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Application of Liquid Crystals for Gas-Liquid Chromatography

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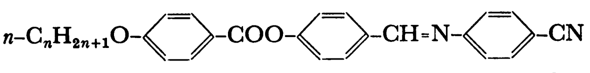
Synopsis. A liquid crystalline homologous series of *N*-[4-(4-alkoxybenzoyloxy)benzylidene]-4-cyanoanilines was applied as a stationary liquid phase for the gas-liquid chromatographic separation of various positional isomers. It is shown that the nematic phase has higher selectivity for several positional isomers compared with the other mesomorphic phases.

Liquid crystals are anisotropic liquids and they exhibit interesting solvent properties due to the rod-like shape and the ordered arrangement of their molecules. These unique solvent properties of liquid crystals were used for the first time as the stationary phase in gas-liquid chromatography (GLC) for the separation of the positional isomers of various disubstituted benzenes.[1] Recently, the separation of various solutes such as polycyclic aromatic hydrocarbons,[2] steroid epimers,[3] and Z/E mixtures of fatty alcohols[4] has been carried out with good success using liquid crystalline stationary phases in GLC.

Most GLC studies reported so far have been made with the use of nematic liquid crystals. However, from the viewpoint of practical application there exists a disadvantage that the use of the nematic stationary phases is confined to their limited mesomorphic temperature ranges. In connection with an attempt to obtain liquid crystals with a wide mesomorphic temperature range the smectic[5,6] and re-entrant nematic phases[7] have been recently applied to the separation of the various positional isomers.

In order to develop GLC using liquid crystals as the liquid phase it seems worthwhile to study the solubility and selective affinity of the various solutes in these different liquid crystalline phases. In this report we describe a study of the separation of some positional isomers in different mesomorphic phases by use of a homologous series of *N*-[4-(4-alkoxybenzoyloxy)benzylidene]-4-cyanoanilines.



(n=7, 9, and 12)

Experimental

Materials. 4-Dodecyloxybenzoic acid was synthesized according to the known method[8] while the other lower homologues were commercially obtained. These 4-alkoxybenzoic acids were converted to acid chlorides by treatment with thionyl chloride, and then esterified by a reaction with 4-hydroxybenzaldehyde in ether solution including triethylamine. Finally, the substituted benzaldehydes formed were coupled with 4-cyanoaniline in ethanol solution. The crude liquid crystals were purified by successive recrystallization from ethanol. The solutes chosen were commercially obtained and used without further purification.

Apparatus and Procedure. The liquid crystalline texture and the transition temperatures were determined by a Nikon polarizing microscope equipped with a Mettler FP 52 microfurnace and control unit. Checks on the transition temperatures were made using a Rigaku differential scanning calorimeter.

The support material employed was 100—120 mesh Chromosorb W HP. The support was coated with the liquid crystalline compounds by using chloroform as solvent, followed by gradual elimination of the solvent by evaporation. The concentration of the liquid phase in the packing of the coated support was 2.5 wt%. The columns were conditioned at 240 °C for 2 h prior to initial use.

A Hitachi 163 gas chromatograph equipped with a flame-ionization detector was used. The flow-rate of the carrier gas (nitrogen) was measured using a soap-bubble flow meter.

Results and Discussion

The transition temperatures and the liquid crystalline phases of the compounds studied are given in Table 1. The C_7 and C_9 homologues have been reported by Weissflog *et al.*[9] and the transition temperatures determined in this study are in good agreement with the published data. The C_7 member exhibits both the smectic A and nematic phases while another liquid crystalline phase, *i.e.*, re-entrant nematic phase is monotropically observed for the C_9 member. As shown in Table 1, the C_{12} homologue exhibits no nematic phase. This is not surprising because the disappearance of the nematic phase is not unusual, and has been frequently observed as the alkoxy chain length increases in other homologous series of liquid crystalline materials.[10]

To estimate the selective affinity of the different liquid crystalline phases toward the various solutes we have measured relative retention(α) of some positional isomers on the liquid crystalline stationary phases. The chosen solute isomers and their relative retention determined in this study are compiled in Table 2.

The separation of *m*- and *p*-xylenes by GLC is a classically difficult one because of their similar boiling points and polarities. However, it should be stressed that both the nematic phase of the C_7 homologue and the re-entrant nematic phase of the C_9 member can separate this isomeric pair. Separation of compounds on the basis of molecular shape is the most characteristic feature of the liquid crystalline stationary phase in GLC.[11] Roughly, the more rod-like a solute is, the

Table 1. Transition temperatures of liquid crystals studied (°C)

n	Re-entrant nematic	Smectic C	Smectic A	Nematic	Isotropic
7			(72)	113	264
9	(92)		95	224	246
12		(74)	83		245

The parentheses show the monotropic transition.

Table 2. Relative retention of the solute isomers studied

Solutes	Temperature °C	C_7	C_9	C_{12}
m- and *p*- Xylenes	75	1.05(N)	1.02(Re N)	—[a] (S_A)
m- and *p*- Dibromobenzenes	130	1.14(N)	1.08(S_A)	1.09 (S_A)
m- and *p*- Chloroacetophenones	130	1.20(N)	1.14(S_A)	1.14 (S_A)
1- and 2- Chloronaphthalenes	130	1.12(N)	1.07(S_A)	1.07 (S_A)
Phenanthrene and Anthracene	210	1.14(N)	1.12(S_A)	1.12 (S_A)

The relative retention is equal to 1.00 for the *m*- and 1- isomers and phenanthrene, respectively. The parentheses indicate the liquid crystalline phases. N: nematic, S_A: smectic A, Re N: re-entrant nematic.
a) The isomers of *m*- and *p*-xylenes can not be separated at 75 °C in the smectic A phase of C_{12} homologue.

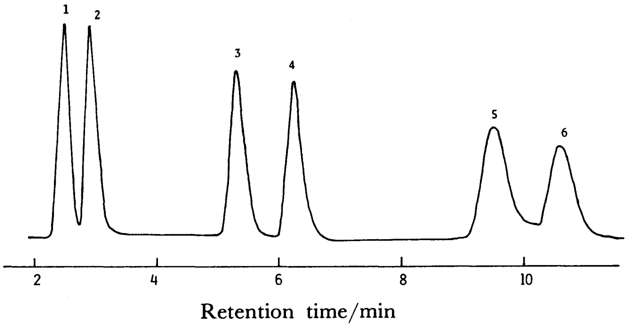


Fig. 1. Gas chromatogram of a mixture of dibromobenzenes, chloroacetophenones and chloronaphthalenes observed in the nematic phase on a C_7 column. Oven temperature, 130 °C; injection temperature, 250 °C; flame-ionization detector; nitrogen flow-rate, 25 ml/min. Peaks 1: *m*-dibromobenzene, 2:*p*-dibromobenzene, 3:*m*-chloroacetophenone, 4:*p*-chloroacetophenone, 5:1-chloronaphthalene, 6:2-chloronaphthalene.

easier it should fit into the liquid crystalline lattice and hence the greater its solubility should be. As is expected, the retention time for the isomer with the more rod-like shape (*p*-isomer) is longer than that for the *m*-isomer. It is also noteworthy to state that the relative retention of xylene isomers observed in the nematic phase is higher than that in the re-entrant nematic state. This result is likely to indicate that the nematic phase has much higher selective affinity toward the positional isomers compared with the re-entrant nematic phase.

Isomeric pairs of dibromobenzenes, chloroacetophenones and chloronaphthalenes can be separated almost completely at 130 °C on all the mesomorphic stationary phases studied, as shown in Fig. 1. As mentioned previously, the length to breadth ratio of the molecules plays an important role for the separation of the solute isomers on the liquid crystalline stationary column. It is apparent in Fig. 1 that the isomer with the more rod-like shape (*p*- and 2-isomer) is retained longer than that with less rod-like shape. Similarly, a complete separation of phenanthrene and anthracene can be achieved at 210 °C using a liquid crystalline column, as shown in Table 2. In addition, it should be emphasized that a value of relative retention toward all the positional isomers obtained in the nematic phase is much higher relative to the corresponding values found in the smectic A and re-entrant nematic phases.

In conclusion, we believe that the C_7 member of the homologous series studied is likely to be most useful stationary liquid phase in GLC because it exhibits a wide nematic temperature range and a unique selectivity for a mixture of various positional isomers.

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