900°C. In order to obtain comparable data, constant operational parameters were kept for all samples.

The molecular simulations were effectuated using Materials Studio[®] 4.0. Software, Inc., San Diego (licensed to Nicolae Hurduc). The dipole moment values corresponding to the compounds **3a-f** were calculated using DMol3 module, AM1 method.

2.3. Synthesis

4-(4-Hydroxyphenylazo) benzoic acid (2): A mixture of 27.4g (0.2 mol) of 4-aminobenzoic acid and 57.5 ml (0.6 mol) HCl 32% was cooled to 0-5⁰C with an ice-salt bath to which 13.8 g (0.2 mol) of NaNO₂ dissolved in H₂O (20%) was added dropwise under stirring. After the addition was finished, the mixture was stirred for 30 minutes at 0 °C. The diazonium salt was slowly added over a solution containing 19.36 g (0.206 mol) phenol and 272 g (2 mol) CH₃COONa*3H₂O in 5 ml water at 5⁰C. After 3 h, the orange precipitate was filtered off and washed several times with water. η=90%, m.p = 283⁰C. ¹H-NMR δ_H ppm (DMSO): 13.01 (s, 1H, -COOH), 10.47 (s, 1H, -OH) 8.11 (d, 2H, Ar), 7.88 (m, 4H, Ar), 6.97 (d, 2H, Ar). m/z: 242 [M]⁺.

General method for the preparation of 4-(4-alkoxyphenylazo) benzoic acids (3a-f). Compounds were prepared by adapting literature data [5, 6], *via* etherification between 4-(4-hydroxyphenylazo) benzoic acid and the corresponding *n*-bromoalkanes in the presence of potassium hydroxide. Compound **2** (3g, 12.3 mmol) was dissolved in a solution containing 1.85g (33 mmol) KOH, 2 ml H₂O and 8 ml EtOH. A trace of potassium iodide was added and the solution was heated and stirred while 13.6 mmols of the appropriate

n-bromoalkane was added slowly. The mixture was refluxed for 15 h; the solvent was evaporated and the solid residue was dissolved in water. The solution was washed with diethyl ether for three times and then was made strongly acidic with HCl 32%. The precipitate was extracted with ethyl ether, affording the pure compounds. Yields = 44.9÷69.7%

4-(4-Hexyloxyphenylazo) benzoic acid (3 a)

Quantities: 1.9 ml (13.6 mmol) 1-bromohexane. Red product, prismatic crystals, $\eta = 44.9\%$ (1.8 g), m.p = 272.12^oC. ¹H-NMR δ_{H} ppm (DMSO): 13.18 (s, 1H, -COOH), 8.12 (d, 2H, ArH), 7.92 (m, 4H, ArH), 7.14 (d, 2H, ArH), 4.09 (t, 2H, -OCH₂-), 1.75 (cv, 2H, CH₂), 1.43 (cv, 2H, CH₂), 1.32 (m, 4H, CH₂), 0.89 (t, 3H, CH₃). ¹³C-NMR δ_{C} ppm (DMSO): 166.70, (COOH), 162.06, 154.42, 146.06, 132.08, 130.54, 124.97, 122.17, 115.10, (8C, aromatic), 68.04, (O-CH₂), 30.92, 28.48, 25.08, 22.01, 13.86 (5C, aliphatic). FT-IR (KBr, cm⁻¹): 3442.93 (v OH, carboxylic acid), 2924.08, 2860.43 (v CH, aliphatic), 1681.92 (vC=O), 1600.91 (v C-C, aromatic), 1247.94, 1139.93 (vC-O, R-O-Ar). m/z (CHCl₃): 326 [M]⁺.

4-(4-Heptyloxyphenylazo) benzoic acid (3 b)

Quantities: 2.1 ml (13,6 mmol) 1-bromoheptane. Orange product, fine needles, $\eta = 49.8\%$ (2.1 g), m.p = 266.1^oC. ¹H-NMR δ_{H} ppm (DMSO): 13.00 (s, 1H, -COOH), 8.13 (d, 2H, ArH), 7.91 (m, 4H, ArH), 7.11 (d, 2H, ArH), 4.06 (t, 2H, -OCH₂-), 1.74 (cv, 2H, CH₂), 1.42 (cv, 2H, CH₂), 1.28 (m, 6H, CH₂), 0.87 (t, 3H, CH₃). ¹³C-NMR δ_{C} ppm (DMSO): 166.31, (COOH), 161.77, 154.34, 146.01, 131.95, 130.09, 124.52, 121.71, 114.82, (8C aromatic), 67.88, (O-CH₂), 30.78, 28.24, 27.98, 25.01, 21.56, 13.37, (6C, aliphatic). FT-IR (KBr, cm⁻¹): 3437.14 (v OH, carboxylic acid), 2954.94 - 2858.50 (v CH, aliphatic), 1681.92 (vC=O), 1600.91 (vC-C, aromatic), 1249.87, 1145.71 (vC-O, R-O-Ar). m/z (CHCl₃): 340 [M]⁺.

4-(4-Octyloxyphenylazo) benzoic acid (3 c)

Quantities: 2.35 ml (13.6 mmol) 1-bromooctane. Orange product, fine needles, $\eta = 50.9\%$ (2.23 g), m.p = 262.6^oC. ¹H-NMR δ_{H} ppm (DMSO): 12.84 (s, 1H, -COOH), 8.12 (d, 2H, ArH), 7.90 (m, 4H, ArH), 7.12 (d, 2H, ArH), 4.10 (t, 2H, -OCH₂-), 1.76 (cv, 2H, CH₂), 1.43 (cv, 2H, CH₂), 1.28 (m, 8H, CH₂), 0.87 (t, 3H, CH₃). ¹³C-NMR δ_{C} ppm (DMSO): 167.12, (COOH) 162.60, 155.16, 146.83, 132.77, 130.93, 125.36, 122.55, 115.69, (8C, aromatic) 68.72, (O-CH₂), 31.61, 29.09, 29.04, 28.99, 25.87, 22.42, 14.22 (7C, aliphatic). FT-IR (KBr, cm⁻¹): 3437.14 (v OH, carboxylic acid), 2954.64 - 2854.64 (v CH, aliphatic), 1685.78 (vC=O), 1600.91 (v C-C, aromatic), 1249.87, 1143.79 (vC-O, R-O-Ar). m/z (CHCl₃): 354 [M]⁺.

4-(4-Nonyloxyphenylazo) benzoic acid (3 d)

Quantities: 2.6 ml (13.6 mmol) 1-bromononane. Orange, fine needles product, $\eta = 49.3\%$ (2.25 g), m.p = 258.0^oC. ¹H-NMR δ_{H} ppm (DMSO): 12.92 (s, 1H, -COOH), 8.13 (d, 2H, ArH), 7.90 (m, 4H, ArH), 7.12 (d, 2H, ArH), 4.09 (t, 2H, -OCH₂-), 1.75 (m, 2H, CH₂), 1.43 (m, 2H, CH₂), 1.28 (m, 10H, CH₂), 0.87 (t, 3H, CH₃). ¹³C-NMR δ_{C} ppm (DMSO): 166.27, (COOH), 161.75, 154.31, 146.00, 131.92, 130.09, 124.51, 121.70, 114.83, (8C, aromatic) 67.87, (O-CH₂), 30.83, 28.48, 28.31, 28.20, 28.17, 25.02, 21.60, 13.37 (8C, aliphatic). FT-IR (KBr, cm⁻¹): 3433.28 (v OH, carboxylic acid), 2954.64 - 2854.64 (v CH, aliphatic), 1685.78 (vC=O), 1600.91 (v C-C, aromatic), 1249.87, 1143.79 (vC-O, R-O-Ar). m/z (CHCl₃): 368 [M]⁺.

4-(4-Decyloxyphenylazo) benzoic acid (**3 e**)

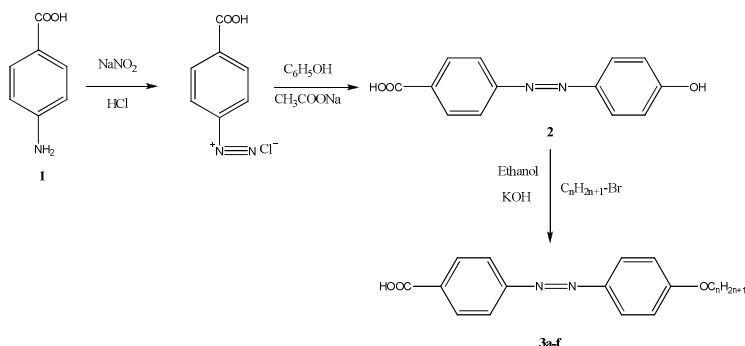
Quantities: 2.8 ml (13.6 mmol) 1-bromodecane. Orange product, flakes, $\eta = 69.7\%$ (3.3 g), m.p = 254.8 $^{\circ}$ C. $^1\text{H-NMR}$ δ_{H} ppm (DMSO): 12.88 (s, 1H, -COOH), 8.12 (d, 2H, ArH), 7.89 (m, 4H, ArH), 7.10 (d, 2H, ArH), 4.07 (t, 2H, -OCH₂-), 1.74 (cv, 2H, CH₂), 1.42 (cv, 2H, CH₂), 1.27 (m, 12H, CH₂), 0.85 (t, 3H, CH₃). $^{13}\text{C-NMR}$ δ_{C} ppm (DMSO): 166.30, (COOH), 161.76, 154.33, 146.02, 131.95, 130.10, 124.51, 121.70, 114.81, (8C, aromatic), 67.88, (O-CH₂), 30.87, 28.55, 28.51, 28.33, 28.27, 28.23, 25.04, 21.61, 13.38, (9C, aliphatic). *FT-IR* (KBr, cm⁻¹): 3433.28 (v OH, carboxylic acid), 2954.64 - 2850.78 (v CH, aliphatic), 1685.78 (vC=O), 1602.84 (v C-C, aromatic), 1251.80, 1143.79 (vC-O, R-O-Ar). m/z (CHCl₃): 382 [M]⁺.

4-(4-Octadecyloxyphenylazo) benzoic acid (**3 f**)

Quantities: 4.5 g (13.6 mmol) n-octadecylbromide. Orange product, flakes, $\eta = 50.6\%$ (3.1 g), m.p = 237 $^{\circ}$ C. $^1\text{H-NMR}$ δ_{H} ppm (DMSO): 12.88 (s, 1H, -COOH), 8.11 (d, 2H, ArH), 7.88 (m, 4H, ArH), 7.09 (d, 2H, ArH), 4.10 (t, 2H, -OCH₂-), 1.75 (cv, 2H, CH₂), 1.44 (cv, 2H, CH₂), 1.27 (m, 28H, CH₂), 0.85 (t, 3H, CH₃). $^{13}\text{C-NMR}$ δ_{C} ppm (DMSO): 166.07, (COOH), 161.61, 154.29, 145.99, 131.90, 129.87, 124.26, 121.46, 114.69, (8C, aromatic), 67.80, (O-CH₂), 30.66 - 13.08 (17C, aliphatic). *FT-IR* (KBr, cm⁻¹): 3433.28 (v OH, carboxylic acid), 2920.22, 2850.78 (vCH, aliphatic), 1687.71 (vC=O), 1600.91 (v C-C, aromatic), 1253.73, 1145.71 (vC-O, R-O-Ar). m/z (CHCl₃): 493 [M-1]⁺.

3. Results and discussion

The mesogenic groups were prepared using the synthetic route presented in **Scheme 1**. The synthesis involved the Williamson etherification of 4-(4-hydroxyphenylazo) benzoic acid with different *n*-alkyl bromides, with yields between 44.9 ÷ 69.7 %.



Scheme 1 Synthesis of the mesogenic compounds:

3a, *n* = 6; **3b**, *n* = 7; **3c**, *n* = 8; **3d**, *n* = 9; **3e**, *n* = 10; **3f**, *n* = 18

3.1. Liquid-crystalline properties

DSC and POM indicated for all compounds **3a-f** the presence of liquid crystalline properties. All compounds present enantiotropic nematic phases, with characteristic Schlieren textures, and smectic phases.

The liquid crystalline properties of **3a-f** compounds containing azo linkage are schematically presented in Table 1. The domains of temperatures in which the mesophases are stable are quite large, between 107- 178⁰C on heating and 11-147⁰C on cooling (Table 1).

Table 1 Transition temperatures (⁰C) and transition enthalpies (J/g) of compounds **3a-f**

No	K/Sm ₁	Sm ₁ /Sm ₂	Sm ₂ /Sm ₃	Sm ₃ /Sm ₄	Sm ₄ /N	N/I	I/N	N/Sm ₄	Sm ₄ /Sm ₃	Sm ₃ /K
3a	110 [-2.54]	199 [-5.7]	226 [-52.8]	-	-	272*	-	224 [48.4]	143 [2.77]	106 [3.31]
3b	141 [-26]	-	-	-	230 [-66]	266*	231 [7.63]	228 [49.3]	-	84 [23.3]
3c	154 [-3]	-	222 [-25]	-	235 [-3.43]	262 [-12.2]	250 [6.49]	235 [1.04]	221 [0.73]	214 [0.14]
3d	151 [-10.5]	194 [-1.61]	204 [-0.75]	223 [-1.09]	245*	258*	-	-	218 [0.35]	196 [0.14]
3e	77 [-5.1]	183 [-11.2]	218 [-13.9]	-	246 [-33]	255*	245 [32.8]	217 [13.4]	178 [11.5]	70 [5.59]
3f	95 [-4.68]	130 [-2.28]	147 [-3.7]	-	-	237*	-	-	137 [0.4]	126 [0.51]

Abbreviation: K-crystalline, Sm-smectic, N-nematic, I-isotropic

* Data obtained from POM investigations

Fig. 1 presents, as an example, the DSC curves of compound **3e**.

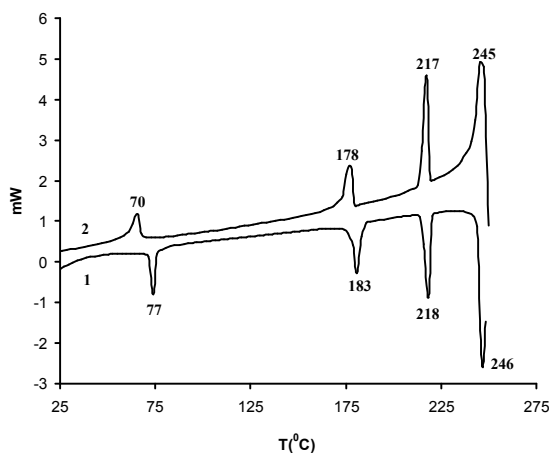


Fig. 1 The DSC curves of **3e**: 1 – second heating, 2 – first cooling.

Both on heating and cooling cycles, the DSC curves of the compound **3e** show 4 peaks corresponding to different transitions: K – Sm₁, Sm₁ – Sm₂, Sm₂ – Sm₃ and Sm₃ – N. The N – I transition has been attributed from optical microscopy studies. On cooling, compound **3e** presents nematic droplets that arise from isotropic liquid at 245⁰C (Fig. 2a) and which join immediately into characteristic Schlieren textures at 244⁰C (Fig. 2b). The nematic range maintains down to 217⁰C when reorders into smectic mesophases (Fig. 2c) which continue down to 70⁰C when crystallization begins.

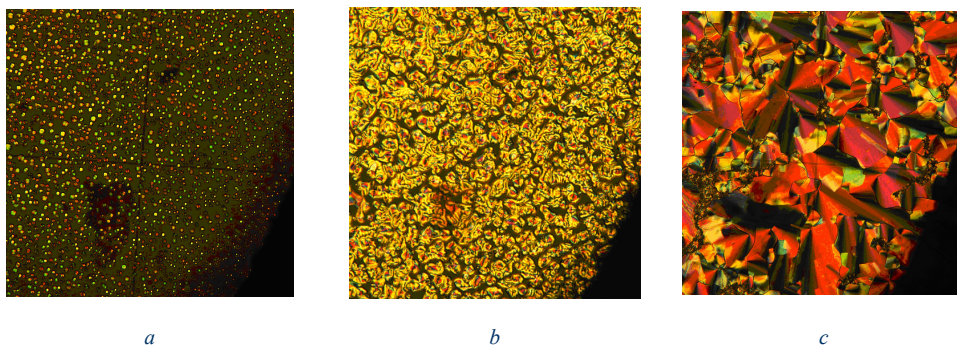


Fig. 2 Optical textures of 4-(4-decyloxyphenylazo) benzoic acid (**3e**) on cooling: a) nematic droplets from isotropic liquid at 245°C; b) Schlieren texture at 244°C and c) smectic texture at 176°C.

The minimum energy conformation of all compounds exhibited a common arrangement since only small changes in their structures have been made (Fig. 3).

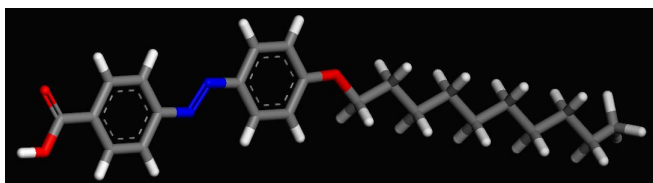


Fig. 3 Molecular geometry of **3e**.

Data presented in Table 1 evidence the diminishing of the range of nematic mesophases with the increasing of the length of the terminal chain. This may be explained by the slight increase of calculated dipole moments (from 5.9D to 6.1D) with the increase of the number of carbon atoms in the terminal chains, which leads to stronger collateral interactions between molecules (the last compound of the series does not present a nematic mesophases).

3.2. Thermal stability of 4-(4-alkoxyphenylazo) benzoic acids (3a-f)

The summary of the thermogravimetric data obtained from thermograms (T_{onset} – the initial temperature of thermal degradation for each stage, T_{peak} – the temperature corresponding to the maximum degradation rate, T_{endset} - the final temperature at which the degradation process for each stage ends, mass loss (W%) and residue at the end of decomposition processes) are listed in Table 2.

According to the thermogravimetric data presented in Table 2, thermal degradation occurs in one or three stages, with various mass percent losses, depending on the chemical structure. For all the samples, the degradation processes are not complete, in all cases a residue being left. Data presented in Table 2 reveal that the initial temperature at which thermal degradation for the first stage begins is above 300 °C (with the exception of sample **3f**), which proves a good thermal stability, above the isotropisation temperatures.

The samples **3a**, **3c**, **3d** and **3e** exhibited one step of degradation, with T_{onset} between 340 and 353°C, while the other compounds exhibited three steps of degradation, with T_{onset} for the first stage between 198 and 303°C.

Table 2 Thermogravimetric data for compounds **3a** ÷ **3f**.

Sample	Stages of thermal degradation	DTA characteristic data	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	Mass loss (%)
3a	I	exo	340	374	414	78.53
	residue					21.47
3b	I	exo	370	381	390	24.96
	II					28.44
	III residue					19.57 27.03
3c	I	exo	345	373	394	72.00
	residue					28.00
3d	I	exo	347	373	390	88.96
	residue					11.04
3e	I	exo	353	369	450	71.81
	residue					28.19
3f	I	exo	198	235	255	14.36
	II		350	368	402	39.28
	III residue		423	441	468	40.94 5.42

Using as thermal stability criteria the onset temperatures (T_{onset}) for the first stage, the thermal stability series was established as being the following:

$$3f < 3b < 3a \approx 3c \approx 3d \approx 3e.$$

A similar conclusion regarding thermal stability may be obtained if the temperature of degradation at maximum degree rate (T_{max}) is considered as criteria of stability.

4. Conclusions

The paper presents synthesis, characterization and thermal behaviour of some 4-(4-alkoxyphenylazo) benzoic acids (**3a**÷**f**) which may be used as mesogenic groups in the synthesis of banana shaped liquid crystals.

Compounds have been obtained by Williamson alkylation and were structurally characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, IR spectroscopy and mass spectra. All the reported compounds presented enantiotropic liquid crystalline properties, mainly with smectic and nematic textures. The mesophases stabilities correlates with molecular modelling study and decrease with dipole-moment increasing. Thermogravimetric studies evidenced that all compounds show a good thermal stability in the mesophases domain.

Acknowledgements. This work was supported by CNCSIS–UEFISCSU (Romania), project number PNII – IDEI 356/2008.

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