

## Gas Chromatographic Separation of Isomeric Phenols by Schiff's Base Liquid Crystalline Stationary Phases

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### Abstract

The chromatographic behaviour of liquid crystalline compounds 4-(propyloxybenzylidene)-4'-p-aminoazobenzene (1) and 4-(butyloxybenzylidene)-4'-p-aminoazobenzene (2) as stationary phases for the separation of cresol isomers was investigated. These isomers were analysed on 4-(propyloxybenzylidene)-4'-p-aminoazobenzene within a nematic range of 142- 153° C with a temperature interval of 5° C. Better peak resolution was at a column temperature of 147° C. The analysis was repeated on a and 4-(butyloxybenzylidene)-4'-p-aminoazobenzene column at a nematic temperature of 176° C, which represented the end of the nematic range, and gave the optimum peak resolution. It was found that isomer better separation was obtained at 20% loading for both liquid crystal materials. Other columns of different liquid crystalline percentages (15% and 25%) were used. A chromatogram with unoverlapped peaks was only obtained in both cases at 20% column loading. The order of elution isomers under the applied chromatographic conditions is discussed. The separation of these isomers is also discussed on the basis of stereo chemical conformations.

Keywords: Gas chromatography, Stationary phase, Liquid crystals.

### Introduction

Thermotropic liquid crystal have drawn the attention of the chromatographers to be as stationary phases in gas chromatography follows from their unique separating properties, which are due to the structure and ordering of their molecules [1].

At a certain temperature range (from the melting point to the point of transition to the isotropic liquid phase) thermotropic liquid crystal have some degree of orientation molecular ordering, and thus have properties that are intermediate between the solid and the isotropic liquid [2].

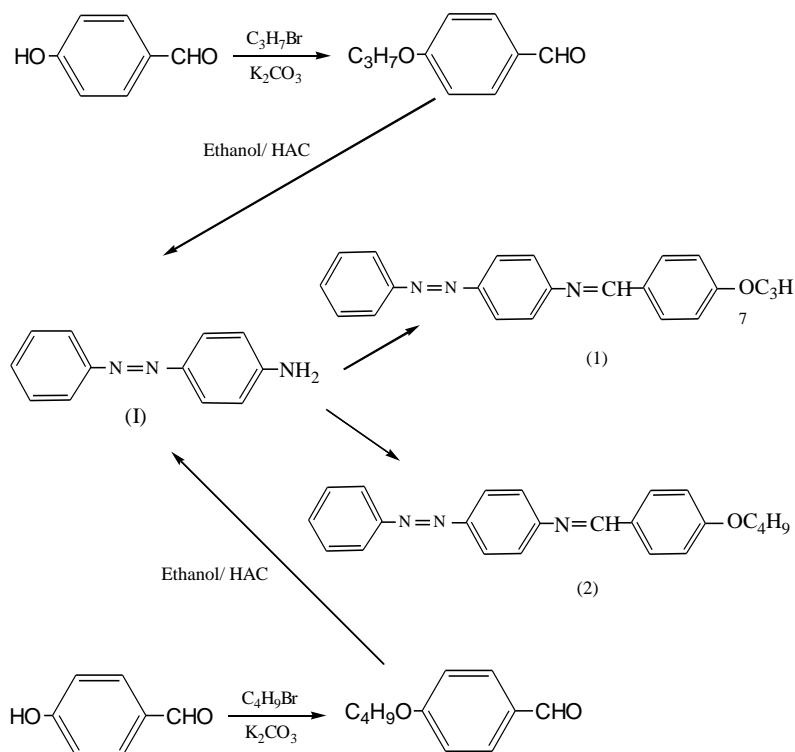
The liquid crystal compounds that are used as stationary phases belong to many chemical-groups such as Schiff bases, azo and azoxy compounds, esters, isothiocyanates, and biphenyl and terphenyl derivatives [3].

These phases can either be monomeric [4] or polymeric [5], the latter being more thermally stable. Elsewhere, the physical and chemical properties of liquid crystal polymers have been studied by various analytical techniques [6, 7]. The retention mechanism on this kind of stationary phases is complex and temperature dependent. In addition to the polarity and the volatility of the solutes, their geometry and molecular structure play a role

in the interactions with the liquid crystalline stationary phase.

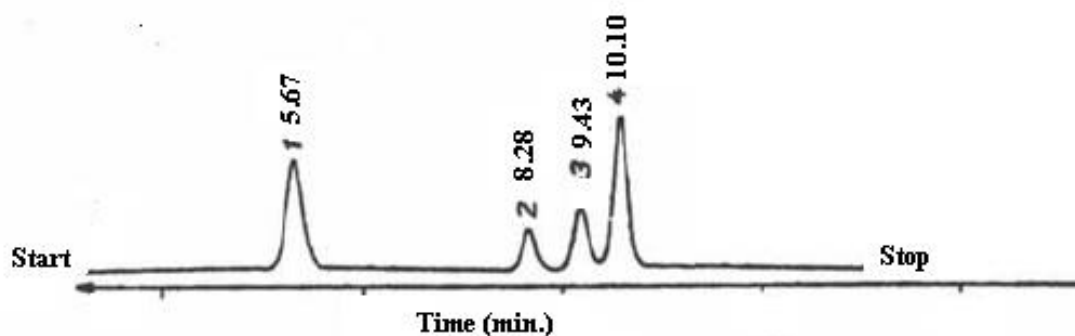
### Experimental

All chemicals and solvents were of analar grade and were used without further purification. A Shimadzu GC-9A gas chromatographer equipped with a flame ionization detector (FID) linked to a data processor (Shimadzu C-R6A) capable of plotting a chromatogram and printing data on the same recording thermal chart paper was used. High purity nitrogen gas (99.99%) was used as a carrier gas. The flow rate was measured with a soap bubble flowmeter. The FID and injector port were maintained at 240° C. Samples of 0.5-1.0 µL were injected into the column by calibrated hypodermic syringes. The nematic liquid crystals 4-(propyloxybenzylidene)-4'-p-aminoazobenzene (1) and 4-(butyloxybenzylidene)-4'-p-aminoazobenzene (2) were prepared according to well-defined procedures for the liquid crystal preparation of the Schiff's base structure Scheme (1).



The identities of the prepared compounds were confirmed by the measurement of their infrared spectra (8300 shimadzo spectrophotometer). The transition temperatures were recorded by hot stage polarized microscope (Meiji MT9000). The preparation of liquid crystalline columns was performed by dissolving the liquid crystalline compound in chloroform and mixing with solid support Chromosorb W/AW (80-100 mesh) for around 2 h. The solvent was removed and the solid residue was dried in an oven. The procedure was repeated for the

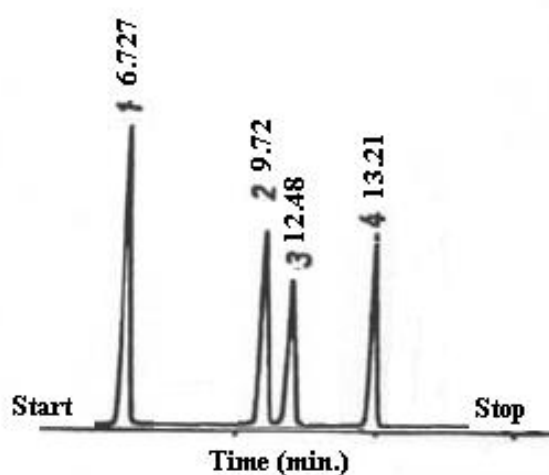
preparation of three loading percentages: 15%, 20% and 25% w/w (liquid crystal: support). Glass columns (2.1 m × 3.2 mm i.d.) were packed with the prepared stationary phases and were conditioned overnight in GC-oven at temperatures 10° C below the melting point of the used liquid crystal with a flow of carrier gas. Samples were injected into the columns at the measured nematic transition temperature ranges with column temperature intervals of 5° C under specified chromatographic conditions (Figs. (1) and (2)).



**Fig. (1) Gas Chromatogram of phenol isomers mixture on 20% 4-(propyloxy- benzylidene)-4'-p-aminoazobenzene Conditions: OvenTemp. = 190° C, Flow rate = 40 mL/min, Det. and Inj. = 240° C. Sample size 1 µL. Peaks: 1 = Ethanol (solvent), 2 = o-cresol, 3 = p-cresol, 4 = m-cresol.**

**Table (1)**  
Adjusted retention times ( $t'_R$  / minute) for mixture A on 20% 4-(propyloxybenzylidene)-4'-p-aminoazobenzene.

Temp.°C \ Comp.	Retention Time ( $t'_R$ / min.)								
	130°C	140°C	150°C	160°C	170°C	180°C	190°C	200°C	210°C
o -cresol	8.660	8.280	7.813	7.447	7.388	7.206	6.922	6.663	6.381
p-cresol	9.791	9.430	8.838	8.389	8.289	7.961	7.641	7.191	6.712
m-cresol	10.721	10.100	9.823	9.165	9.132	8.751	8.331	7.881	7.255



**Fig. (2)** Gas Chromatogram of phenol isomers mixture on 20% 4-(butyloxybenzylidene)-4'-p-aminoazobenzene Conditions: Oven Temp. = 256° C, Flow rate = 30 mL/min, Det. and Inj. = 270° C. Sample size 1  $\mu$ L. Peaks: 1 = Ethanol (solvent), 2 = o-cresol, 3 = p-cresol, 4 = m-cresol.

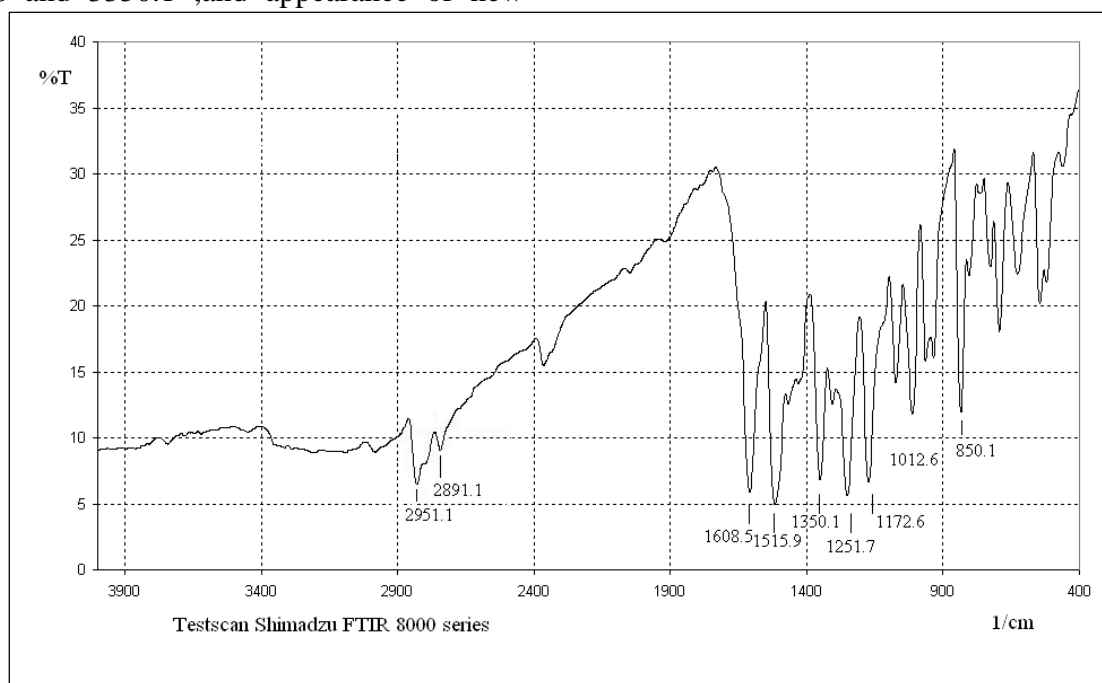
**Table (2)**  
Adjusted retention times ( $t'_R$  / minute) for mixture A on 20% 4-(butyloxybenzylidene)-4'-p-aminoazobenzene.

Temp.°C \ Comp.	Retention Time ( $t'_R$ / min.)								
	140°C	150°C	160°C	170°C	180°C	190°C	200°C	210°C	220°C
o -cresol	9.160	9.051	8.913	8.847	9.720	9.606	9.022	8.874	8.751
p-cresol	13.191	13.012	12.872	12.712	12.481	12.361	12.041	11.891	11.480
m-cresol	14.721	14.337	13.823	13.465	13.210	12.751	12.331	11.881	11.255

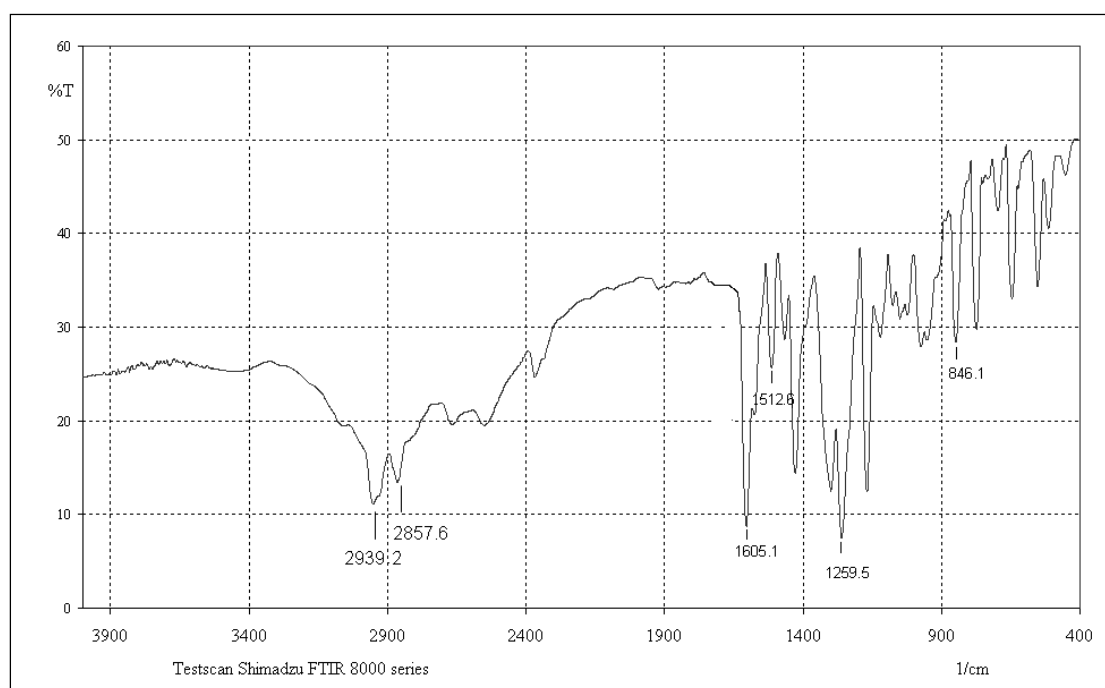
## Results and Discussion

**Synthesis;** the two phases were synthesis according to Scheme (1), the products were characterized using FTIR spectroscopy. The FTIR spectra Fig.(3) and (4) for compounds phase (I) and (II), shows the following characteristic absorption bands, (KBr disc  $\text{cm}^{-1}$ ) : the disappearance of  $\text{NH}_2$  stretching band of amino azo benzene at 3471.6 and 3350.1 ,and appearance of new

band at 1608.5 for  $\text{CH}=\text{N}$  imine group of compound (I) and 1605.1 for compound (II). The spectra also show band at (2951.1, 2891.1, 1608.5, 1515.9, 1350.1 and 850.1) for compound (I) and at (2939.2, 2857.6, 1605.1, 1512.6 and 846.1) for compound (II) for CH aliphatic, N-H bending ,N=N and out of plane bending of P-disubstituted benzene ring respectively.



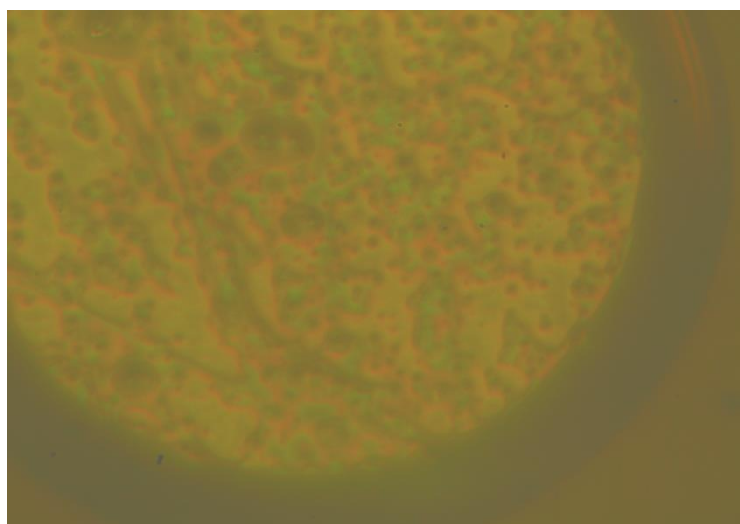
**Fig.(3) FTIR spectrum of 4-(propyloxybenzylidene)-4'-p-aminoazobenzene.**



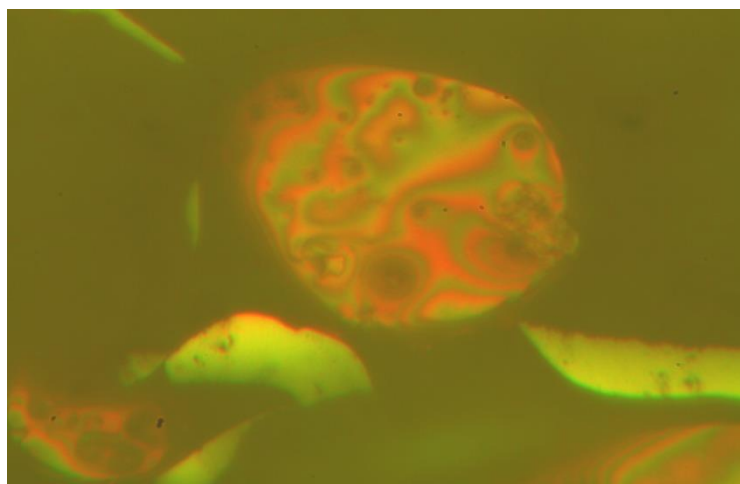
**Fig. (4) FTIR spectrum of 4-(butyloxybenzylidene)-4'-p-aminoazobenzene-  
(butyloxybenzylidene)-4'-p-aminoazobenzene.**

Mesomorphic properties: Nematic liquid crystalline properties of the prepared compounds phases (I & II) were studied using hot stage polarizing microscope. Microscopic

observations of the compounds at liquid crystalline transition temperature displayed a nematic mesophase of typical nematic droplet as shown in Fig. (4 & 5).



*Fig. (4) Nematic texture of phase (I).*



*Fig. (5) Nematic texture of phase (II).*

Gas chromatographic analyses were carried out for a mixture of phenol isomers in ethanol that consisted of o-cresol, m-cresol and p-cresol, by using columns packed first with 4-(propyloxybenzylidene)-4'-p-aminoazobenzene (phase I) and then with 4-(butyloxybenzylidene)-4'-p-aminoazobenzene (phase II). The phenol isomers were analyzed on phase I within the nematic ranges of the liquid crystalline compound 142-153° C with a temperature interval of 5° C. The same analysis was repeated on phase II at a nematic column temperature of 176° C. In both cases the best resolution was obtained from a 20% loading column. On the other hand, better

selectivity for the separation of phenol isomer mixtures was obtained at column temperature 147° C for the liquid crystal phase I (Fig.(1)). The separation by such selectivity at 20% loading could be attributed to the type and quantity of the liquid crystalline compound. The order of elution for these isomers under the applied chromatographic conditions was (1) o-cresol b.p. 191 °C, (2) p-cresol; b.p. 202° C (3) m-cresol ; b.p. 203 °C, (Fig.(1)).

It is clear that the order of elution for these isomers does not depend on their boiling points as is usually expected in ordinary stationary phases [8, 9]. It also seems that the linear and symmetrical molecules are retained

longer on the liquid crystalline column as in *p*-cresol<sup>[10]</sup>. The behaviour of phenol isomers and their order of elution from the column

could also be explained on the basis of stereo conformation.

The selectivity and resolution factors were calculated and are shown in Table (3).

**Table (3)**  
**Selectivity factor ( $\alpha$ ) and resolution  $R_s$  for the mixture on phase (I).**

Compound	Column temp.	Selectivity factor ( $\alpha$ )	Resolution ( $R_s$ )
<i>p</i> -resol / <i>o</i> -cresol	147° C	1.28	1.89
<i>m</i> -cresol / <i>p</i> -resol	147° C	1.20	1.23

Better separation was obtained at the temperature 145°C for phase (I) and 176 for phase (II), this related to the higher order of the liquid crystal stationary phase which makes it easier for molecules of substances are retained stronger and stay longer in the column. As the temperature increase the retention time decrease this arise as the fact that with increase in temperature the order of a liquid crystal decreases which result in a smaller influence of substances which molecules are of the shape hindering their interaction with the structure of liquid crystals of lower order.

The order of elution's of cresol isomers was *ortho*, *para* and *meta*, this could be explained to the ability of the nitrogen atom of imine group to form inter molecular hydrogen bonding.

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**الخلاصة**

تم التحقق من السلوك الكروماتوغرافي للبلورات السائلة ٤- بروبيولكسي بنزلاين-٤-بارا-امينو ازوبنزين (١) و ٤- بيوتلوكسي بنزلاين-٤-بارا-امينو ازوبنزين (٢) كأطوار ثابتة لفصل ايزومرات الكريسول. تم الفصل في درجة حرارة ١٤٢ - ١٥٣ م بالنسبة للطور (١) وتم الحصول على افضل ذروة فصل عند درجة ١٤٧م. تم اعادة التحليل للطور (٢) وتم الحصول على افضل فصل عند درجة ١٧٦° م والتي تمثل نهاية الطور النيماتى. كذلك وجدنا ان افضل فصل للايزومرات هو بنسبة ٢٠% بالنسبة للطور البلورى السائل ومادة الساند (الكروموسورب). تمت مناقشة ترتيب سرعة النزول خلال عمود الفصل بالنسبة للايزومرات وكذلك تأثير الترتيب الفراغى للمركبات.