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Comparison of two azobenzene liquid crystal stationary phases in open tubular column gas chromatography

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Abstract

Comparative applications of two liquid crystals used as stationary phases in gas–liquid chromatography were investigated using different kinds of solutes. These liquid crystal molecules are: 4-(4-*trans*-pentylcyclohexanecarboxyloxy)-2′-methoxy-4′-(4-*trans*-pentylcyclohexanecarboxyloxy)-azobenzene (LC_1) and 4-(4-*trans*-pentylcyclohexanecarboxyloxy)-2′-butoxy-3′-methyl-(4-butoxybenzoyloxy)-azobenzene (LC_2). Their thermal properties were established with differential scanning calorimetry (DSC). The chromatographic separation abilities of LC_1 and LC_2 were studied using capillary glass columns. Interesting analytical performances were obtained in different fields: isomeric separation of alkanes, aromatics, polyaromatics, volatile aromatic compounds and *cis*- and *trans*-isomers. Comparison between LC_1 and LC_2 is presented. Elution properties of LC_1 and LC_2 showed some differences. LC_2 exhibited a higher separation efficiency especially for alkanes, light aromatics and polyaromatics, and the elution orders of some solutes were reversed compared with LC_1. Then, the two liquid crystals are efficient before and after solid–solid or solid–nematic transitions. Nevertheless, they present higher plate numbers in the nematic state. Nice separations of volatile aromatic compounds are obtained by the two liquid crystals.

Keywords: Stationary phases, GC; Liquid crystals; Azobenzenes; Aromatic compounds; Alkanes; Volatile organic compounds

1. Introduction

The use of liquid crystals as stationary phases in gas–liquid chromatography was first reported by Kelker [1,2] and Dewar et al. [3]. Liquid crystalline stationary phases are useful in separating close-boiling isomers which are very difficult or impossible to separate on classical stationary phases. These interesting properties are due to the rod-like shape and the ordered arrangement of their molecules within the mesophase. Liquid crystals were used with great success in the separation of naphthalenes [4] and derivatives [5], polycyclic aromatic hydrocarbons [6,7], isomers of benaxaprofen [8], steroid epimers [9], phenol ethers [10] and volatile aromatic compounds [11–17]. We presented the synthesis and the chromatographic applications of four new liquid crystals [18,19].

In this work, we analyse the gas–liquid chromatographic retention characteristics and the analytical performances of two new liquid crystals using a large variety of solutes. The formulas of the two

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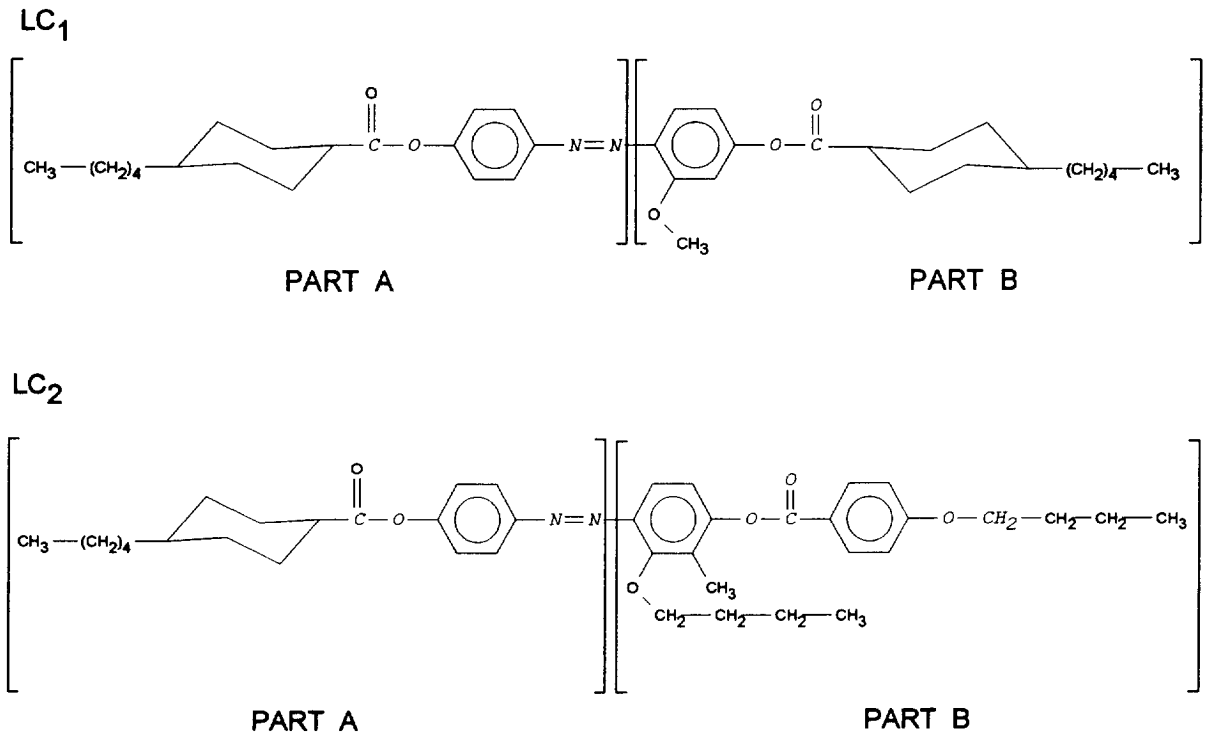

Fig. 1. LC_1 and LC_2 formulas.

Table 1
Transition temperature of liquid crystals LC_1 and LC_2 obtained by differential scanning calorimetry (DSC) measurements

Transition	LC_1	LC_2
Solid–solid ($K_1 \rightarrow K_2$)	89.5°C	99.6°C
Solid–nematic ($K_2 \rightarrow N$)	93.8°C	110.3°C
Nematic–liquid ($N \rightarrow I$)	274.5°C	245.4°C

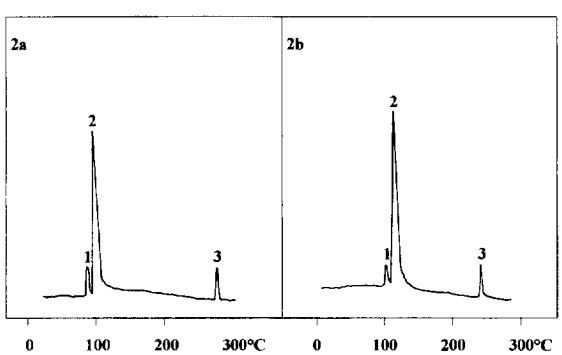

Fig. 2. Thermograms of LC_1 (a) and LC_2 (b). $1 = K_1 \rightarrow K_2$ transition; $2 = K_2 \rightarrow N$ transition; $3 = N \rightarrow I$ transition.

following compounds are shown in Fig. 1. The liquid crystals are: 4-(4-*trans*-pentylcyclohexanecarboxyloxy)-2′-methoxy-4′-(4-*trans*-pentylcyclohexancarboxyloxy)-azobenzene (LC_1) and 4-(4-*trans*-pentylcyclohexanecarboxyloxy)-2′-butoxy-3′-methyl-(4-butoxybenzoyloxy)-azobenzene (LC_2).

They have a common part, A, but differ in part B, LC_2 bearing a lateral alkoxy chain and having one of the aliphatic rings replaced by an aromatic one.

2. Experimental

Details concerning the synthesis of the two liquid crystals are given in [21–26].

2.1. Reagents

Alkanes, aromatics and other solutes were purchased from Chrompack (Netherlands) and volatile

Table 2
Relative retention times of different compounds on LC_1 and LC_2 capillary columns

Compounds	Temperature (°C)		Relative retention times	
	LC_1	LC_2	LC_1	LC_2
Alkanes				
5 *n*-Nonane	50	60	1	1
1 2,3,5-Trimethylhexane	50	60	0.70	0.17
2 2,2,4-Trimethylhexane	50	60	0.70	0.33
3 3-Methyloctane	50	60	0.80	0.67
4 2-Methyloctane	50	60	0.85	0.75
4 *n*-Tridecane	90	110	1	1
1 5-Methyldodecane	90	110	0.73	0.71
2 4-Methyldodecane	90	110	0.78	0.74
3 2-Methyldodecane	90	110	0.81	0.79
5 *n*-Octadecane	180	170	1	1
1 8-Methylheptadecane	180	170	0.83	0.77
2 4-Methylheptadecane	180	170	0.86	0.83
3 3-Methylheptadecane	180	170	0.86	0.83
4 2-Methylheptadecane	180	170	0.88	0.84
3 *n*-Eicosane	210	220	1	1
1 2,6,10,14-Tetramethylhexadecane	210	220	0.62	0.66
2 3-Methylnonadecane	210	220	0.92	0.93
Aromatics				
1 Toluene	60° during 12 min then 4°/min		1	1
2 Ethylbenzene	60° during 12 min then 4°/min		1.92	1.89
3 *m*-Xylene	60° during 12 min then 4°/min		2.31	2.11
4 *p*-Xylene	60° during 12 min then 4°/min		2.31	2.22
5 *o*-Xylene	60° during 12 min then 4°/min		2.77	2.67
6 Isopropylbenzene	60° during 12 min then 4°/min		3.08	2.89
7 1,3,5-Trimethylbenzene	60° during 12 min then 4°/min		4.31	3.56
8 1,2,4-Trimethylbenzene	60° during 12 min then 4°/min		5.08	3.17
9 Paracymene	60° during 12 min then 4°/min		5.15	3.83
10 *tert.*-Butylbenzene	60° during 12 min then 4°/min		5.38	4.28
11 Isobutylbenzene	60° during 12 min then 4°/min		5.84	4.66
12 1,3-Diethylbenzene	60° during 12 min then 4°/min		6.46	5.00
Cis and trans-isomers				
2 *trans*-Decalin	110° then 4°/min		1	1
1 *cis*-Decalin	110° then 4°/min		0.89	0.90
2 *trans*-Isoeugenol	120° then 4°/min		1	1
1 *cis*-Isoeugenol	120° then 4°/min		0.73	0.74
Polyaromatics				
1 Naphthalene	110° then 4°/min		1	1
2 2-Methylnaphthalene	110° then 4°min		1.45	1.41
3 1-Methylnaphthalene	110° then 4°/min		1.53	1.47
4 Acenaphtene	110° then 4°/min		4.10	3.14
5 Fluorene	110° then 4°/min		4.16	3.28
6 *trans*-Stilbene	110° then 4°/min		4.43	3.43
7 Anthracene	110° then 4°/min		4.63	3.57
8 Phenanthrene	110° then 4°/min		4.63	3.75

(*Continued on p.* 250)

Table 2 (*continued*)

Compounds	Temperature (°C)		Relative retention times	
	LC_1	LC_2	LC_1	LC_2
Halogen compounds				
1 *m*-Dichlorobenzene	100° during 10 min then 4°/min		1	1
2 *o*-Dichlorobenzene	100° during 10 min then 4°/min		1.22	1.19
3 1,3-Dichloropropanol 2	100° during 10 min then 4°/min		2.38	2.27
4 1-Bromo-3-chloropropanol 2	100° during 10 min then 4°/min		2.84	2.59
5 1,3-Dibromopropanol 2	100° during 10 min then 4°/min		3.16	3.08
Volatile aromatic compounds				
1 α-Pinene	120° then 4°/min	110° then 4°/min	0.32	0.36
2 β-Pinene	120° then 4°/min	110° then 4°/min	0.42	0.42
3 Eucalyptol	120° then 4°/min	110° then 4°/min	0.53	0.48
4 Limonene	120° then 4°/min	110° then 4°/min	0.53	0.48
5 Camphor	120° then 4°/min	110° then 4°/min	0.68	0.54
6 Linalol	120° then 4°/min	110° then 4°/min	1	1
7 Linalyl acetate	120° then 4°/min	110° then 4°/min	1.05	1.40
8 Nerol	120° then 4°/min	110° then 4°/min	1.18	1.44
9 Eugenol	120° then 4°/min	110° then 4°/min	1.21	1.52
10 Geranyle acetate	120° then 4°/min	110° then 4°/min	1.34	1.80
11 α-Cedren	120° then 4°/min	110° then 4°/min	1.45	1.65
12 *cis*-Isoeugenol	120° then 4°/min	110° then 4°/min	1.47	1.88
13 Geraniol	120° then 4°/min	110° then 4°/min	1.50	1.64
14 β-Cedrene	120° then 4°/min	110° then 4°/min	1.55	1.72
15 *trans*-Isoeugenol	120° then 4°/min	110° then 4°/min	2.00	2.34
16 Estragole	120° then 4°/min	110° then 4°/min	2.34	2.08
17 Thymol	120° then 4°/min	110° then 4°/min	2.39	2.28
18 Carvacrol	120° then 4°/min	110° then 4°/min	2.53	2.40
19 Anethole	120° then 4°/min	110° then 4°/min	2.63	2.48

The numbers given before each product refer to their elution order in the LC_1 phase as shown for some of them in Figs. 3–6

aromatic compounds from Meyreau-Boiveau (France).

2.2. Apparatus

Thermal analysis measurements were made using a GA 44 Mettler DSC apparatus. A HP 5730A gas chromatograph equiped with dual flame ionization detector and split/splitless injector was used with a single-channel HP 7130A recorder. High-purity nitrogen was used as carrier gas. Each glass capillary column was made of borosilicate glass (35 m×0.25 mm I.D.). After etching according to the method of Rijks et al. [20], the capillary was deactivated with Carbowax 20M and coated dynamically with a solution of 10% of the liquid crystals dissolved in dichloromethane. The column was then conditioned overnight at 10°C above the nematic-isotropic transition temperature.

3. Results and discussion

3.1. Thermal characteristics of LC_1 and LC_2

The different phase transitions of LC_1 and LC_2 compounds were determined by DSC and their corresponding temperatures are listed in Table 1. The two liquid crystals exhibit a solid–solid phase transition ($K_1 \rightarrow K_2$) and a nematic phase within a large temperature range. Thermograms of the two liquid crystals are shown in Fig. 2.

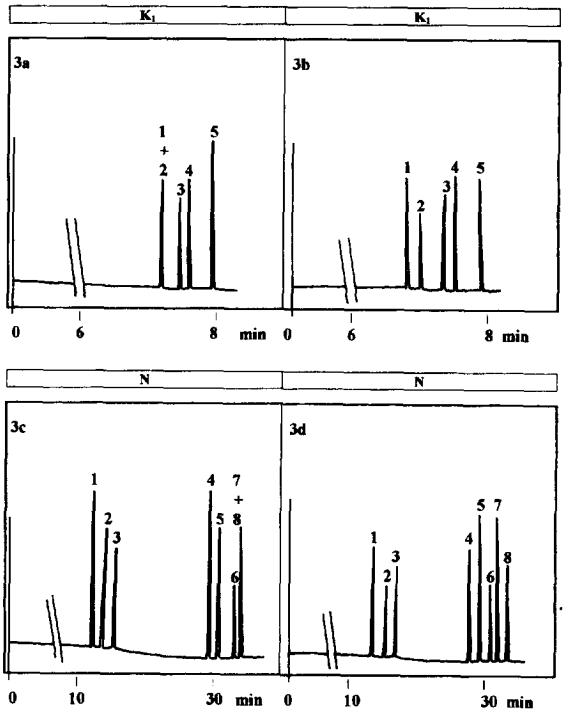

Fig. 3. Typical analytical performances of LC_1 and LC_2. Separation of positional isomers of nonanes in the solid state K_1 using LC_1; column temperature: 50°C (3a) and LC_2; column temperature: 60°C (3b). 1: 2,3,5-trimethylhexane. 2: 2,2,4-trimethylhexane. 3: 3-methyloctane. 4: 2-methyloctane. 5: *n*-nonane. Polyaromatics separation in the nematic phase (N) using LC_1 (3c) and LC_2 (3d); column temperature: programmed from 110° at 4°C/min. 1: naphthalene. 2: 2-methylnaphthalene. 3: 1-methylnaphthalene. 4: acenaphtene. 5: fluorene. 6: *trans*-stilbene. 7: anthracene. 8: phenanthrene.

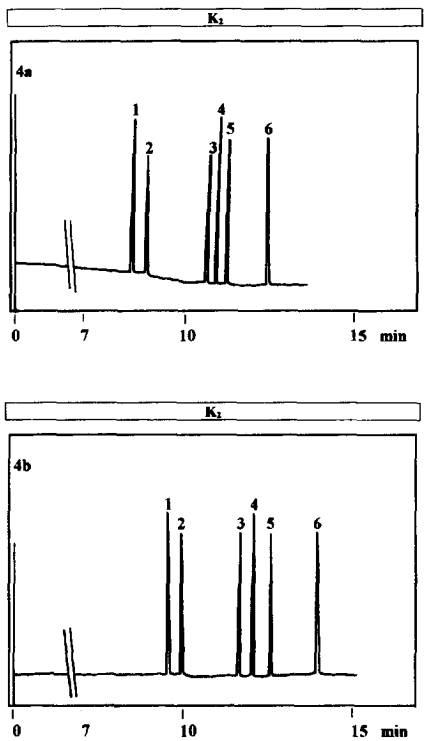

Fig. 4. Analytical performances in the solid state K_2 of LC_1 (a) (column temperature 90°C) and LC_2 (b) (column temperature 105°C). 1: *cis*-2-hexen-1-ol. 2: *cis*-3-hexen-1-ol. 3: 5-methyldodecane. 4: 4-methyldodecane. 5: 2-methyldodecane. 6: *n*-tridecane.

3.2. Comparative analytical applications of the two liquid crystals

In our opinion, parts A and B in the structures (Fig. 1a and b) explain the differences and the similarities between LC_1 and LC_2. In Table 2, relative retention times were preferred to retention times or more complex presentations [17]. Briefly, the characteristics of LC_1 and LC_2 are listed below.

3.3. Differences

LC_2 shows a higher separation ability with alkanes, aromatics and polyaromatics, probably due to the last aromatic ring and the lateral alkoxy chain in part B (see Fig. 1a and b). Fig. 3a and b indicate that 2,3,5- and 2,2,4-trimethylhexane are well separated only on LC_2.

Another difference between LC_1 and LC_2 is shown in Fig. 3c and d. Phenanthrene and anthracene which appeared in one peak on LC_1 are separated into two peaks on LC_2.

In Fig. 5a and b and Table 2, we see that LC_2 succeeded in separating xylene isomers while LC_1 is not able to differentiate between *m*- and *p*-xylene.

Some other minor differences are observed in the elution orders of the following solutes: (i) 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene are eluted in this order on LC_1 and in the reverse order on LC_2; (ii) geraniol is eluted before geranyl acetate on LC_2 and after it on LC_1. Other differences in elution order can be seen in Fig. 6a and b.

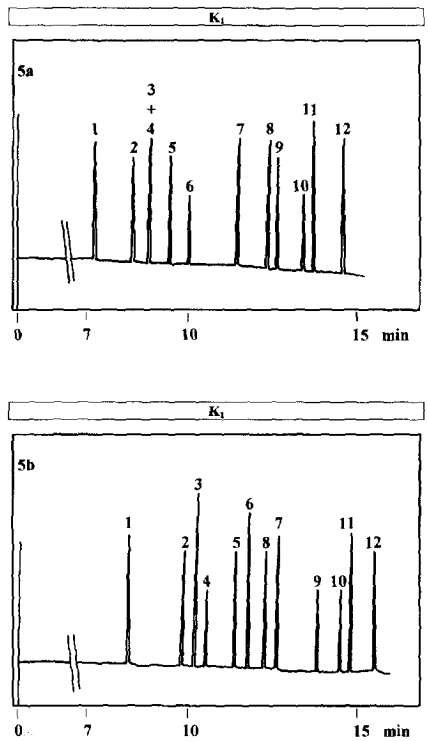

Fig. 5. Separations of aromatic hydrocarbons on LC_1 (5a) and LC_2 (5b); column temperature: isotherm at 60°C during 12 min then 4°C/min. 1: toluene. 2: ethylbenzene. 3: *m*-xylene. 4: *p*-xylene. 5: *o*-xylene. 6: isopropylbenzene. 7: 1,3,5-trimethylbenzene. 8: 1,2,4-trimethylbenzene. 9: paracymene. 10: *tert.*-iobutylbenzene. 11: isobutylbenzene. 12: 1,3-diethylbenzene.

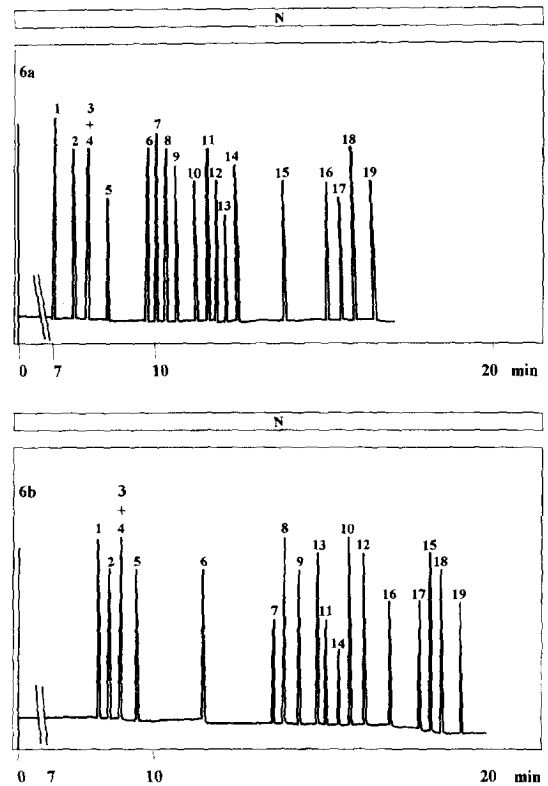

Fig. 6. Separation of volatile aromatic compounds. 6a: LC_1. Column temperature: programmed from 120°C at 4°C/min. 6b: LC_2. Column temperature: programmed from 110°C at 4°C/min. 1: α-pinene. 2: β-pinene. 3: eucalyptol. 4: limonene. 5: camphor. 6: linalol. 7: linalyl acetate. 8: nerol. 9: eugenol. 10: geranyle acetate. 11: α-cedrene. 12: *cis*-isoeugenol. 13: geraniol. 14: β-cedrene. 15: *trans*-isoeugenol. 16: estragole. 17: thymol. 18: carvacrol. 19: anethole.

3.4. Similarities

Plates number of the capillary columns packed with the two liquid crystals are comparable, largest values are found in the nematic phase (Table 3).

The two liquid crystals exhibit a satisfactory separation ability below solid–solid or solid–nematic temperature transition. For example, nonanes are well separated at 50°C on LC_1 and at 60°C on LC_2

Table 3
Plates number of LC_1 and LC_2 in the solid, nematic and isotropic phases

Liquid crystal	State	Solute	Retention temperature (°C)	Plate number/m
LC_1	Solid	*n*-Nonane	60	2620
	Nematic	*n*-Tridecane	120	3100
	Liquid	*trans*-Stilbene	280	2510
LC_2	Solid	*n*-Nonane	60	2815
	Nematic	*n*-Tridecane	120	3200
	Liquid	*trans*-Stilbene	250	2620

(Fig. 3a and b). Light aromatics are well resolved at 60°C on both LC_1 and LC_2 (Fig. 5a and b). Solid-phase K_2 also allows the separation of tridecane isomers, *cis*-2-hexen-1-ol and *cis*-3-hexen-1-ol using LC_1 (Fig. 4a) or LC_2 (Fig. 4b).

Because of the large temperature range of their nematic phase, LC_1 and LC_2 separate a large variety of alkanes having from 9 to 20 carbon atoms (Table 2).

Chromatographic behaviour of the two liquid crystals are comparable in different fields, particularly in the separation of volatile aromatic isomers (Table 2, Fig. 6) such as thymol–carvacrol, estragole–anethole, eugenol–isoeugenols, α- and β-pinene and α- and β-cedrene.

It is known that estragole and anethole are eluted before thymol and carvacrol on polyethylene glycol [27]. With the two liquid crystals (Fig. 6, Table 2), elution order is estragole, thymol, carvacrol and finally anethole. It seems that the double bond conjugated with the aromatic ring present in anethole is preferentially retained over the aromatic ring with protruding polar oxygen present in thymol [28]. The elution order is more complex when the two phenomena (conjugated double bonds and protruding oxygen) are present, for example *trans*-isoeugenol is eluted before thymol and carvacrol on LC_1 and in-between on LC_2. But *trans*-isoeugenol is always eluted before anethole (Table 2, Fig. 6a and b).

Interesting separations are obtained for *cis–trans* isomers. In Table 2, we report the relative retention times of *cis*- and *trans*-decalin and those of *cis*- and *trans*-isoeugenol. The two columns elute *trans*- before *cis*-isomers.

4. Conclusion

The separation properties of the two liquid crystals can be summarized as:

1. LC_1 and LC_2 are convenient stationary phases in order to separate different kinds of solutes such as alkanes, aromatics, polyaromatics isomers, volatile aromatic compounds and halogen compounds.
2. LC_1 and LC_2 exhibit interesting separation properties in the solid state as well as in the nematic state.

Because they contain the same part A in their structures, LC_1 and LC_2 present similarities in the separation of (i) positional isomers of alkanes, aromatics, polyaromatics and volatile aromatic compounds, (ii) some geometrical isomers.

The variation in part B of their structures explains the differences in the separation abilities of LC_1 and LC_2. It appears that the introduction of an aromatic ring and a lateral alkoxy chain in part B, leads to better analytical performances for LC_2. Indeed LC_2 achieved the separation of xylenes, positional nonane isomers, anthracene and phenanthrene where LC_1 did not.

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