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Preparationand Thermodynamic Behaviourof New Nematic Sulphur-Containing Liquid Crystal

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Abstract: In the last few years, liquid crystalswere used as stationary phases in gas chromatography for the separation of close-boiling isomers.In this paper new nematic liquid crystalbased on Schiff basewasprepared by the condensation between amino group of 4-(5-(ethylthio)-1,3,4-oxadiazole-2-yl)aniline and the aldehyde group of para-methoxybenzaldehyde. In summary, a facile and high yielding synthesis of liquid crystal (6) has been developed. Utilization of the liquid crystal as stationary phase in gas chromatography, results confirmed that this liquid crystal has the ability to separate many of close-boiling and geometrical isomers, such as benzene derivatives, ionone and decaline, through the nematic phase. This work forms the basis of the design of new liquid crystals stationary phases for analytical purposes and related applications.

Key words: Gas chromatography, liquid crystal, nematic phase, stationary phase

INTRODUCTION

A liquid crystal is a state of matter neither liquid nor crystal but a state inbetween(Van Hecke *et al*. 2005). Liquid crystals are often called mesophases after the Greek (μεσος) mesos for middle (Chandrasekhar, 1992; de Gennes, 1993). A crystal is a collection of molecules (or atoms) positioned and oriented in space in a regular and repeated manner. An ordinary liquid is a collection of molecules neither positioned nor oriented in any regular manner. Normally when a crystal melts it forms an ordinary liquid phase without order, that is, isotropic. However, a substance that exhibits liquid crystalline behaviour “melts” at least twice, first into the liquid crystalline (LC) or mesophase, and second into the ordinary liquid (Chandrasekhar, 1994).

All molecules in a mesophase orient with respect to each other and, in certain types of liquid crystals, further exhibit some regular position with respect to each other. Thus, mesophases are described by degrees of orientational and positional order. Using ordering as a basis, liquid crystals fall into two types: nematic and smectic. A nematic mesophase possesses only orientational order while smectic mesophases possess orientational and some positional order(Chandrasekhar, 1994). The general structure of LC (Figure 1) consists of two or more central rings (almost aromatic) A_1, A_2, and these rings are bonded directly to one another or connected by linking groups X like: azo, ester, imine.....

Many of LCs have terminal substituents R_1, R_2 like: alkyl, alkoxy, nitro, amino,….(Gray, 1976).

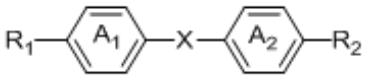

Fig. 1: General structure of Liquid Crystal

Liquid crystalline behaviour of an organic compound is essentially dependent on its molecular architecture, in which a slight change in its molecular geometry brings about considerable changes in its mesomorphic properties. Detailed studies by liquid crystal researchers have led to empirical rules, one of which includes the effect of the chemical constitution in the formation of nematogenic and smectogenic mesophases (Gray, 1962).

Most of these studies focus mainly on Schiff’s bases since the discovery of 4-methoxybenzylidene-4'-butylaniline which exhibited a nematic phase at room temperature (Kelker and Scheurle, 1969).

Methods for the preparation of liquid crystals and their utilization as stationary phases in gas chromatography columns have been developed (Berdagué, 1995; Judeinstein, 1999; Bélaïdi, 2003).In 1963 KELKER was the first who used para.para-azoxyphenetol as stationary phase in gas chromatography for separating the hydrocarbons isomers. While many studies confirmed that nematic phases of LCs have higher efficiency in the separation of isomers from the other phases of liquid crystals(Habboush *et al*. 1991).

BENALIA, *et al*., (2003) was mentioned that LC monomer (I) was used in GC as stationary phase. Results gave that this kind of nematic LC had an efficacy of separating isomers.

So it could be argued that 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 solvent

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properties are due to the rod-like shape and the ordered arrangement of their molecules.

Thus the possibility of using the ordered LC structures for analytical purposes was realized some years ago and it was suggested that the best separation and column efficiency would be obtained in a nematic phase (Haky and Muschik, 1981). Kelker (1963) first recognized that mesophases should provide good separation of geometric isomers and resolved all three xylene isomers.

Since then, mesophases have been widely applied to a wide range of separations (Janini, 1979; Witkiewicz, 1979; Witkiewicz, 1989) include separations of benzene isomers, alkanes, alkenes, heterocycles, polyaromatic hydrocarbons, polychlorinated biphenyls and benoxaprofen isomers, as reviewed by Witkiewicz and Mazur (Witkiewicz and Mazur, 1989).

In order to examine the physicochemical properties of a wide range of systems including polymers (Ward, 1989; Guillet *et al*. 2000), Inverse gas chromatography (IGC) has been used.While it is a dynamic method, it was shown some years ago that measurements recorded under the correct conditions could give accurate equilibrium thermodynamic information (Ashworth, 1984; Summers, 1972).The retention of an extremely small amount of a solvent or ‘‘probe’’ molecule in the stationary phase is recorded and the measurements being made effectively at infinite dilution of the probe. Parameters such as activity coefficients, enthalpies and entropies of a solution can then be calculated.

The basis of the IGC is the recording, under accurately controlled conditions, of the specific retention volume, V^O_g, the volume of a carrier gas at standard temperature and pressure needed to elute a probe molecule from the column per gram of stationary phase (Conder and Young, 1978).

Isothermal operation allows determination of thermodynamic parameters such as activity coefficients and interaction parametersand investigation of the chemical nature of polymeric surfaces (Patterson *et al*. 1971).

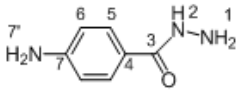
For this aim, this paper has achieved preparation of new nematic LC based on Schiff base. This new nematic LCwas used as stationary phase in GC andgave best efficacy of separating isomers.

MATERIALS AND METHODS

Synthesis And Characterization:

All reagents and solvents were supplied by Aldrich and used as received without further purification if not stated otherwise. The purity of the compounds was established by ^{1}H- and ^{13}C NMR spectroscopy, infrared spectroscopy. The ^{1}H- and ^{13}C NMR were recorded on a MERCURY 400 (400 MHz) instrument using DMSO-d6 as the solvent. The δ values in parts per million (ppm) are relative to external standard TMS. Infrared spectra were obtained on a Jasco-300E-FTIR spectrophotometer operating in the 4000-600 cm^{-1} region using KBr discs. Melting points were measured with Stuart SMP3. Spectroscopic data were compared with typical spectral data (Pretsch, 2009).

4-aminobenzoic hydrazide (2):

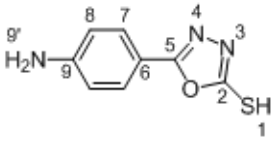


(2)

Ethyl 4-aminobenzoate (1) (9.9 g, 0.06 moles) and Hydrazine hydrate (30 mL) dissolved in an absolute EtOH (25 mL), were refluxed for 5 hours. After being cooled to room temperature, a white crystal participate **(2)** is formed with (6.68 g, 67.48%) yield. 1-H NMR (DMSO-d6), 4.27 (2 H, s, NH_2-NH), 5.55 (2 H, s, C-NH_2), 6.49-7.53 (4 H, dd, $J_{1,2}$ 8, $J_{1,2}$ 8, H-5, H-6), 9.24 (1 H, s, NH-NH_2). 13-C NMR (DMSO-d6), 112.6 (2C, C-6), 119.95 (1C, C-4), 128.4 (2C, C-5), 151.5 (1C, C-7), 166.48 (1C, C-3)

IR, ν_{max}/cm^{-1}: 3234, 3345.8, 3426.8 (-NH_2, NH Hydrazide), 1603.5 (CO-NH). mp 222.8 ºC.

5-[4-amino phenyl] 1,3,4-oxadiazole -2- thiol (3):



(3)

4-aminobenzoic hydrazide**(2)** (3.0 g, 0.02 moles) was dissolved in an absolute EtOH (20 mL) and cooled to 0°C.

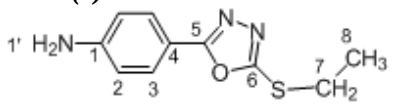
A solution of Potassium hydroxide (1.5 g, 0.027 moles) in absolute EtOH (10 mL) was added, the mixture stirred for 15 min, then CS_2 (1.21 mL, 0.02 moles) was added dropwise. The reaction was stirred for a further 7 hours under reflux. Solvent was removed by rotary evaporator. The resulting solid was dissolved in cold water

(25 mL) and acidified with 10% HCl until participation of light yellow crystals **(3)** with (1.8 g, 60%) yield.

1-H NMR (DMSO-d6), 6.00 (2 H, bs, NH_2), 6.63-7.52 (4 H; dd, $J_{1,2}$ 8, $J_{1,2}$ 8, CH; Ar). 13-C NMR (DMSO-d6), 108.4 (1C; C-6), 113.5 (2C; C-8), 127.6 (2C; C-7), 152.6 (1C; C-9), 161.57 (1C; C-5), 176.54 (1C; C-2)

IR, ν_{max}/cm^{-1}: 3349.7, 3424.9 (-NH_2), 2769.2 (SH). mp 240-244 ºC.

4-(5-(ethylthio)-1,3,4-oxadiazole-2-yl)aniline (4):



(4)

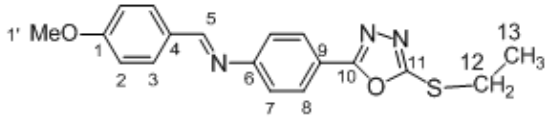
5-[4-amino phenyl] 1,3,4-oxadiazole-2-thiol **(3)** (3.0 g, 0.016 moles) and Potassium hydroxide (2.74 g, 0.042 moles) dissolved in absolute EtOH (30 mL), were refluxed for half an hour. After being cooled to room temperature, bromoethyl (1.2 mL, 0.016 moles) was added carefully via a syringe. The reaction was stirred for further three hours under reflux. The solvent was removed *in vacuo* and the residue poured into cold water to obtain a white solid **(4)** (2.26 g, 75.3%).

1-H NMR (DMSO-d6), 1.36-1.39 (3 H, t, $J_{1,2}$7.2, H-8), 3.21-3.27 (2 H, q, $J_{1,2}$ 7.2, H-7), 5.91 (2 H, s, NH_2), 6.64-6.66 (2 H, d, $J_{1,2}$ 8.8, 2H-2), 7.58-7.60 (2 H, d, $J_{1,2}$ 8.8, 2H-3).

13-C NMR (DMSO-d6), 14.90 (1C; C-8), 26.63 (1C; C-7), 109.38 (1C; C-4), 113.52 (2C; 2C-2), 127.86 (2C; 2C-3), 152.31 (1C; C-1), 161.40 (1C; C-6), 165.86 (1C; C-5)

IR, ν_{max}/cm^{-1}: 2960 (CH, aliphatic), 1630.5 (C=N, oxadiazole), 1114.6 (C-O, oxadiazole). mp 98 ºC.

1-[4-methoxy benzylidene amino]-4-[2-ethylthio-1,3,4-oxadiazole-5-yl] benzene (6):



(6)

(500 mg, 2.26 mmoles) of **(4)** and *para*-methoxy benzaldehyde **(5)** (313.9 mg, 2.26 mmoles), were dissolved in absolute EtOH (10 mL) and glacial acetic acid (1 mL). The reaction mixture was refluxed for three hours with stirring before it was filtered. The solvent was removed from the filtrate by evaporation. The yellowish solid of liquid crystal **(6)** thus obtained was recrystallized from ethanol till the constant transition temperatures were obtained (401.5 mg, 80.3%).

1-H NMR (DMSO-d6), 1.40-1.43 (3 H, t, $J_{1,2}$ 7.2, H-13), 3.28-3.32 (2 H, q, $J_{1,2}$ 7.2, H-12), 3.84 (3 H, s, H-1'), 7.07-7.09 (2 H, d, $J_{1,2}$ 8.4, 2H-2), 7.38-7.40 (2 H, d, $J_{1,2}$ 8.4, 2H-7), 7.90-7.92 (2 H, d, $J_{1,2}$ 8.4, 2H-8), 7.96-7.99 (2 H, d, $J_{1,2}$ 8.4, 2H-3), 8.58 (1 H, s, H-5; imine).

13-C NMR (DMSO-d6), 14.90 (1C; C-13), 26.69 (1C; C-12), 55.46 (1C; C-1'), 114.36 (2C; 2C-2), 119.93 (1C; C-9), 121.97 (2C; 2C-7), 127.53 (2C; 2C-8), 128.59 (1C; C-4), 130.87 (1C; C-5; imine), 154.73 (1C; C-6), 161.48 (2C; 2C-3), 162.31 (1C; C-1), 163.47 (1C; C-11), 164.98 (1C; C-10).

IR, ν_{max}/cm^{-1}: 2800-2960 (CH, aliphatic), 1594.5 (C=N, oxadiazole), 1566.0 (CH=N, imine), 1245.2 (CH3-O), 1165.5 (C-O, oxadiazole). mp 125.9 ºC.

Differential Scanning Calorimetry (DSC) Analysis:

Differential scanning calorimetry measurements were made on a DSC-7 model Perkin Elmer apparatus equipped with an electronic computer TADS (thermal analysis dated station) with a heating rate of 20 °C min^{-1}.

Inverse Gas Chromatography:

Chromatographic measurements were performed on an Auto System XL Perkin Elmer gas chromatography equipped with:

–A split-splitless manual injector at 250 °C, in split mode (split ratio: 50)

–A flame ionization detector at 250 °C

–A Perkin Elmer Nelson model 1022 integrator

–An OkidataMicroline 320 printer

–Argon as the carrier gas.

The probe molecules were of analytical grade or better and were obtained from commercial sources. The injections were performed isothermally with temperature intervals of 2 °C from 100 to 170 °C.

The experimental gas chromatography conditions are listed below:

– Injector temperature: 250 °C

– Detector temperature: 250 °C

– Carrier gas: argon with a flow rate of 1.45 mL min^{-1}

– Hydrogen flow rate: 25 mL min^{-1}
– Air flow rate: 250 mL min^{-1}
– Pressure inlet: 4.8 psi

The theoretical plates numbers calculated for the capillary column packed with the synthesized liquid crystal **(6)** are comparable, largest values are found in the nematic phase (Table 2).

Table 2: The theoretical plates of liquid crystal (6)

Column	Phase	Solute	Temperature (°C)	N (plates/m)
LC (6)	Solid(S)	1,3-diethylbenzene	55	2600
	Nematic (N)	Ethyl phenol	115	3250
	Isotropic (I)	Bromonaphtalene	170	3050

Column Preparation:

The glass capillary column was made of borosilicate glass. It was coated by the method known as ''dynamic technique'' used for the impregnation of the stationary phase on the inner glass wall.

After treatment of the internal glass surface by sodium chloride deposit, this wall was then deactivated by polyethylene glycol impregnation (PEG) then conditioned by heating. The stationary phase was then impregnated on the internal wall of the column by flushing of a solution of the liquid crystal **(6)** in dichloromethane under nitrogen pressure. The solvent (dichloromethane) was then evaporated and finally the column was conditioned during 8 h in the gas chromatograph oven from 60 to 175°C with a heating rate of 2 °C min^{-1}. The optimum flow-rates for this column were determined by plotting the Van Deemter curve.

Inverse gas chromatography has been used to study phase transitions for the liquid crystal **(6)**. This method has shown that transition temperatures between the entire mesophase can be detected and their temperatures measured with an accuracy and precision comparable to that of more conventional techniques.

The used column has dimensions of 30 m length and 0.25 mm internal diameter.

RESULTS AND DISCUSSION

A facile, high yielding synthesis of liquid crystal (**6**)has been developed. Reaction paths have shown in Scheme **1** usingEthyl 4-aminobenzoate **(1)**the starting material. The desired liquid crystal is formed directly when the amino group of 4-(5-(ethylthio)-1,3,4-oxadiazole-2-yl)aniline **(4)**is condensate with the aldehyde group of para-methoxy benzaldehyde**(5)**.

All the compounds were purified by crystallization from ethanol, and characterized from their FTIR, NMR. Spectral data of all compounds were in good agreement with their structures, indicating the high purity.

4-aminobenzoic hydrazide**(2)** was synthesized in agreement with the procedure reported earlier (Kömürcü *et al*. 2003). The position of the amide group was confirmed by FTIR spectrum at 1603.5 cm^{-1}. The ^{1}H NMR of product **(2)** shows new peaks related with hydrazide group protons at [δ (NH_2) = 4.27 ppm, δ(NH) = 9.24 ppm].

The structural features associated with the formation of the oxadiazole ring moiety in **(3)**appear clearly in FTIR spectrum from the presence of two bands C=N, C-O at 1684.5, 1172.5 cm^{-1} respectively (Zamani, 2003), while^{13}C NMR spectrum showed new peaks corresponding to C-SH, C=N at 176.54, 161.57 ppm respectively. ^{13}C NMR spectrumwas confirmed the expected structure of (**4**).The reaction of **(4)** with para-methoxybenzaldehyde**(5)** gave the expected Schiff base**(6)** (Yeap *et al*. 2006).Thisliquid crystal **(6)** was submitted to FTIR and NMR analyses, revealed the presence of -CH=N- double bond ($\upsilon_{(CH=N)}$ 1566.0 cm^{-1};$\delta_{(C\underline{H}=N)}$ = 8.58 ppm, $\delta_{(\underline{C}H=N)}$ = 130.87 ppm), wherefore NMR analysis method showed high purity of the reaction product**(6)**.

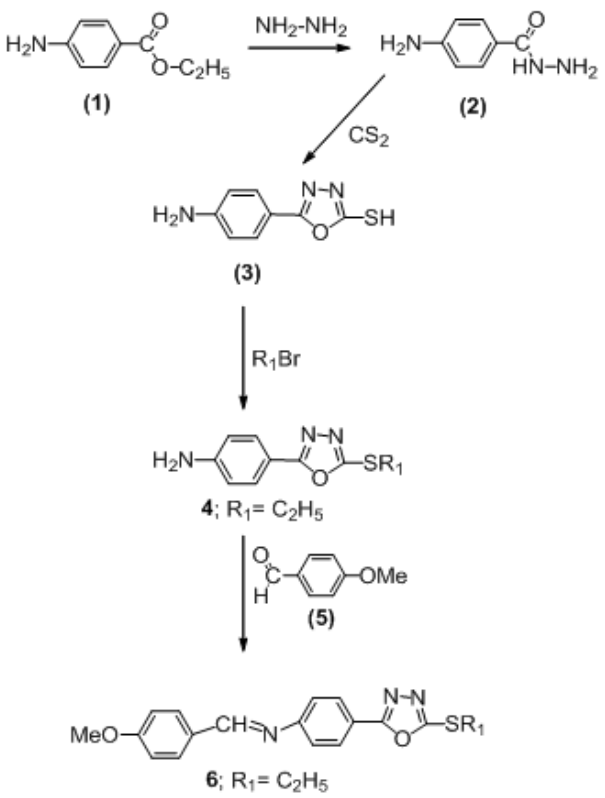
In the HMQC-NMR spectrum of **(6)**, one distinct correlation is shown. The carbon resonance at δ = 130.87 ppm, which corresponds to an imine function, correlates with one proton at δ = 8.58 ppm. This interaction is the imine carbon and its attached imine proton.

Thermal Properties Of Liquid Crystal (6):

Table (1) shows the characteristic parameters of the liquid crystal **(6)** phase transitions. Only the heating data of Differential scanning calorimetry (DSC) measurements are presented (Figure 2). During the heating, the *Solid (S) – Nematic (N)* phase transition occurs at 116 °C and the *(N) – isotropic liquid (I)* phase transition occurs at 132 °C, in this case, the nematic mesophase exists in 16 °C temperature interval. The analysis of the data reveals that there are no significant differences between the data of DSC and gas chromatography.

Table 1: Phase transition temperatures of liquid crystal (6)

Temperature (T/ °C)		Transition
DSC	GC	
116	118	Solid (S)→Nematic (N)
132	130	Nematic (N)→Isotropic (I)



Scheme 1: Synthesis of liquid crystal (6)

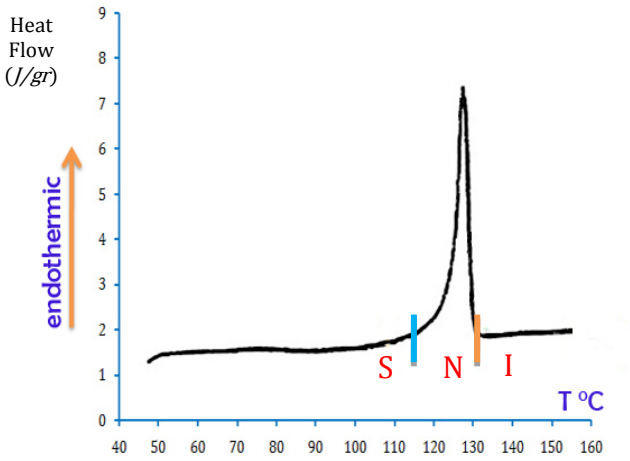


Fig. 2: DSC thermogram of liquid crystal (6)

Data Reduction:

The primary datum in IGC is the specific retention volume $V_g°$, the volume of the carrier gas at standard temperature and pressure (STP) per gram of stationary phase required to elute the probe (Ward *et al*. 1989),this is related to the probe retention time by equation:$\boldsymbol{V_g^\circ = F(t_r - t_m)/w}$

Where $\boldsymbol{t_r}$and $\boldsymbol{t_m}$are the retention times of the solvent and an inert marker, respectively, $\boldsymbol{w}$ is the weight of LC on the column, and $\boldsymbol{F}$ is the flow rate of the carrier gas, corrected to (STP). The flow rate is calculated from equation:

$$F = F'\left(\frac{273.2}{T_f}\right)\left(\frac{P_0}{760}\right)\left(\frac{P_0 - P_w}{P_0}\right)\left(\frac{3[(P_i/P_0)^2 - 1]}{2[(P_i/P_0)^3 - 1]}\right)$$

Where $\boldsymbol{F'}$is the flow rate measured at a flowmeter temperature $\boldsymbol{T_f}$, and atmospheric pressure $\boldsymbol{P_o}$(measured in Torr; 1 Torr =133.3 Pa). Thus, the first three terms of the above equation represent $\boldsymbol{F'}$corrected to (STP), while the last two account, respectively, for the vapour pressure of water in the flow meter, $\boldsymbol{P_w}$and the compressibility of the gas as it passes through the column, $\boldsymbol{P_i}$ being the pressure at the column inlet.

Retention diagrams were recorded for a range of hydrocarbon probes in the LC and examples are shown in Figures 3-6.

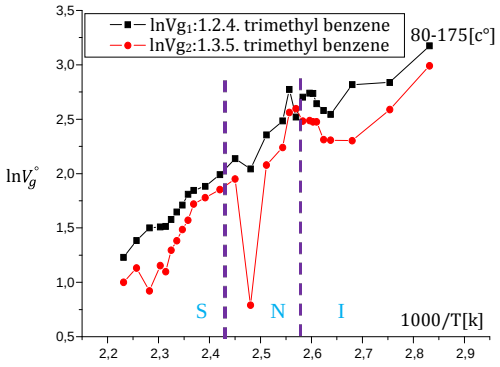


Fig. 3: Retention diagram for probes in LC (6). 1.2.4. trimethyl benzene, 1.3.5. trimethyl benzene

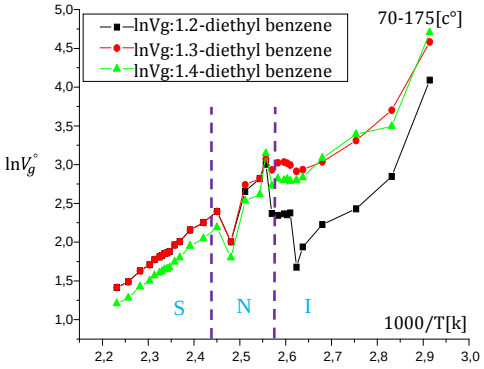


Fig. 4: Retention diagram for probes in LC (6). 1.4-diethyl benzene 1.2-diethyl benzene, 1.3-diethyl benzene,

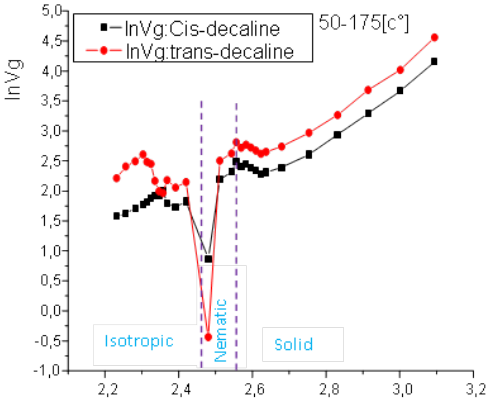


Fig. 5: Retention diagram for probes in LC (6). *cis*-decaline, *trans*-decaline

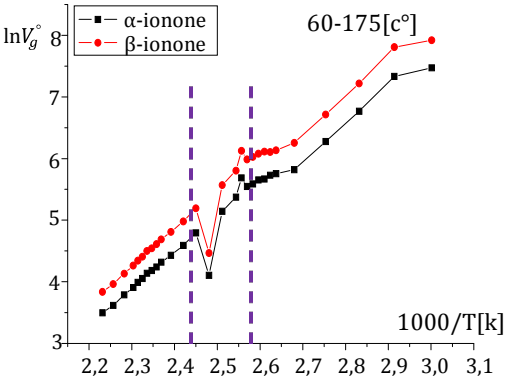


Fig. 6: Retention diagram for probes in LC (6). α-ionone, β- ionone

Each of the diagrams clearly shows the function; $\ln(V_g) = f(1000/T)$and the nematictransition in the results recorded on heating the samples.It can also be that, trimethyl benzene and diethyl benzene derivatives were successfully separated in the nematic phase of the liquid crystal **(6)**. However, it is notable that all of the various mesophase transitions in the accessible temperature range could be seen in the retention.

Analytical Applications:

Benzene Derivatives:

The retention time of the benzene derivatives on the liquid crystal stationary phase depends on the number of methyl substituents, and it is increases with this number; as for trimethylbenzene following the same order of their respective boiling points. Also it can be noticed that 1,2,3-trimethylbenzene is more retained in the stationary phase than 1,2,4-trimethylbenzene.Whereas the geometrical isomers such as 1,2-diethylbenzene and 1,3-diethylbenzene, the firstone is less retained than thelatter on the column.

Volatile Aromatics Compounds:

α-ionone was separated before it's isomer β-ionone, while *trans*-decaline was more retained than *cis*-decaline in the column.

Generally, IGC could be valuable since a number of other parameters(Kozłowska*et al*. 2005) can be measured in the same experiment, amongst which are thermodynamic properties such as activity coefficients; that yield information on the interactions between the components in the chromatographic system.

Conclusion:

In summary, a facile and high yielding synthesis of liquid crystal (**6**) has been developed. When applying the liquid crystal **(6)** as stationary phase in GC, this liquid crystal has the ability to separate many of close-boiling and geometrical isomers, such as benzene derivatives, ionone and decaline, through the nematic phase of this liquid crystal. Inverse gas chromatography has been used to study phase transitions of this liquid crystalline compound, this technique has shown that thermal transitions between all of the various mesophases can be detected and their temperatures measured with an accuracy and precision comparable to that of more conventional techniques. This work forms the basis of the design of new liquid crystals stationary phases for analytical purposes and related applications.

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