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Synthesis and properties of two new liquid crystals: an analytical and thermodynamic study

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Abstract

Synthesis, analytical performances, thermodynamic and surface properties of two new liquid crystals substituted with poly(ethylene oxide) chains are described. The first of them is *N,N'*-diphenyl-[4-{2,3,4-tri[2-(2-methoxyethoxy)ethoxy]-benzylidene}imine]piperidine (**LC**₁) and the second is 2-hydroxy-3-methyl-4-{4-[2-(2-butoxyethoxy)ethoxy]} 4'-{4-[2-(2-butoxyethoxy)ethoxy]styryl}azobenzene (**LC**₂). The nematic ranges of the two liquid crystals, determined by differential scanning calorimetry do not interfere. The analytical and thermodynamic studies of **LC**₁ and **LC**₂ in the solid, nematic and liquid state were done using a series of appropriate solutes. Comparison of the analytical performances shows a better efficiency in the nematic state. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermodynamic parameters; Stationary phases, GC; Liquid crystals

1. Introduction

In this study, we report the synthesis, analytical performances and thermodynamic properties of two new liquid crystals substituted with poly(ethylene oxide) (POE) chains. The first of them was *N,N'*-diphenyl-[4-{2,3,4-tri[2-(2-methoxyethoxy)ethoxy]-benzylidene}imine]piperidine (**LC**₁) and the second was 2-hydroxy-3-methyl-4-{4-[2-(2-butoxyethoxy)ethoxy]} 4'-{4-[2-(2-butoxyethoxy)ethoxy]-styryl}azobenzene (**LC**₂). Due to the presence of

POE chains, both compounds have amphiphilic character. The aromatic hydrophobic core and hydrophilic POE chains induce formation of the ordered phase and lead to a narrow liquid crystal range [1].

Liquid crystals were used as gas chromatography stationary phases for the first time by Kelker [2,3] and Dewar [4]. At present, the use of capillary columns coated with liquid crystals combining the efficiency and the shape selectivity [5] is widespread in analytical chemistry. Recently, analytical applications of liquid crystals were reviewed by Mazur and Witkiewicz [6]. In previous works [7–12], we presented the synthesis and chromatographic applica-

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tions of some new liquid crystals, including Schiff bases, azo bridge, lateral alkoxy chains, etc. In this study thermodynamic properties of liquid crystals **LC₁** and **LC₂** in the solid, nematic and liquid state were investigated by inverse gas chromatography [13–20], using a series of appropriate solutes.

2. Experimental

2.1. Reagents

All chemicals used for the liquid crystal synthesis

were obtained from Jansen Chemica (Netherlands). Compounds used in analytical and thermodynamic studies were purchased from Chrompack (alkanes) and from Meyreau-Boiveau (volatile aroma compounds). All other compounds were from Fluka.

2.2. Liquid crystals synthesis

2.2.1. **LC₁** synthesis (Fig. 1a)

N,N'-Di(4-nitrobenzene)piperidine was obtained reacting 2 equiv. 4-fluoronitrobenzene with 1 equiv. piperidine and 2 equiv. NaOH. The crude product was extracted with ether and recrystallized in etha-

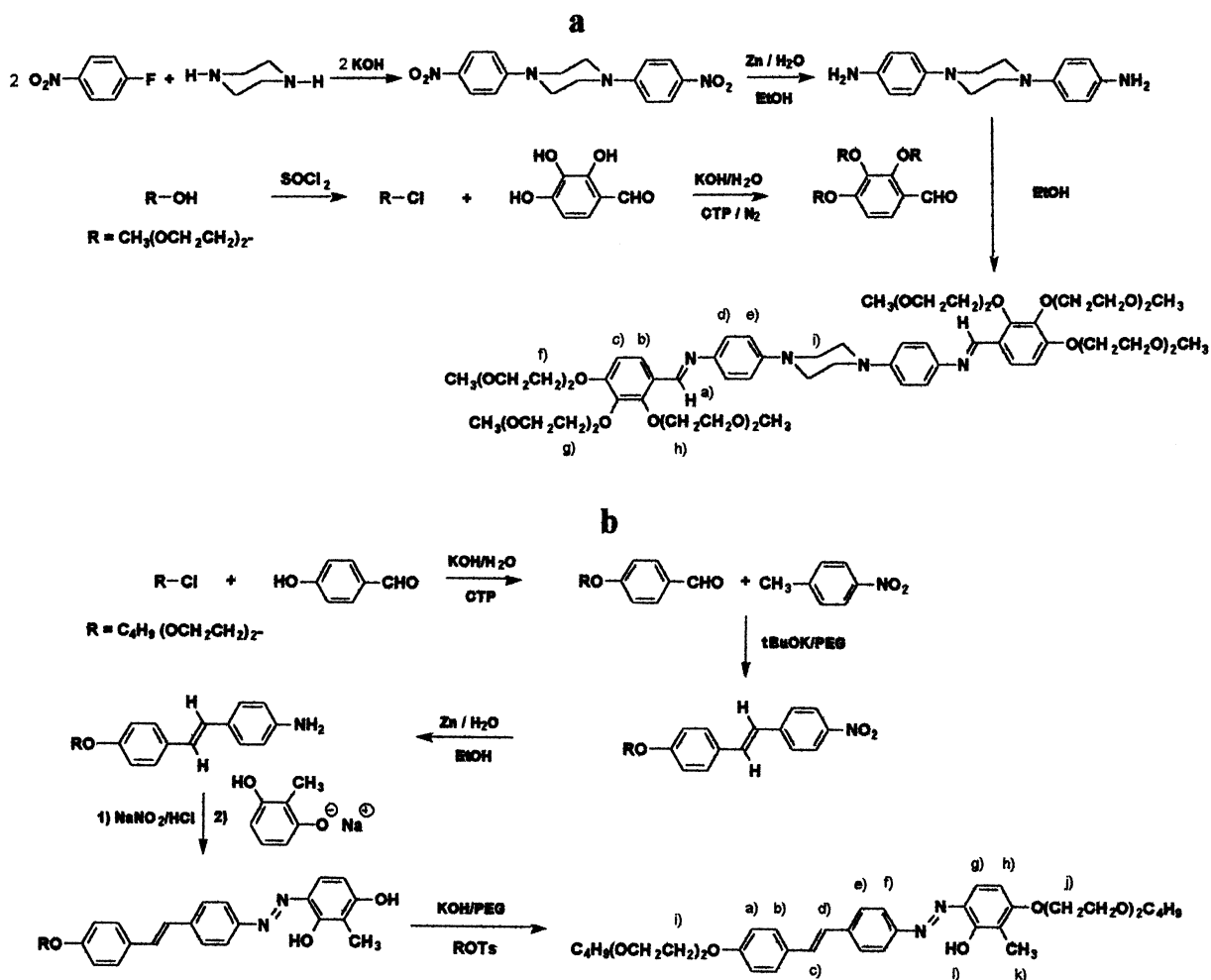


Fig. 1. Synthesis of the **LC₁** (a) and **LC₂** (b) liquid crystals. (a) NMR: (a) 8.92 ppm (2H, s); (b) 7.87 ppm (2H, d); (c) 6.75 ppm (2H, d); (d) 7.29 ppm (4H, d); (e) 7.02 ppm (4H, d); (f) 4.41 ppm (2H, m); (g+h) 4.22 ppm (4H, m); (i) 3.5 ppm and 2.2 ppm (8H, m). (b) NMR: (a) 6.92 ppm, (2H, d); (b) 7.47 ppm, (2H, d); (c) 7.15 ppm, (1H, d); (d) 7.0 ppm, (1H, d); (e) 7.62 ppm, (2H, d); (f) 7.85 ppm, (2H, d); (g) 7.72 ppm, (1H, d); (h) 6.62 ppm, (1H, d); (i) 4.17 ppm (2H, t); (j) 4.27 ppm (2H, t); (k) 2.22 ppm (3H, s); (l) 13.8 ppm (1H, s).

nol. Then, the diamino derivative was obtained by reduction of the nitro group using zinc in ethanol under neutral conditions. The solution was filtered and the ethanol was evaporated to yield pure *N,N'*-di(4-aminobenzene)piperidine.

[2-(2-Methoxyethoxy)ethoxy]ethanol was reacted with 1.2 equiv. of thionylchloride (1 h, 80°C) to give the respective chloro compound. 2,3,4-Tri[2-(2-methoxyethoxy)ethoxy]benzaldehyde was prepared in one step by total etherification of 2,3,4-trihydroxybenzaldehyde (THB) using the phase transfer catalysis method. The reaction was carried out in water under nitrogen by mixing the aldehyde, 3.5 equiv. of 2-(2-methoxyethoxy)chloroethane and Aliquat 336 as phase transfer catalyst. The solution was brought to 80°C, 3.5 equiv. of aqueous NaOH were added over a period of 4 h and the mixture was left to react over 12 h. After chloroform extraction, the aldehyde was chromatographed on silica gel (0.071–0.25 mm) with CH₂Cl₂–methanol (8:92) as eluent. The Schiff base was obtained by reacting 2,3,4-trialkoxybenzaldehyde with the corresponding diamine in boiling ethanol. The final product was recrystallized from heptane–ethanol (80:20) until constant transition points were obtained.

2.2.2. LC₂ synthesis (Fig. 1b)

The 4-[2-(2-butoxyethoxy)ethoxy]benzaldehyde and 1.5 equiv. of 4-nitrotoluene were dissolved in poly(ethylene glycol) of *M_r* 200 (PEG 200) at room temperature. A homogeneous solution of 1.5 equiv. of potassium *t*-butoxide in PEG was then added to the latter mixture. The temperature was raised to 80°C and the reaction mixture was left at this temperature over 12 h. After cooling, the mixture was extracted 3 times with dichloromethane and the organic solution was washed with acidic water. Evaporation of CH₂Cl₂ and recrystallization from ethanol led to a pure 4-[2-(2-butoxyethoxy)ethoxy]-4'-nitrostilbene. The amino derivative was obtained by reduction of the nitro group using zinc in ethanol under neutral conditions. The solution was filtered and the compound was chromatographed on silica gel (0.071–0.25 mm) with CH₂Cl₂–ethyl acetate (50:50) as eluent to pure 4-[2-(2-butoxyethoxy)ethoxy]-4'-aminostilbene. Coupling of the diazonium salt with the 2,6-dihydroxytoluene monoanion was performed in a water–dioxane (50:50) mixture. The

product was extracted with CH₂Cl₂ and chromatographed on silica gel (0.071–0.25 mm) with CH₂Cl₂–ethyl acetate (50:50) as eluent. In the next step, one equivalent of 4-[2-(2-butoxyethoxy)ethoxy]-tosylate derivative was added to the modified stilbene in PEG 200 with an equimolar amount of KOH to give LC₂. The pure liquid crystalline product was chromatographed on silica gel (0.071–0.25 mm) with ethyl acetate–chloroform (50:50) and recrystallized from pure ethanol until constant transition points were obtained.

2.3. Differential scanning calorimetry (DSC) analysis

A Setaram DSC 111 system was used to determine temperature and enthalpy effects of the phase transitions. LC₁ and LC₂ samples (25 mg) were heated from the ambient temperature up to the temperature above the nematic–liquid transition with the rate of 0.5 K min⁻¹.

2.4. Gas chromatography

Two gas chromatography devices were used. A Carlo-Erba Fractovap GC 4130 equipped with a flame ionization detection (FID) system was used for physicochemical measurements. Columns manufactured with stainless steel tubing (0.91 m×0.6 mm I.D.) were packed with stationary phase prepared by coating the Chromosorb W HP (0.125–0.14 mm) with 10% (w/w) of liquid crystal-forming compound. The rate of the carrier gas (nitrogen) was controlled with a soap bubble debimeter and was 30 ml/min. Analytical experiments were performed using a HP 5730A gas chromatograph equipped with FID, split/splitless injector and an HP 7130A recorder. Helium of high purity at the rate of 1 ml/min was used as a carrier gas. Borosilicated glass capillary columns (30 m×0.25 mm I.D.) were etched using the Rijks et al. method [21] and deactivated with Carbowax 20M. Dynamic coating of capillaries was performed using 10% solution of the liquid crystals in dichloromethane. The coated columns were conditioned overnight at a temperature 10 K higher than the temperature of the nematic–liquid transition.

3. Results and discussion

3.1. Characterization of new compounds

Both compounds studied can exist in a nematic state. Temperatures of corresponding solid–liquid crystal and liquid crystal–liquid transitions were determined by gas chromatography and DSC. Fig. 2a and b show variations of the logarithm of the specific retention volume ($\ln V_g$) of selected solutes in function of the inverse absolute temperature $1/T$. Transition temperatures correspond to the function discontinuities. Results obtained using the gas chromatography and DSC are in good agreement and are reported in Table 1. In the same table, the enthalpy of transitions determined by DSC is given.

3.2. Analytical applications

Table 2 reports the number of theoretical plates corresponding to the three physical states of the stationary phases. It can be seen that the solid, as well as the nematic and liquid phases have separation capability. The best efficiency is observed, however, in the nematic phase. Analytical performances of LC_1 and LC_2 were tested by separating various families of solutes. Relative retention times of volatile aroma compounds, alkanes, aromatics, polyaromatics, phenols and *cis* and *trans* isomers are listed in Table 3. It can be observed that the selectivity of the solid stationary phases is poor in the case of isomer separations. LC_1 does not discriminate between hexane isomers and LC_2 is not selective in the case of octane and tridecane isomers. Similarly, bad separations were obtained with *para*- and *meta*-xylenes, *para*- and *meta*-diethylbenzenes, *para*- and *meta*-cresols. It should be stressed, however, that in many cases, satisfactory results were obtained with solid-phase LC_1 and LC_2 .

In the nematic state, the increased discrimination in respect to the shape of molecules led to remarkable analytical performances (see Table 3). The full separation of (i) octane and tridecane isomers by LC_1 , (ii) octadecanes by LC_2 , (iii) diethylbenzenes with LC_1 , (iv) phenols by LC_2 is to be noted. Both mesogenic LC_1 and LC_2 separate *cis* and *trans* isomers, with the *cis* eluted always before the *trans* isomer, as found in our preceding work [7–12]. It is

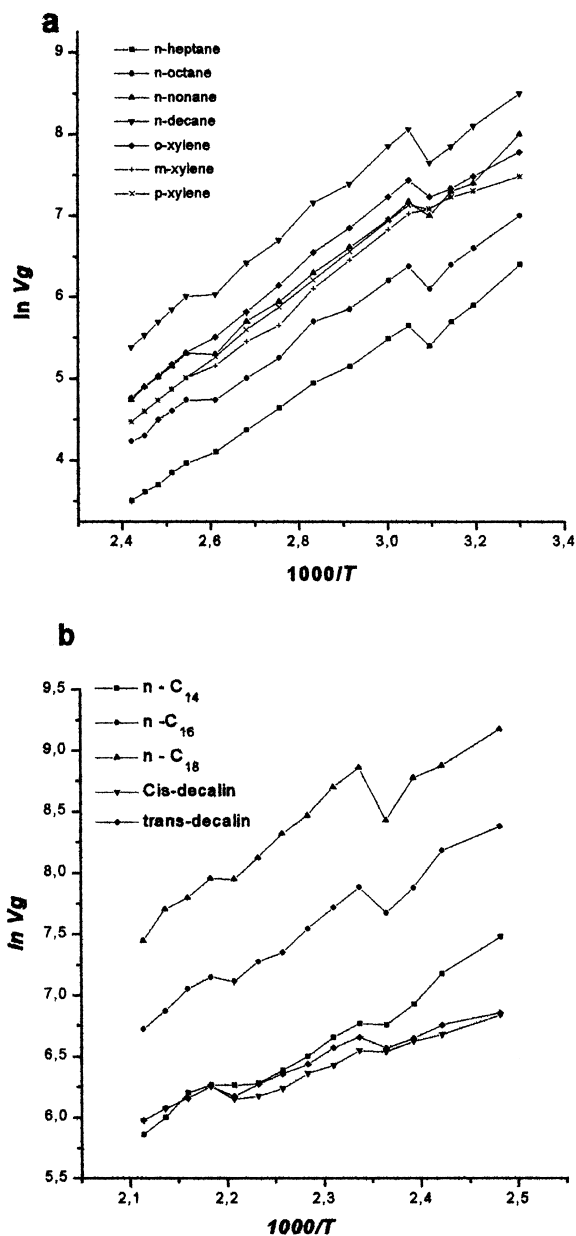


Fig. 2. Variation of $\ln V_g$ with the reciprocal absolute temperature. (a) LC_1 , (b) LC_2 .

well known that estragol and anethol are eluted before thymol and carvacrol on the polyethylene glycol stationary phase [22]. When LC_1 or LC_2 are used, the elution follows the order: estragol, thymol, carvacrol, anethol. The double bound conjugated

Table 1
Transition temperatures of **LC**₁ and **LC**₂ obtained with DSC and GC

Transition	Method		LC ₁	LC ₂
Solid–nematic K→N	DSC	Temperature (°C)	56.2	155.2
		ΔH (K→N) (kJ mol ⁻¹)	16.86	15.16
	GC	Temperature (°C)	55	155
Nematic–liquid N→I	DSC	Temperature (°C)	120.5	179.2
		ΔH (N→I) (kJ mol ⁻¹)	8.13	10.99
	GC	Temperature (°C)	120	180

with the aromatic ring present in anethol seems to be more retained than the aromatic ring with a protruding polar oxygen present in thymol [23]. When **LC**₁ and **LC**₂ stationary phases are used in the temperature range corresponding to the liquid state, their analytical performances decrease as compared to the nematic state. As in the case of the solid stationary phase, the separation of isomers is poor, e.g. no separation of octadecane isomers on the **LC**₁ was observed. The chromatograms corresponding to the separation of the volatile aroma compounds are given in Fig. 3. At the temperature range considered, **LC**₁ is in the nematic state (Fig. 3a) and **LC**₂ is in the solid and in the nematic state. The solid–nematic transition of **LC**₂ appears as a vertical line in Fig. 3b. These results lead to the conclusion that **LC**₁ and **LC**₂ in the nematic state display similar analytical performances.

3.3. Thermodynamic analysis

Plots of $\ln V_g$ presented in Fig. 2a and 2b indicate that it is possible to determine enthalpy of transition according to the equation:

$$\ln V_g = -\Delta H/RT + \text{constant.}$$

The physical meaning of ΔH depends on the physical state of the stationary phase. For a solid state, ΔH corresponds to the molar enthalpy of adsorption ΔH_a . For the nematic and liquid state, it is assumed that the solute is dissolved in the stationary phase and ΔH corresponds to the molar enthalpy of dissolution ΔH_s . In the three cases considered, ΔH corresponds to the enthalpy change of the solute in infinite dilution conditions (without solute–solute interactions). The enthalpy of adsorption or dissolution calculated using the experimental chromatographic data (Fig. 2a and b) are given in Table 1. It is interesting to compare ΔH data obtained on **LC**₁ and **LC**₂ with the condensation enthalpy, corresponding to the negative value of the vaporization enthalpy, ΔH_v . The condensation enthalpy roughly corresponds to the liquid cohesion energy and can be used to establish a scale of the energy of molecular interactions involved in adsorption or dissolution processes. It is particularly interesting when the enthalpy of solute transfer from the gas to liquid, liquid crystal or solid are to be compared. Mean values of ΔH_v in the temperature range considered

Table 2
Plates numbers of **LC**₁ and **LC**₂ in the anisotropic, nematic and isotropic state

Stationary phase	States	Solutes	Temperature (°C)	<i>k</i>	Plates number/m
LC ₁	Anisotropic solid	<i>n</i> -hexane	40	1.5	2700
	Nematic	<i>n</i> -tridecane	100	2.1	4200
	isotropic liquid	<i>n</i> -octadecane	170	2.8	2500
LC ₂	Anisotropic solid	<i>n</i> -tridecane	100	1.8	3100
	Nematic	<i>n</i> -octadecane	170	2.2	4900
	isotropic liquid	<i>n</i> -eicosane	200	2.9	3600

Table 3
Relative retention times $r = (tr_2/tr_1)$ of the tested solutes

No.	Compounds	LC ₁			LC ₂		
		T (°C)	r	State	T (°C)	r	State
<i>Volatile aroma compounds</i>							
1	α-Pinene	4°C/min from 60°C	0.15	N	8°C/min from 70°C	0.21	K
2	β-Pinene	4°C/min from 60°C	0.30	N	8°C/min from 70°C	0.21	K
3	Eucalyptol	4°C/min from 60°C	0.71	N	8°C/min from 70°C	0.62	K
4	Limonène	4°C/min from 60°C	0.61	N	8°C/min from 70°C	0.62	K
5	d-Camphor	4°C/min from 60°C	0.93	N	8°C/min from 70°C	1.14	K
6	Linalool	4°C/min from 60°C	1	N	8°C/min from 70°C	1	K
7	Linalyl acetate	4°C/min from 60°C	1.20	N	8°C/min from 70°C	1.55	K
8	Citronellal	4°C/min from 60°C	1.41	N	8°C/min from 70°C	1.10	K
9	Terpineol	4°C/min from 60°C	2.20	N	8°C/min from 70°C	1.55	K
10	Menthol	4°C/min from 60°C	2.32	N	8°C/min from 70°C	1.66	K
11	Borneol	4°C/min from 60°C	2.51	N	8°C/min from 70°C	1.65	K
12	Nerol	4°C/min from 60°C	2.83	N	8°C/min from 70°C	2.75	N
13	Citronellol	4°C/min from 60°C	2.86	N	8°C/min from 70°C	2.11	K
14	Geraniol	4°C/min from 60°C	3.25	N	8°C/min from 70°C	2.95	N
15	Estragole	4°C/min from 60°C	3.47	N	8°C/min from 70°C	4.11	N
16	Thymol	4°C/min from 60°C	3.60	N	8°C/min from 70°C	4.50	N
17	Carvacrol	4°C/min from 60°C	3.72	N	8°C/min from 70°C	4.95	N
18	cis-Isoeugenol	4°C/min from 60°C	5.05	N	8°C/min from 70°C	4.20	N
19	Anethole	4°C/min from 60°C	5.76	N	8°C/min from 70°C	5.20	N
20	trans-Isoeugenol	4°C/min from 60°C	5.84	N	8°C/min from 70°C	4.63	N
<i>Alkanes</i>							
21	n-Hexane	40	1	K	40	1	K
22	2-Methyl-pentane	40	0.63	K	40	0.35	K
23	3-Methylpentane	40	0.63	K	40	0.35	K
24	n-Octane	60	1	N	60	1	K
25	2,3-Dimethylhexane	60	0.55	N	60	0.72	K
26	3,4-Dimethylhexane	60	0.67	N	60	0.72	K
27	2-Methylheptane	60	0.82	N	60	0.93	K
28	3-Methylheptane	60	0.93	N	60	0.93	K
29	Tridecane	100	1	N	100	1	K
30	2-Methyldodecane	100	0.81	N	100	0.88	K
31	4-Methyldodecane	100	0.78	N	100	0.85	K
32	5-Methyldodecane	100	0.73	N	100	0.85	K
33	Octadecane	170	1	I	170	1	N
34	2-Methylheptadecane	170	0.85	I	170	0.90	N
35	3-Methylheptadecane	170	0.88	I	170	0.85	N
36	4-Methylheptadecane	170	0.88	I	170	0.83	N
37	8-Methylheptadecane	170	0.92	I	170	0.70	N
38	Eicosane				190	1	I
39	3-Methylnonadecane				190	0.87	I
<i>Aromatics</i>							
40	Ethylbenzene	50	1	K	50	1	K
41	o-Xylene	50	1.75	K	50	1	K
42	m-Xylene	50	1.05	K	50	0.77	K
43	p-Xylene	50	1.05	K	50	0.77	K
44	Isopropylbenzene	70	1	N	70	1	K
45	Propylbenzene	70	0.94	N	70	1.06	K
46	4-Ethyltoluene	70	1.1	N	70	1.03	K
47	1,2,4-Trimethyl benzene	70	0.94	N	70	1.07	K
48	Tertiobutyl-benzene	80	1	N	80	1	K
49	Isobutyl benzene	80	0.95	N	80	0.96	K
50	Paracymene	80	0.85	N	80	0.94	K
51	1,3-Diethylbenzene	80	0.89	N	80	0.81	K
52	1,2-Diethylbenzene	80	0.97	N	80	0.74	K
53	1,4-Diethylbenzene	80	1.05	N	80	0.81	K
54	1,2,4,5-Tetramethylbenzene	80	1.08	N	80	1.29	K

Table 3 (continued)

No.	Compounds	LC ₁			LC ₂		
		T (°C)	r	State	T (°C)	r	State
<i>Polyaromatics</i>							
56	Naphtalene	130	1	I	4°C/min from 130°C	1	K
57	2-Methylnaphtalene	130	1.42	I	4°C/min from 130°C	1.59	K
58	1-Methylnaphtalene	130	1.49	I	4°C/min from 130°C	1.80	K
59	Acenaphtene				4°C/min from 130°C	4	N
60	Fluorene				4°C/min from 130°C	4.70	N
61	Acenaphthylene				4°C/min from 130°C	4.31	N
62	Phenanthrene				4°C/min from 130°C	5.72	N
63	Anthracene				4°C/min from 130°C	5.22	N
64	<i>cis</i> -Stilbene				4°C/min from 130°C	3.91	N
65	<i>trans</i> -Stilbene				4°C/min from 130°C	4.24	N
<i>Phenols and derivatives</i>							
66	Phenol	130	1	I	130	1	K
67	<i>o</i> -Cresol	130	1.35	I	130	1.84	K
68	<i>m</i> -Cresol	130	1.46	I	130	2.76	K
69	<i>p</i> -Cresol	120	1.46	I	130	2.76	K
70	2,6-Dimethylphenol				140	2.76	K
71	2,5-Dimethylphenol				140	2.15	K
72	2,4-Dimethylphenol				140	2.25	K
73	2,3-Dimethylphenol				140	2.94	K
74	3,5-Dimethylphenol				140	3.69	K
76	3,4-Dimethylphenol				140	4.30	K
77	2,4,6-Trimethylphenol				170	1	N
78	2,4,5-Trimethylphenol				170	1.04	N
79	2,3,5-Trimethylphenol				170	1.15	N
80	<i>o</i> -Chlorophenol				170	1.85	N
81	<i>m</i> -Chlorophenol				170	2	N
82	<i>p</i> -Chlorophenol				170	2.21	N
83	<i>o</i> -Nitrophenol				170	3.52	N
84	2,4,6-Trichlorophenol				170	4.5	N
85	4-Chloro-3-methylphenol				170	3.83	N
86	2,4-Dinitrophenol				170	5.24	N
<i>cis and trans isomers</i>							
87	Nerol	100	1	N	160	1	N
88	Geraniol	100	1.15	N	160	1.18	N
89	<i>cis</i> -Isoeugenol	110	1	N	160	1	N
90	<i>trans</i> -Isoeugenol	110	1.16	N	160	1.12	N
91	<i>cis</i> -Decalin	100	1	N	120	1	K
92	<i>trans</i> -Decalin	100	1.75	N	120	1.05	K
93	<i>cis</i> -Stilbene				160	1	N
94	<i>trans</i> -Stilbene				160	1.09	N

were calculated using the Antoine equation with parameters given in TRC tables [24]. According to Table 4 the enthalpy of adsorption of *n*-heptane, *n*-octane, *n*-nonane and *n*-decane on LC₁ are only 5–10% lower than corresponding condensation enthalpies. Enthalpies of adsorption of *n*-alkanes (*n*-tetradecane, *n*-hexadecane and *n*-octadecane) on LC₂

are significantly smaller than their enthalpies of condensation and, surprisingly, seem to be independent of the *n*-alkane chain length. The values of about 50 kJ mol⁻¹ were found with three *n*-alkanes considered. ΔH_a of xylenes on LC₁ and decalines on LC₂ phase are small as compared to the condensation enthalpy ($-\Delta H_v$). In the case of *m*- and *p*-

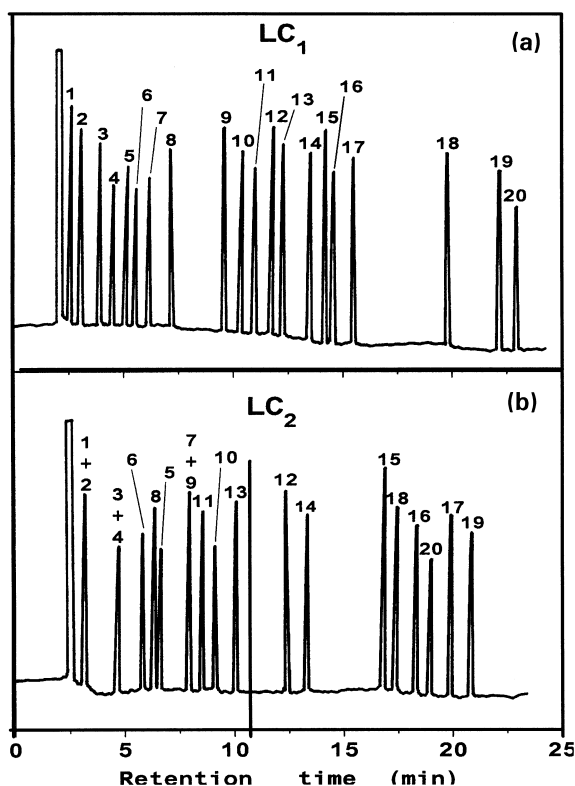


Fig. 3. Chromatograms of the volatile aroma compounds; LC_1 is in the nematic state (a). The vertical line appearing in (b) corresponds to LC_2 solid–nematic transition. Experimental conditions and compound numbers are given in Table 3.

Table 4
Thermodynamical values of the compounds tested on LC_1 and LC_2

Compound	Solid ΔH_a	Nematic ΔH_s	Liquid ΔH_s
LC_1			
Heptane	–39.8	–29	–30.9
<i>n</i> -Octane	–35.6	–30.9	–35.5
<i>n</i> -Nonane	–39.5	–34.0	–37.6
<i>n</i> -Decane	–34.8	–37.8	–42.4
<i>o</i> -Xylene	–22.7	–36.5	–40.7
<i>m</i> -Xylene	–15.6	–35.9	–38.2
<i>p</i> -Xylene	–15.6	–35.1	–38.2
LC_2			
<i>n</i> -Tetradecane	–51.5	–40.0	–48
<i>n</i> -Hexadecane	–50.0	–48.7	–50.7
<i>n</i> -Octadecane	–49.0	–59.8	–61.4
<i>cis</i> -Decaline	–20.9	–29	–33.2
<i>trans</i> -Decaline	–20.6	–31.2	–33.2

xylene, ΔH_a represents only 40% of the condensation enthalpy and about 50% with *cis*- and *trans*-decaline. Strong differences of ΔH_a observed with various solutes explain the interesting chromatographic separations observed in the solid range. ΔH_s for the liquid phase is lower than the condensation enthalpy of about 5–10% with LC_1 and 10–15% with LC_2 . In the case of the nematic phase, these deviations are about 10–20% and 15–25% respectively. These differences are due to the strongly endothermic partial molar enthalpy of mixing.

4. Conclusion

In this study the synthesis, analytical performances and thermodynamic properties of two new liquid crystals substituted with POE chains are reported. Both compounds have an amphiphilic character due to the presence of POE chains. However, LC_1 is more hydrophilic than LC_2 . The aromatic hydrophobic core and hydrophilic POE chains give rise to formation of ordered phases and lead to a narrow liquid crystal range.

Analytical studies show that isomer separation on the stationary phases in the solid and in the liquid state is generally poor. The good separations of certain solutes observed with the supports being in the solid state could be explained by important differences of their ΔH_a . This is probably due to an amphiphilic character of both compounds studied. In the nematic state, the increased discrimination in respect to the shape of molecules leads, however, to remarkable analytical performances.

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