Effect of the chain length on the thermal and analytical properties of laterally biforked nematogens

Mohamed Dahmane [a], Fatiha Athman [a], Saïd Sebih [a], Moulay-Hassane Guermouche [a], Jean-Pierre Bayle [b], Soulimane Boudah [a],[*]

[a] *Laboratoire de Chromatographie, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediène, B.P. 32, El-Alia, 16111 Bab-Ezzouar, Alger, Algeria*
[b] *Laboratoire de Chimie Structurale Organique, Bt. 410, Orsay, Université Paris Sud., 91405 Paris, France*

ARTICLE INFO

ABSTRACT

Three laterally substituted liquid crystals were synthesized in order to investigate the effect of a lateral biforked chain on the thermal and analytical properties. The mesogenic molecules have the same core containing four aromatic rings connected by two ester and one diazo linkages, they differ by the length of one chain within the lateral biforked substituent. The phase transition temperatures were obtained by polarized light microscopy and differential scanning calorimetry (DSC). The clearing temperature and the nematic range decrease with increasing length of the lateral biforked chain. The stationary phases derived from these nematogens provide excellent resolution of various classes of compounds, including aromatic hydrocarbons (AH), substituted benzenes, polycyclic aromatic hydrocarbons (PAH), phenols and volatile organic compounds (VOC) present in the essential oils. The selectivities of the stationary phases were found to decrease according to the length of the side chain.

1. Introduction

Within the chromatographic techniques, no single phase is likely to separate all components of a complex mixture of isomers, each stationary phase has a particular set of interactions within the solute molecules. Nevertheless, liquid crystal phases exhibit interesting solvent properties because of their rode-like shape and the ordered arrangement of their individual molecules. An advantage of capillary gas chromatography (GC) columns is their high column efficiency and inertness towards sample compounds, capillary columns with liquid crystalline phases permit to achieve a good separation within a short time. Since the pioneering work of Kelker [1] and Dewar and Schröeder [2] in the sixties a large number of publications describe the analytical performance of liquid crystals [3–27]. The mechanism of the chromatographic separation on LCSPs is mostly connected with the differentiation of the solute molecular by the ordered arrangement of these stationary phases [11,28,29] that obviously depends on the type of mesophase. Several reviews outlining the fundamentals and applications of liquid crystal stationary phases in both packed and capillary columns are available [30–38]. As shown in these reviews, nematic liquid crystals possess the highest structural selectivity. Liquid crystals were used with great suc-

cess in the separation of naphthalenes [39] and derivatives [40], polycyclic aromatic hydrocarbons [41–47], pyridine derivatives [48], phenol derivatives [49–51] and volatile aromatic compounds [9,11,29,52–55].

The selection of a gas chromatographic stationary phase is one of the most critical aspects of this technique. Chemical nature of the stationary phase is very important when considering the overall behaviour and performance of a column as the structure of the stationary phase influences the separation of the compounds. The effect of the chemical structure of liquid crystalline compounds on separation potential is reported in the literature [56]. These studies have shown that the separation factor for a particular pair of isomers is also dependent on the chemical structure of the liquid crystalline compound used as stationary phase. This correlation between structure and separation provided very important clues for the development of specific liquid crystalline compounds to be used in chromatographic separation of isomers of a compound. Sojak et al. [57] examined regularities and irregularities in the values of retention of chromatographed substances, affecting the selectivity of separation, with regard to the retention of a chromatographed substance versus the structure of a liquid crystal.

If the core of mesogen molecule is large enough it is possible to introduce flexible lateral substituents without destroying the mesophase stability even if the final compound deviates from the classical road-like shape [58]. Many useful materials have been synthesized by a suitable choice of the lateral substituents.

* Corresponding author. Tel.: +213 21247311; fax: +213 21247176.
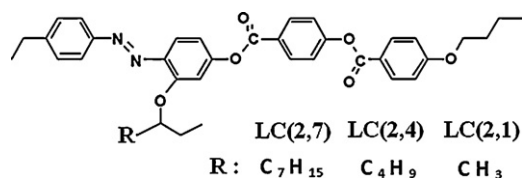 *E-mail address:* sboudah@yahoo.fr (S. Boudah).

Fig. 1. Structures of LC(2,7), LC(2,4) and LC(2,1) liquid crystals. LC(2,7): 2-(1-ethyloctyloxy)-4-(4ï-(4-butoxybenzoyloxy)-benzoyloxy)-4ï-ethyl-azobenzene, LC(2,4): 2-(1-ethylpentyloxy)-4-(4ï-(4-butoxybenzoyloxy)-benzoyloxy)-4ï-ethyl-azobenzene, and LC(2,4): 2-(1-methylpropyloxy)-4-(4ï-(4-butoxybenzoyloxy)-benzoyloxy)-4ï-ethyl-azobenzene.

To establish the correlation between the structure and properties of liquid crystals, it is necessary not only to study the physico-chemical properties of selected compounds but also to follow the variation of these properties in homologous series, since the configuration of substituents may have a marked effect on anisotropic molecular interaction.

To allow the comparison of the different effects the mesogenic core is the same in all the compounds. There are several aspects to discuss the influence of lateral substituents on the thermal and analytical properties.

The present investigation aims to compare the gas chromatographic behaviour of three monomeric liquid crystals presented in Fig. 1. They have the same mesogenic core with different biforked substituents: 1-ethyloctyloxy for phase LC(2,7), 1-ethylpentyloxy for phase LC(2,4) and 1-methylpropoxy for phase LC(2,1) (Fig. 2).
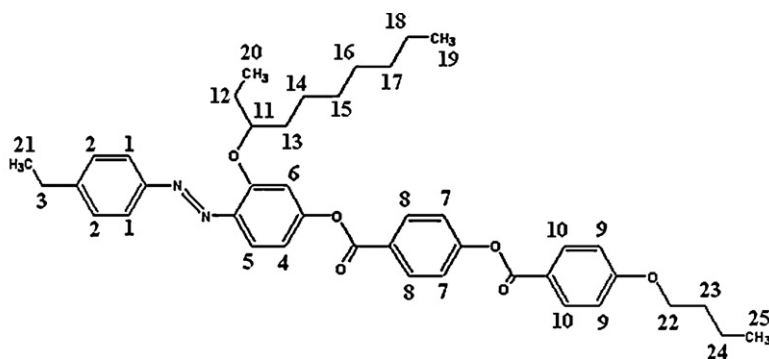
2. Experimental

2.1. Reagents

Chromatographic grade solvents (Janssen Chimica, Amsterdam, The Netherlands) and analytical grade solutes (Chrompack, Middelburg, The Netherlands) were used in the analytical study.

2.2. Synthesis

Procedure for the synthesis of the studied liquid crystals was given in precedent works [59–62].

The purity of the three LC was checked by NMR. The chemical shifts for LC(2,7) are reported in parts per million (ppm) in Table 1.

Table 1
Transition temperatures (°C) of LC(2,7), LC(2,4) and LC(2,1) found by DSC and microscopy.

	Solid → nematic		Nematic → isotropic		Nematic range
	DSC	Microscopy	DSC	Microscopy	
LC(2,7)	113.6	113.9	135.3	135.5	21.7
LC(2,4)	95.5	95.5	152.6	152.1	57.1
LC(2,1)	109.4	109.7	201.4	201.8	92.0

2.3. Differential scanning calorimetry and microscopy analysis

Differential scanning calorimetry (DSC) measurements were performed using TA 2920 device (TA Instruments, New Castle, USA). All scans were carried out using a heating rate of 10 °C min⁻¹. Heating of LC(2,7), LC(2,4) and LC(2,1) was also followed by microscopy using a polarizing microscope (Olympus) with a rate of 10 °C min⁻¹ from room temperature to 220 °C.

2.4. Gas chromatography

The gas chromatograph used was an HP model 6890 equipped with split/splitless injector and a flame ionization detector while using and HP3395 integrator for data collection (Agilent Technologies, Palo Alto, CA, USA). Fused silica columns with intermediate polarity (30 m × 0.32 mm I.D.) were purchased from Supelco (Bellafonte, PA, USA). Deactivation of the column inner surface was made by the manufacturer (Intermediate Polarity Fused Silica Tubing L 9 I.D. 30 m × 0.32 mm (reference 25774 from Supelco), with methylphenyl silylating reagent. The column was coated dynamically with liquid crystalline LC(2,7), LC(2,4) and LC(2,1) (5% in dichloromethane) at a speed of 1 cm s⁻¹. It was then conditioned overnight at 10 °C above the nematic–isotropic transition temperature.

Before starting each experiment, to be sure that the stationary phase was in the solid state, the column was cooled to room temperature and left overnight.

3. Results and interpretation

3.1. Thermal behaviour of the liquid crystals

The transition temperatures of liquid crystals have been determined by polarized light microscopy and differential scanning

H position	1	2	3	4	5	6	7	8	9	10	11	12
δ (ppm)	7.89	7.04	2.77	6,93	7.77	7.04	7.42	8.33	7.32	8,20	4,40	1.85

H position	13	14	15-18	19	20	21	22	23	24	25
δ (ppm)	1.57	1.57	1.34	0.90	1.06	1.34	4.12	1.85	1.85	1.06

Fig. 2. ¹H NMR chemical shifts *d* (ppm) of LC(2,7) liquid crystal.

Fig. 3. Differential scanning calorimetry thermograms of LC(2,7), LC(2,4) and LC(2,1).

Table 2
Plate numbers observed for the analysis of the given analytes on LC(2,7), LC(2,4) and LC(2,1) liquid crystal based phases in the anisotropic, nematic and isotropic states. Plate number per meter was calculated by the classical equation $N = 16\, t'_r{}^2/\omega^2$ (where t'_r and ω are the corrected retention time and baseline peak width, respectively).

Stationary phases	Status	Solute	T isothermal (°C)	Plate number (per meter)
LC(2,7)	Anisotropic solid	Fenchone	60	2257
	Nematic	Geraniol	125	3386
	Isotropic liquid	Phenanthrene	210	2418
LC(2,4)	Anisotropic solid	Fenchone	60	2822
	Nematic	Geraniol	125	3870
	Isotropic liquid	Phenanthrene	210	2967
LC(2,1)	Anisotropic solid	Fenchone	60	2338
	Nematic	Geraniol	125	3628
	Isotropic liquid	Phenanthrene	210	2515

The results obtained reveal that:

- the temperatures of transition obtained by DSC and microscopy are practically identical;
- the morphological observations under polarized light microscopy at different temperatures were consistent with those described in the thermal analysis;
- the three compounds exhibited a single nematic phase;
- the effect of the lateral substituent length on the melting point is similar for the three LC, indicating that the spacing of molecules and so the interactions in the solid phase are similar. In fact, it has been shown that flexible substituents in the solid or nematic phases are usually bent along the core whatever the chain length is;
- the influence of the chain length on the clearing temperature is more pronounced. The mesomorphic range decreases strongly with the number of carbons within the chain. Even if each part of the biforked chain is folded back along the mesogenic core, the increase of the number of methylene groups in one of the chains brings considerable entropy change that causes the decrease of the mesogenic properties.

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, nematic and liquid phases have separation capability. The best efficiency is observed, however, in the nematic phase.

In the nematic phase the liquid crystal molecules are oriented with the long axis parallel and, owing to their rod-like molecular structure in the nematic temperature range, longer (or more rod-like) isomers can interact more strongly with the aligned nematic phase than isomers with bulkier molecules. Especially positional isomers, owing to differences in their molecule shapes, show retention differences. To elucidate possible effects caused by the used mesogenic phases, more compounds belonging to various families having different polarities and volatilities were injected. It was proved that mesogens can be used in all the domains of their existence: solid, mesomorphic, and isotropic liquid. The selectivities of the stationary phases were found to vary according to the chain length of the liquid crystalline. The retention times of all compounds tested are listed in Table 3.

3.2.1. Aromatic compounds

The most satisfactory results were obtained at an oven temperature of 60 °C in the solid state for the three coated liquid crystals (Table 3). The effects of the separation of components of mixtures,

calorimetry. Thermograms of the three liquid crystals are shown in Fig. 3 and the transition temperatures in Table 1.

The thermodynamic stability of nematic phase is strongly influenced when a lateral group is attached to a mesogenic core. Considering the steric hindrance, a lateral substituent effectively widens the core and increases the intermolecular separation. This leads to a reduction in the intermolecular interactions and hence the nematic phase stability is reduced [62,58,63]. There are several reports in the literature that indicate that large flexible lateral substituents depress the clearing temperature less than do rigid ones [64–67] and that increasing the length of the flexible substituent also depresses the clearing temperature.

Table 3
Retention times (tr) of the tested solutes on the three capillary columns.

	LC(2,7)[I] tr[e]	LC(2,4)[II] tr[e]	LC(2,1)[III] tr[e]
Aromatic hydrocarbons[a]			
Benzene	3.05	3.02	2.94
Toluene	3.36	3.32	3.47
Ethylbenzene	3.94	3.75	4.26
p-Xylene	4.01	4.01	4.64
m-Xylene	4.11	3.91	4.56
o-Xylene	4.45	4.35	5.08
t-Butylbenzene	4.48	5.29	6.19
Iso-Butylbenzene	5.40	5.74	6.75
1,3,5-Trimethylbenzene	5.60	6.03	6.79
1,2,4-Trimethylbenzene	6.05	6.26	8.16
1,3-Diethylbenzene	6.42	7.46	8.82
1,4-Diethylbenzene	6.49	7.85	9.70
1,2-Diethylbenzene	6.86	8.01	9.92
1,2,3-Trimethylbenzene	7.30	7.35	9.88
1,2,4,5-Tetramethylbenzene	9.55	12.65	16.44
Polyaromatic hydrocarbons[b]			
Naphtalene	5.31	4.28	4.77
2-Methylnaphtalene	6.10	4.92	6.03
1-Methylnaphtalene	6.45	5.18	6.31
Chloronaphtalene	8.04	5.99	7.96
2,6-Dimethylnaphtalene	8.16	6.04	8.24
1,6-Dimethylnaphtalene	8.61	6.34	8.46
Acenaphtylene	10.09	7.45	10.59
Acenaphtene	10.32	7.50	10.79
Bromonaphtalene	10.89	8.24	11.73
Fluorene	13.40	10.35	15.83
Phenanthrene	19.44	15.96	26.99
Anthracene	20.01	16.41	29.51
Phenols[c]			
Phenol	8.49	5.10	6.95
2-Bromorophenol	9.07	5.50	7.08
2,6-Dimethylphenol	9.65	5.79	7.70
o-Cresol	9.77	5.75	7.77
m-Cresol	10.81	6.58	8.90
p-Cresol	10.92	6.58	9.10
2-Ethylphenol	12.08	6.37	9.15
2,5-Dimethylphenol	12.43	7.13	9.94
2,4,6-Trimethylphenol	12.89	7.34	9.94
2,3-Dimethylphenol	13.47	7.93	10.96
3-Ethylphenol	13.59	8.19	11.03
3,5-Dimethylphenol	13.82	8.02	11.15
3,4-Dimethylphenol	14.86	8.80	12.24
t-Butylphenol	15.56	9.10	12.04
2,4,5-Trimethylphenol	16.60	9.87	13.26
2,3,5-Trimethylphenol	16.95	10.03	13.44
3-Chlorophenol	17.30	10.58	14.49
4-Chlorophenol	17.30	10.78	14.78
2,6-Dibromophenol	20.54	13.00	16.79
3-Bromophenol	21.24	13.86	18.21
4-Bromophenol	21.24	13.85	18.30
Volatile aroma compounds[d]			
Cis-hex-3-ene-1-ol	3.88	3.35	3.54
Cis-hex-2-ene-1-ol	3.96	3.40	3.56
α-Pinene	3.96	3.47	3.45
Eucalyptol	4.59	3.63	3.69
Limonene	4.77	3.68	3.75
Fenchone	5.21	4.25	4.76
Linalol	5.39	4.26	4.75
1,3-Dichloro-2-propanol	5.48	4.00	4.70
1-Bromo-3-chloropropen-2-ol	7.18	4.63	5.95
Camphor	7.27	4.94	5.62
Linalyl acetate	7.27	5.26	5.90
Borneol	8.52	5.16	6.30
Menthol	8.97	5.30	6.54
Cis-myrtanol	9.05	5.26	6.31
1,3-Dibromopropan-2-ol	9.59	6.01	8.04
α-Terpineol	9.86	5.89	7.24
β-Citronellol	10.04	5.68	7.25
Nerol	10.13	6.30	7.58
Cis-citral	10.75	6.50	7.92
Geraniol	10.93	6.96	8.51
Trans-myrtanol	11.73	7.24	9.02
Citronellyl acetate	11.82	6.76	7.86
Trans-citral	12.18	7.32	9.00

Table 3 (*Continued*)

	LC(2,7)[I] tr[e]	LC(2,4)[II] tr[e]	LC(2,1)[III] tr[e]
Neryl acetate	12.36	7.18	8.51
Carvone	12.36	7.63	9.52
Terpenyl	13.07	7.52	8.88
Geranyl acetate	13.52	8.10	9.39
Anethol	14.86	9.91	11.42
Bisabolene	15.48	9.62	11.01
Thymol	16.29	9.63	12.84
Carvacrol	16.56	9.98	13.05
Eugenol	17.18	10.84	13.69
Cis-jasmone	18.07	11.51	13.77
Cis-isoeugenol	19.59	12.25	15.53
Trans-isoeugenol	22.27	14.67	18.27

[a] I, II and III Column temperature: isotherm 60 °C.
[b] I Column temperature programmed from 160 °C (8 min) at 4 °C min⁻¹ to 225 °C; II Column temperature programmed from 160 °C (8 min) at 8 °C min⁻¹ to 225 °C; III Column temperature programmed from 160 °C (10 min) at 4 °C min⁻¹ to 225 °C.
[c] I Column temperature programmed from 80 °C at 4 °C min⁻¹ to 190 °C; II and III Column temperature programmed from 100 °C at 4 °C min⁻¹ to 190 °C.
[d] I Column temperature programmed from 80 °C at 4 °C min⁻¹ to 190 °C; II and III Column temperature programmed from 100 °C at 4 °C min⁻¹ to 190 °C.
[e] Compounds.

including isomers, on LCSPs at temperatures below their melting points, in the solid, similar to the effects of the separation within the temperature mesophase range are difficult to explain [40], but may be due to the similar arrangement of molecules between the two phases when cooling from the nematic to the solid phase.

Below melting point, the stationary phase was solid; the separation of the solutes was due to their adsorption on the solid surface. The compounds were not always separated, but when the separation occurred, generally, the more retained was the more polar with the highest boiling point.

For instance, if we considered xylene isomers, partial separation was obtained for meta and para homologues in this order on the LC(2,7)-based column and in a different order on the two other columns while the compound with the highest boiling point (o-xylene) was more retained on the three liquid crystal based stationary phases. The second example was relative to diethylbenzenes. In Table 3, it is clear that LC(2,4) and LC(2,1) succeed in separating diethylbenzene isomers while LC(2,7) is not able to differentiate between meta and para isomers (1,3/1,4-diethylbenzene). As for xylene isomers, it can be noticed that 1,2-diethylbenzene is more retained than 1,3-diethylbenzene and 1,4-diethylbenzene on the three columns. 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene were eluted in this order on all the columns with a good resolution (Table 3). Greater retention of the analytes with LC(2,1) stationary phase than with the other phases was observed (Table 3). This phenomenon may be related to the fact that the molecules under investigation interact in the nematic phase more pronouncely with the core than with the lateral biforked chain.

3.2.2. Polyaromatic compounds

Because of the wide boiling range for the analytes (PAHs), it is not easy to separate all of them isothermally within a reasonable time. Hence, several temperature programmings were studied.

For the separations of PAHs (Table 3) some differences were observed with respect to elution orders for the three columns. A similar elution order but a longer retention time was observed for each corresponding analyte on LC(2,1) and LC(2,7) comparatively with LC(2,4).

Methylnaphthalenes and dimethylnaphthalenes are more difficult to separate on conventional phases, but on our columns 2- and 1-methylnaphthalene as well as 2,6- and 1,6-dimethylnaph-talene were successfully separated on the three stationary phases with identical elution orders.
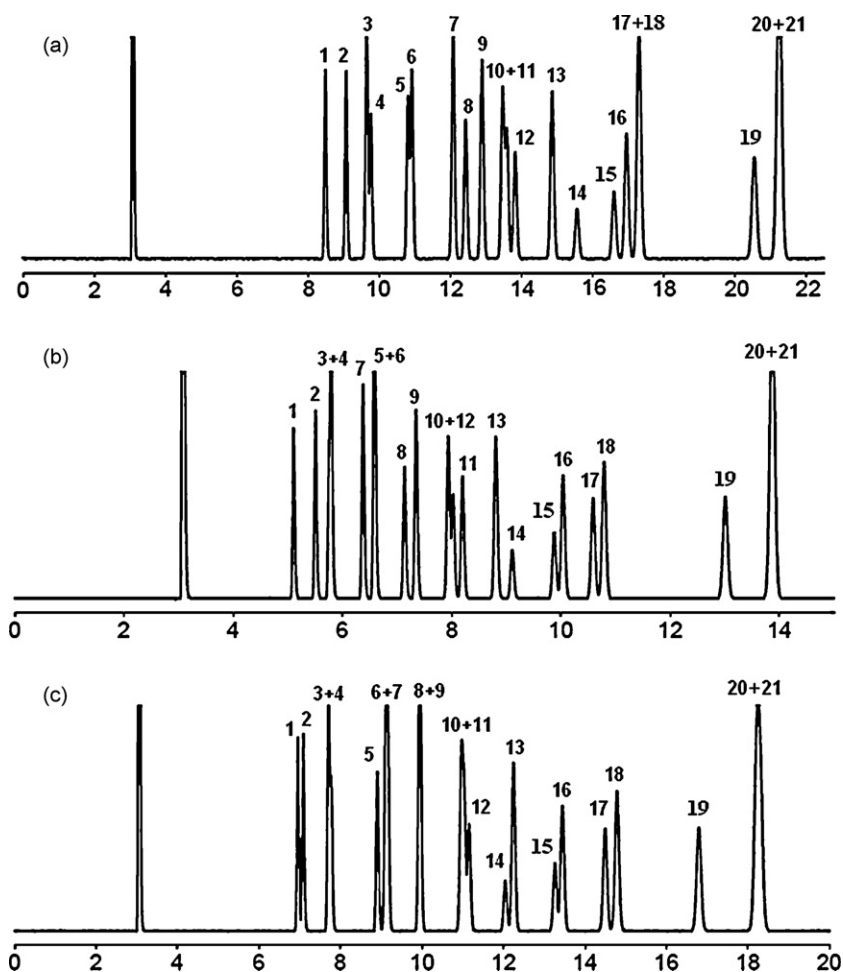
Fig. 4. Chromatograms obtained for a mixture of phenols on the LC(2,7)-, LC(2,4)- and LC(2,1)-based phase (a–c, respectively); column temperatures: from 80 °C at 4 °C min⁻¹ to 190 °C for LC(2,7), and from 100 °C at 4 °C min⁻¹ to 190 °C for LC(2,4) and LC(2,1). (1) Phenol; (2) 2-bromophenol; (3) 2,6-dimethylphenol; (4) o-cresol; (5) m-cresol; (6) p-cresol; (7) 2-ethylphenol; (8) 2,5-dimethylphenol; (9) 2,4,6-trimethylphenol; (10) 2,3-dimethylphenol; (11) 3-ethylphenol; (12) 3,5-dimethylphenol; (13) 3,4-dimethylphenol; (14) t-butylphenol; (15) 2,4,5-trimethylphenol; (16) 2,3,5-trimethylphenol; (17) 3-chlorophenol; (18) 4-chlorophenol; (19) 2,6-dibromophenol; (20) 3-bromophenol; and (21) 4-bromophenol.

Table 3 shows that the separation of acenaphtylene (bp = 280.0 °C) from acenaphtene (bp = 279.0 °C) was achieved only by LC(2,1) and LC(2,7) in this order, although the L/B ratios are identical for the two molecules.

The high structural selectivity of nematic mesophases provided a basis for the solution of problems in the chromatographic analysis of mixtures containing closely boiling aromatic isomers. The complete separation of phenanthrene/anthracene was easily obtained on the three columns with a good resolution. The molecular sizes of these two PAHs are the same, but their shapes are different (anthracene's L/B = 1.57, phenanthrene's L/B = 1.46), anthracene is more elongated than phenanthrene and is therefore retained longer (Table 3).

3.2.3. Phenols

The analysis of phenols in environmental samples is of great importance because of their widespread occurrence in the environment. Especially, it is hard to separate p-cresol and m-cresol. The experiments made showed that partial separation (Fig. 4a) of this isomers occurred on LC(2,7). The mesogen LC(2,4) was not able to separate them (Fig. 4b). The results showed that the capillary column coated with LC(2,1) was excellent for separating these compounds. Meta and para-cresol were only separated in this order on the nematic LC(2,1)-based phase, while the ortho isomer is eluted first (Fig. 4c). The more elongated compound (para-isomer) better

interacts in a liquid crystal arrangement giving a higher retention time compared to meta- and ortho-isomers.

We first observe that retention times are shorter on the liquid crystal LC(2,4) than on the other stationary phases (Table 3). This is consistent with the lower interaction of the solutes within the mesogen cores.

It seems that the LC(2,4) and LC(2,1) compounds have similar chromatographic capabilities particularly when 2,4,5- and 2,3,5-trimethylphenol, 3- and 4-chlorophenol were chromatographied While 3- and 4-chlorophenol appeared as one peak on the LC(2,7)-based column in the liquid state (see Fig. 4).

The presence of bulky methyl groups in 2,6-positions increases the steric hindrance, this means that the methyl groups do not allow bond formation between the OH group and the polar linkages of the liquid crystal stationary phase. Therefore the retention of 2,6-dimethylphenol is the lowest and is eluted first. For the five isomers of dimethylphenol a good resolution was obtained on LC(2,7) and LC(2,1), while the LC(2,4)-based column could only poorly separate 2,3/3,5-dimethylphenols (Fig. 4b).

Only one inversion of the elution order of phenol substituted on LC(2,1) comparatively with LC(2,7) was observed: o-t-butylphenol was retained on LC(2,7) stronger than the 3,4-dimethyphenol, although it has a lower boiling point.

Most of the compounds were eluted conversely with the order of their boiling points. We also note that 3,4-dimethylphenol and
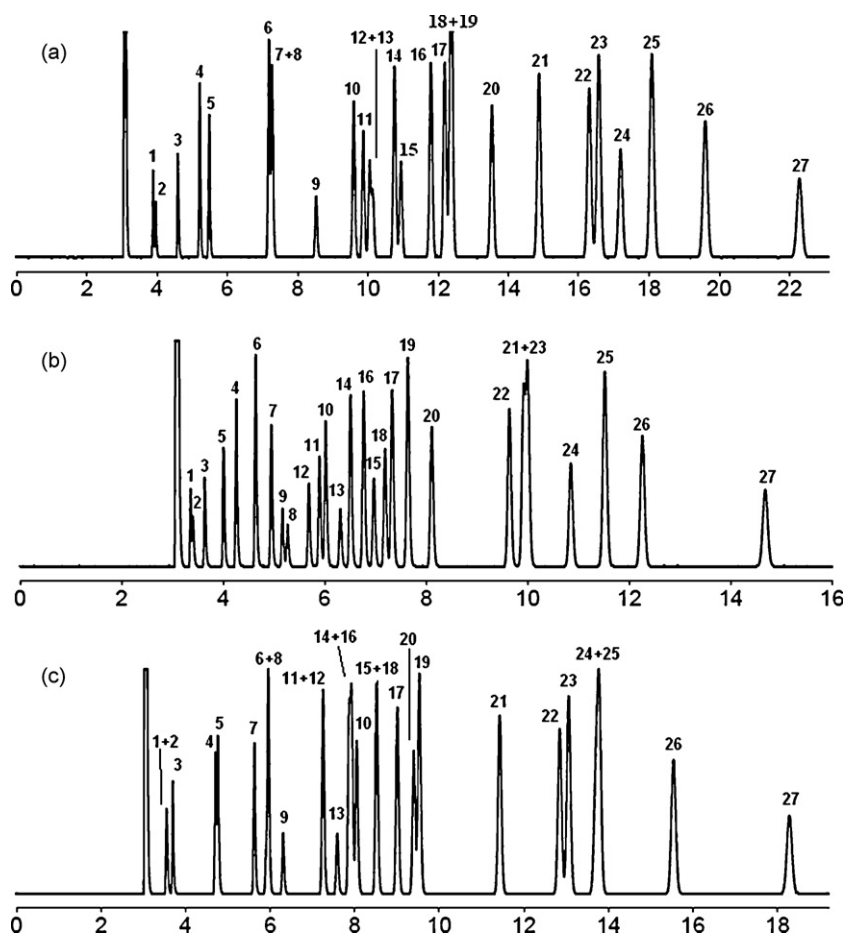
Fig. 5. Chromatograms obtained for a mixture of Volatile aromatic compounds on the LC(2,7)-, LC(2,4)- and LC(2,1)-based phase (a–c, respectively); column temperatures: from 80 °C at 4 °C min⁻¹ to 190 °C for LC(2,7), and from 100 °C at 4 °C min⁻¹ to 190 °C for LC(2,4) and LC(2,1). (1) Cis-hex-3-ene-1-ol; (2) cis-hex-2-ene-1-ol; (3) eucalyptol; (4) fenchone; (5) 1,3-dichloro-2-propanol; (6) 1-bromo-3-chloropropen-2-ol; (7) camphor; (8) linalyl acetate; (9) borneol; (10) 1,3-dibromopropan-2-ol; (11) α-terpineol; (12) β-citronellol; (13) nerol; (14) cis-citral; (15) geraniol; (16) citronellyl acetate; (17) trans-citral; (18) neryl acetate; (19) carvone; (20) geranyl acetate; (21) anethol; (22) thymol; (23) carvacrol; (24) eugenol; (25) cis-jasmone; (26) cis-isoeugenol; and (27) trans-isoeugenol.

2,4,5- and 2,3,5-trimethylphenol (bp = 227.0, 232.0 and 233.0 °C respectively) were eluted before 3- and 4-chlorophenol (bp = 214.0 and 220.0 °C respectively), and it is the same one in the case of 2,6-dibromophenol (bp = 255.0 °C) which was eluted before 3-bromophenol (bp 236.5 °C) and 4-bromophenol (bp = 238.0 °C), and we noticed that 2-ethylphenol (bp = 204.5 °C) is eluted before p-cresol and m-cresol (202.0 and 202.3 °C respectively) only on LC(2,4).

The separation of phenolic compounds obtained under the conditions described was satisfactory with the exception of the isomers of 3- and 4-bromophenol which are not separate on the three studied stationary phases.

3.2.4. Volatile aromatic compounds

Very interesting separations have been achieved on the LC stationary phases in the separation of volatile aromatic compounds (Table 3 and Fig. 5).

As can be seen from Fig. 5, the selectivity factor is affected by carbon numbers in alkoxy chains. Our results show that the capability of the three columns to separate volatile aromatic compounds isomers decreases in the order LC(2,4) > LC(2,7) > LC(2,1).

The positional isomers cis-hex-3-ene-1-ol and cis-hex-2-ene-1-ol, polar compounds having close boiling points (respectively 156.5 and 157.0 °C), are not separated on LC(2,7)-based phase. A gradual increase of resolution with increasing side chain is observed within a single phase state (Fig. 5a-c).

It is well known that on polyethylene glycol (a conventional polar phase), anethol (bp = 235.0 °C) are more retained than thymol (bp = 232.5 °C) and carvacrol (bp = 237.7 °C) [38]. On the nematic LC(2,1), this elution order is preserved, however, it is inverted on LC(2,7)-based phase, while on LC(2,4)-based phase, elution order is thymol, anethol and finally carvacrol according to their boiling points. (Fig. 5 and Table 3)

The characteristic separative properties of liquid crystals are observed for the nematic phase of the three stationary phases, which enables the separation of the geometrical isomers: cis/trans-citral, nerol/geraniol, neryl acetate/geranyl acetate and cis/trans-isoeugenol with cis isomers always eluting before trans in the nematic state, indicating that the stretched form of the molecule is more retained. The separation of geometric isomers results in an elution order according to the length-to-breadth ratio and planarity of the solute and in the case of positional isomers: fenchone/camphor, thymol/carvacrol, linalool/nerol and eugenol/isoeugenol were well separated on the three columns.

Some polar compounds pairs, e.g. 1-bromo-3-chloropropen-2-ol and camphor, and β-citronellol and nerol, are separated on LC(2,4) and LC(2,1) but not on LC(2,7). We also noticed that the increase of lateral chain gives rise to a change of total selectivity, which is expressed in the inversion of the elution order: 1,3-dibromopropan-2-ol and α-terpineol, geraniol and citronellyl acetate. Trans-citral and neryl acetate were eluted in this order on LC(2,7). This order is reversed on the other columns that may

result from chain–chain interactions between the mesogen and the solute. In conclusion, LC(2,4) seems to be more selective for volatile aroma compounds, as shown in Fig. 5b.

4. Conclusion

In this study, the chain length effect of a lateral biforked substituent mesogens on the thermal and analytical chromatographic properties was investigated.

Despite the lateral substituent, the three synthesized mesogens present a single nematic phase which a mesomorphic range that decreases with the chain length.

The resultant columns demonstrate excellent analytical capability and performance at solid, nematic and liquid states. The nematic state possess high structural selectivity.

The lengthening of the lateral chain seems induces a lower structural selectivity due to the fact the chain partially masks the more polar core of the mesogen to the solute molecule.

A compromise has to be done between the nematic range and the chromatographic properties. The crystal liquid LC(2,4), which has a side chain of medium length, gave good separations for the majority of the compounds in a very short time.

The obtained results demonstrate the importance of substituted liquid crystalline stationary phases in capillary gas chromatography for separation of a wide variety of analytes such as phenols and volatile organic compounds (VOC) present in the essential oils.

References

[1] H. Kelker, Fresen. Z. Anal. Chem. 198 (1963) 254.
[2] M.J.S. Dewar, J.P. Schröeder, J. Am. Chem. Soc. 86 (1964) 5239.
[3] H. Kelker, E. Von Schivizhoffen, Adv. Chromatogr., vol. 6, Marcel Dekker, New York, 1968, p. 247.
[4] W.L. Zielinski Jr., G.M. Janini, J. Chromatogr. 186 (1979) 237.
[5] L. Sojak, G. Kraus, J. Ostrovsky, E. Kralovicova, J. Krupcik, J. Chromatogr. 206 (1981) 463.
[6] L. Sojak, G. Kraus, J. Ostrovsky, E. Kralovicova, J. Chromatogr. 234 (1982) 347.
[7] F. Janssen, Chromatographia 17 (1983) 477.
[8] L. Sojak, P. Parkas, J. Janak, S. Rang, O. Eisen, J. Chromatogr. 287 (1984) 271.
[9] T.J. Betts, J. Chromatogr. 588 (1991) 231.
[10] J. Mazur, Z. Witkiewicz, R. Dabrowski, J. Chromatogr. 600 (1992) 123.
[11] T.J. Betts, J. Chromatogr. 605 (1992) 280.
[12] P. Berdagué, J.P. Bayle, F. Perez, J. Courtieu, O. Abdelhadi, S. Guermouche, M.H. Guermouche, J. High Resolut. Chromatogr. 18 (1995) 304.
[13] G. Kraus, J.M. Thierfelder, L. Sojak, J. Chromatogr. A 677 (1994) 197.
[14] P. Berdagué, J.P. Bayle, F. Perez, J. Courtieu, O. Abdelhadi, S. Guermouche, M.H. Guermouche, Chromatographia 40 (1995) 581.
[15] F. Perez, P. Berdagué, J.P. Bayle, J. Courtieu, S. Boudah, M.H. Guermouche, J. Chromatogr. A 746 (1996) 247.
[16] F. Perez, P. Berdagué, J.P. Bayle, J. Courtieu, S. Boudah, M.H. Guermouche, S. Sebih, Bull. Soc. Chim. Fr. 133 (1996) 427.
[17] A. Meddour, J. Courtieu, O. Abdelhadi, S. Guermouche, M.H. Guermouche, Chromatographia 43 (1996) 387.
[18] F. Perez, P. Berdagué, J.P. Bayle, J. Courtieu, S. Boudah, M.H. Guermouche, S. Sebih, J. High Resolut. Chromatogr. 20 (1997) 379.
[19] F. Ammar-Khodja, S. Guermouche, M.H. Guermouche, P. Berdagué, J.P. Bayle, Chromatographia 50 (1999) 338.
[20] B. Saïdat, M.H. Guermouche, C. Canlet, P. Berdagué, J.P. Bayle, Chromatographia 55 (2002) 55.
[21] D. Belaidi, S. Sebih, M.H. Guermouche, J.P. Bayle, S. Boudah, C.R. Chim. 5 (2002) 591.
[22] D. Belaïdi, S. Sebih, M.H. Guermouche, J.P. Bayle, S. Boudah, Chromatographia 57 (2002) 207.
[23] S. Boudah, S. Sebih, M.H. Guermouche, M. Rogalski, J.P. Bayle, Chromatographia 57 (2003) 307.
[24] D. Belaïdi, S. Sebih, M.H. Guermouche, J.P. Bayle, S. Boudah, J. Chromatogr. A 1087 (2005) 52.
[25] M. Dahmane, F. Athman, S. Sebih, M.H. Guermouche, J.P. Bayle, S. Boudah, Chromatographia 70 (2009) 489.
[26] F. Athman, M. Dahmane, S. Boudah, M.H. Guermouche, J.P. Bayle, S. Sebih, Chromatographia 70 (2009) 503.
[27] F. Ammar-Khodja, S. Guermouche, M.H. Guermouche, P. Judenstein, J.P. Bayle, Chromatographia 70 (2009) 497.
[28] J. Krupcik, M. Valachovicova, G. Kraus, J. Chromatogr. A 665 (1994) 111.
[29] T.J. Betts, C.M. Moir, A.I. Tassone, J. Chromatogr. 547 (1992) 335.
[30] G.M. Janini, Adv. Chromatogr., vol. 17, Marcel Dekker, New York, 1979, p. 231.
[31] Z. Witkiewicz, J. Chromatogr. 251 (1982) 311.
[32] M.S. Vigdergauz, N.F. Belyaev, M.S. Esin, Fresen. Z. Anal. Chem. 335 (1989) 393.
[33] Z. Witkiewicz, J. Chromatogr. 466 (1989) 37.
[34] Z. Witkiewicz, J. Mazur, LC GC 8 (1990) 224.
[35] Z. Witkiewicz, in: B. Bahadur (Ed.), Liquid Crystals. Applications and Uses, vol. 2, World Scientific, Singapore, 1991, p. 309.
[36] F. Gritti, G. Felix, Chromatographia 55 (2002) 523.
[37] Z. Witkiewicz, J. Oszczudłowski, M. Repelewicz, Chem. Anal. (Warsaw) 48 (2003) 397.
[38] Z. Witkiewicz, J. Chromatogr. A 1062 (2005) 155.
[39] A. Kraus, U. Shumann, G. Kraus, J. Chromatogr. 609 (1992) 277.
[40] S. Wasik, S. Chesler, J. Chromatogr. 122 (1976) 451.
[41] B.B. Ghatge, N.V. Bhalerao, J. Chromatogr. 549 (1991) 423.
[42] M. Nishioka, B.A. Jones, B.J. Tarbet, J.S. Bradshaw, M.C. Lee, J. Chromatogr. 357 (1986) 76.
[43] G.M. Janini, K. Johnston, W.L. Zielinski Jr., Anal. Chem. 47 (1975) 670.
[44] S.A. Wise, L.C. Sander, H. Chang, K.E. Markides, M.L. Lee, Chromatographia 25 (1988) 473.
[45] J.S. Bradshaw, C. Schregenberger, K.H.C. Chang, K.E. Markides, M.L. Lee, J. Chromatogr. 358 (1986) 95.
[46] K.E. Markides, H.C. Chang, C.M. Schregenberger, B.J. Tarbet, J.S. Bradshaw, M.L. Lee, J. High Res. Chromatogr. 8 (1985) 516.
[47] H. Budzinski, M. Radke, P. Garrigues, S.A. Wise, J. Bellocq, H.J. Willsch, J. Chromatogr. 627 (1992) 227.
[48] L.C. Sander, M. Schneider, C. Woolley, S.A. Wise, J. Microcolumn Sep. 6 (1994) 115.
[49] L. Peichang, L.I. Haochun, J. Chromatogr. 184 (1980) 215.
[50] R.J. Dai, R.N. Fu, W. Zhou, J. Microcolumn Sep. 7 (1995) 455.
[51] L.E. Cook, R.C. Spangelo, Anal. Chem. 46 (1974) 122.
[52] T.J. Betts, J. Chromatogr. 587 (1991) 343.
[53] T.J. Betts, J. Chromatogr. 626 (1992) 294.
[54] T.J. Betts, J. Chromatogr. 641 (1993) 189.
[55] T.J. Betts, J. Chromatogr. 513 (1990) 311.
[56] A. Ziolek, A. Witkiewica, R. Dabrowski, J. Chromatogr. 299 (1984) 159.
[57] L. Sojak, P. Farkas, I. Ostrovsky, J. Janak, J.R. Chretien, J. Chromatogr. 557 (1991) 241.
[58] W. Weissflog, D. Demus, Cryst. Res. Technol. 19 (1984) 55.
[59] P. Berdague, F. Perez, J. Courtieu, J.P. Bayle, Bull. Soc. Chim. Fr. 130 (1993) 475.
[60] F. Perez, P. Judeinstein, J.P. Bayle, New J. Chem. 19 (1995) 1015.
[61] A. Hassner, V. Alexanian, Tetrahedron Lett. 46 (1978) 4475.
[62] J.P. Bayle, F. Perez, J. Courtieu, Bull. Soc. Chim. Fr. 127 (1990) 565.
[63] W. Weissflog, D. Demus, Mol. Cryst. Liq. Cryst. 129 (1985) 235.
[64] G.W. Gray, Mol. Cryst. 1 (1966) 333.
[65] G.W. Gray, in: G.H. Brown (Ed.), Advances in Liquid Crystals, vol. 2, Academic Press, New York, 1976, p. 1.
[66] D. Demus, A. Hauser, in: H.-D. Koswig (Ed.), Selected Topics in Liquid Crystal Research, Akademie-Verlag, Berlin, 1990, p. 19.
[67] D. Coates, in: B. Bahadur (Ed.), Liquid Crystals. Applications and Uses, vol. 1, World Scientific, Singapore, 1990 (Chapter 3).