

Note

Liquid crystals

II*. Applications of liquid crystals as stationary phases in gas-liquid chromatography**

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Liquid crystalline stationary phases are being increasingly used for the separation of close-boiling positional isomers by gas-liquid chromatography (GLC)¹⁻¹⁰. In general, liquid crystalline compounds with longer nematic ranges give the best separation of close-boiling positional isomers¹¹. However, our recent investigations¹⁰ using laterally substituted liquid crystalline compounds as substrates showed that higher relative retention values (α) were obtained for positional isomers of disubstituted benzenes than when laterally unsubstituted liquid crystalline compounds were used. Based on these observations, it was concluded that large nematic ranges are not solely responsible for the higher relative retentions of positional isomers of disubstituted benzenes. We synthesized nine laterally substituted liquid crystalline compounds for a detailed study of the effect of lateral substitution on the separation of isomers.

A literature survey of liquid crystalline compounds as substrates in GLC also revealed that certain liquid crystalline compounds could separate the positional isomers well below their crystal-nematic transition temperatures (*i.e.*, in the solid state)^{7, 12, 14}. We therefore studied the behaviour of nine liquid crystalline compounds in both the solid state and the nematic state in the separation of positional isomers of disubstituted benzenes.

EXPERIMENTAL

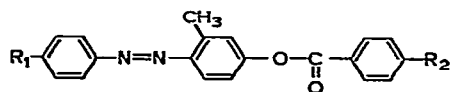
The synthesis of laterally substituted liquid crystalline compounds I-IX is described elsewhere¹³. All of the compounds were purified to give constant transition temperatures. Structures, transition temperatures and nematic ranges of the compounds are given in Table I.

Liquid crystalline compounds I-IX in Table I were used as stationary phases. The solid support used was 80-120-mesh Celite (BDH, Poole, Great Britain). Celite was coated with the liquid crystalline compound using benzene as solvent, followed

* For Part I, see ref. 10.

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TABLE I
PROPERTIES OF LIQUID CRYSTALLINE COMPOUNDS



No.	R ₁	R ₂	Transition temperature (°C)		Nematic range (°C)
			C-N*	N-I*	
I	C ₂ H ₅	OCH ₃	127	199	72
II	C ₂ H ₅	OC ₂ H ₅	121	209	88
III	C ₂ H ₅	<i>n</i> -OC ₄ H ₉	110	181	71
IV	<i>n</i> -C ₄ H ₉	OCH ₃	103	191	88
V	<i>n</i> -C ₄ H ₉	OC ₂ H ₅	107	199	92
VI	<i>n</i> -C ₄ H ₉	<i>n</i> -OC ₄ H ₉	90	175	85
VII	CH ₃	OCH ₃	149	215	66
VIII	CH ₃	<i>n</i> -OC ₄ H ₉	111	193	82
IX	OCH ₃	<i>n</i> -OC ₄ H ₉	108	223	115

* C-N = crystal to nematic; N-I = nematic to isotropic liquid.

by gradual evaporation of the solvent on a water-bath. The coated Celite was dried in an oven at 70°C for 2 h and packed in aluminium columns of 4 mm I.D. The column parameters are given in Table II.

Solutes

Individual positional isomer samples were GLC pure.

Apparatus

The retention times were obtained for all columns using an AIMIL dual-column gas chromatograph equipped with a thermal conductivity detector. Hydrogen was used as the carrier gas.

TABLE II
COLUMN PARAMETERS

Column No.	Stationary phase	Total wt. of packing (g)	Length of column (m)	Concentration of stationary phase (%)
1	I	11.904	1.75	8
2	II	12.790	1.84	16
3	III	12.300	1.75	8
4	IV	12.706	1.84	8
5	V	9.790	1.84	8
6	VI	11.216	1.75	8
7	VII	12.635	1.85	8
8	VIII	9.850	1.84	8
9	IX	9.583	1.84	8
10*	VI	16.249	3.00	5

* Copper column, 5 mm O.D.; solid support, Chromosorb G AW DMCS.

Procedure

All columns were conditioned at 10°C below the nematic to isotropic transition temperature of the stationary phase for 5 h. The injector temperature was 80°C for oven temperatures up to 150°C and 140°C for oven temperatures above 150°C. The detector temperature was 150°C for oven temperatures up to 100°C and 240°C for oven temperatures above 100°C. Retention times (t_R) were measured from air peak maxima to sample peak maxima. The flow-rate of the carrier gas was measured using a soap-film flow meter.

RESULTS AND DISCUSSION

Retention times and relative retention values (α) for positional isomers of disubstituted benzenes were calculated on all columns at different oven temperatures as in a previous paper¹⁰. Additionally here we studied all samples on all columns with both the solid state and the nematic state of liquid crystalline compounds. The stationary phases do not behave in the same manner in the solid and nematic states for a particular sample.

For any sample, at oven temperatures from 50 to 150°C on all columns, it was found that there is an increase in retention time on columns 2, 4, 5, 7 and 8 at the crystal to nematic transition temperature of the stationary phases used. The transition temperatures observed by GLC were 2–8°C lower than the actual transition temperatures, which might be due to uneven heating of the columns at the injector and detector ends.

The retention volumes (V_R) of *m*-xylene on columns 1, 3, 6, 9 and 10 decreased with increase in column temperature. After the crystal to nematic transition temperature there was no observable increase in retention volume, as can be seen in Fig. 1.

It has been indicated that the solubility of a sample should increase in the nematic state, resulting in an increase in retention time at the crystal to nematic transition temperature. Transition temperatures were detected graphically by drawing a graph of t_R against oven temperature or $\log V_R$ against $1/T$. Transition temperatures were not observed clearly for stationary phases I, III, VI and IX, indicating that the solubility of a sample in the solid and nematic states is the same for these compounds and the retention time decreases with increase in oven temperature.

It was found that the retention volumes of any sample on columns 2, 4, 5, 7 and 8 taken into consideration were very small below the crystal to nematic transition temperature, but above that temperature there was a considerable increase in the retention volumes, as can be seen in Fig. 2. It is concluded that on columns 2, 4, 5, 7 and 8 the solubility of sample molecules in the solid state is very poor, while it increases at the crystal to nematic transition temperature and subsequently decreases.

Separations

The separation of close-boiling positional isomers of disubstituted benzene on conventional columns is very difficult, but was successful using liquid crystalline stationary phases. On any liquid crystalline stationary phase, if the separation of xylene isomers is satisfactory then other separations of close-boiling bromotoluenes,

TABLE III
RELATIVE RETENTIONS (α) OF *p*-DISUBSTITUTED BENZENES
 α for *m*-isomer = 1.

Compound	Column No.												
	1	2	3	4	5	6	7	8	9				
	71°C*	132°C	123°C	74°C*	111°C	103°C	106°C	78°C*	115°C	150°C	113°C	74°C*	104°C
<i>p</i> -CH ₃ C ₆ H ₄ CH ₃	1.132	—	1.1080	1.135	1.10	—	—	1.13	—	—	1.137	1.158	1.131
<i>p</i> -ClC ₆ H ₄ CH ₃	—	1.12	1.184	—	1.162	1.169	1.195	—	1.09	—	1.187	—	1.208
<i>p</i> -ClC ₆ H ₄ Cl	—	1.186	1.262	—	1.224	1.228	1.246	—	1.128	1.19	1.252	—	1.274
<i>p</i> -BrC ₆ H ₄ CH ₃	—	1.140	1.234	—	—	1.177	1.200	—	1.15	1.16	1.182	—	1.220
<i>p</i> -CH ₃ C ₆ H ₄ OCH ₃	—	1.265	1.185	—	—	1.207	1.206	—	1.174	1.157	1.188	—	1.242

* Stationary phase in solid state.

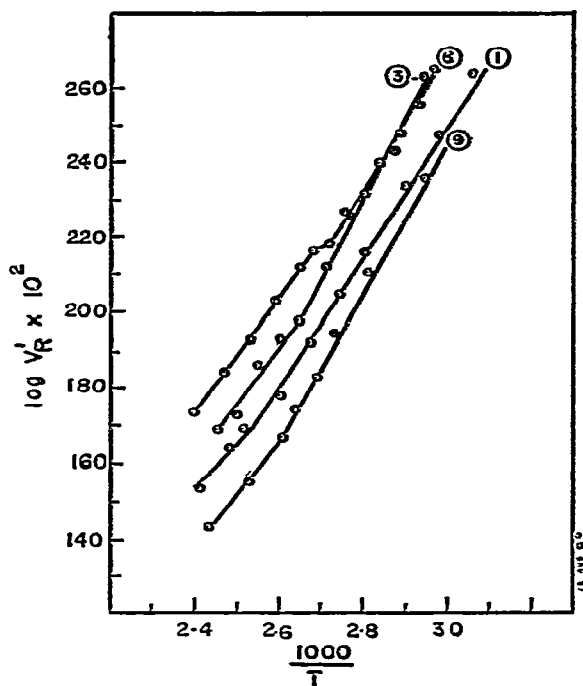


Fig. 1. $\log V_R' \cdot 10^2$ versus $1000/T$ for columns 1, 3, 6 and 9. Test substance: *m*-xylene.

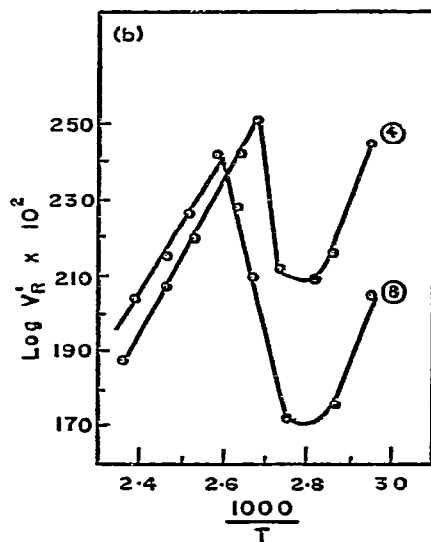
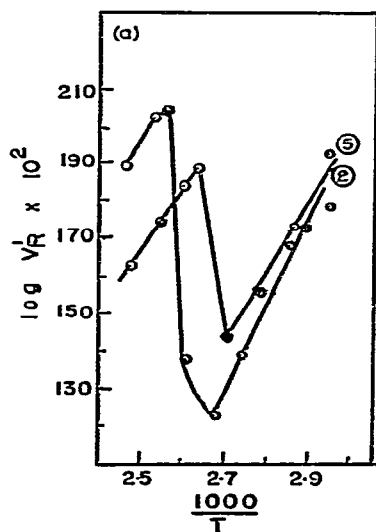


Fig. 2. (a) $\log V_R' \cdot 10^2$ versus $1000/T$ for columns 2 and 5. Test substance: *m*-xylene. (b) $\log V_R' \cdot 10^2$ versus $1000/T$ for columns 4 and 8. Test substances: column 4, *m*-dichlorobenzene; column 8, *m*-bromotoluene.

chlorotoluenes, dichlorobenzenes and methylanisoles can also be effected with great ease.

According to the orienting effect of the nematic state, *p*-xylene should have been retained after *m*-xylene and there should have been a separation in the nematic state. However, from our observations with columns 1, 3, 6, 9 and 10, the solubilities and retention times of xylene isomers increase as the temperature is decreased (*i.e.*, with the stationary phase in the solid state). The relative retention (α) of *p*-xylene (*m*-xylene = 1) varied from 1.16 to 1.10. The relative retention is higher with the stationary phase in the solid state at lower temperatures and decreases as the column temperature is increased.

In contrast, on columns 2, 4, 5, 7 and 8 separations were not observed for positional isomers before the crystal to nematic transition temperature, *i.e.*, with the stationary phase in the solid state.

The separation of close-boiling positional isomers of disubstituted benzenes such as bromotoluenes, chlorotoluenes, dichlorobenzenes and methylanisoles is achieved on all columns however; the maximum α values obtained for a particular column are given in Table III.

Even higher α values for the isomers in Table III can be obtained on columns 1, 3, 6, 9 and 10 in the solid state, but retention times were high and the peaks were broad.

Ethylbenzene and the three xylene isomers were separated on liquid crystalline compounds in the solid state in columns 1, 6 and 9. Their complete separation was obtained at 72°C on column 10 within 16 min (Fig. 3).

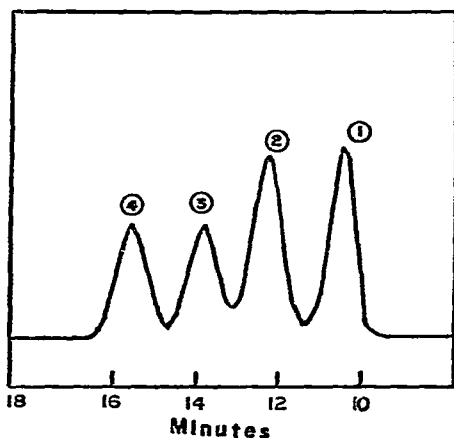


Fig. 3. Gas chromatogram of mixture of ethylbenzene and xylene isomers on column 10. Oven temperature 72°C; injector temperature, 80°C; detector temperature, 180°C. Thermal conductivity detector. Flow-rate of H₂, 20 ml/min. Peaks: 1 = ethylbenzene; 2 = *m*-xylene; 3 = *p*-xylene; 4 = *o*-xylene.

An extensive study of the separation of cresol ethers using liquid crystalline stationary phases was reported by Cook and Spangeld⁶. In comparison in our work higher α values were observed on laterally substituted liquid crystalline stationary phases, resulting in the complete separation of the three isomers of methylanisole (Fig. 4).

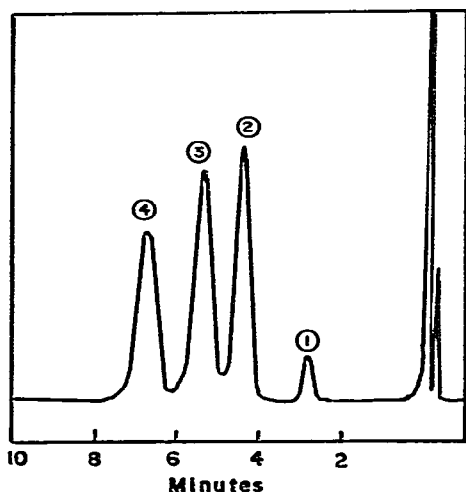


Fig. 4. Gas chromatogram of a mixture of methylanisole isomers on column 9. Oven temperature, 104°C; injector temperature, 80°C; detector temperature, 180°C. Thermal conductivity detector. Flow-rate of H₂, 40 ml/min. Peaks: 1 = anisole; 2 = *o*-methylanisole; 3 = *m*-methylanisole; 4 = *p*-methylanisole.

On column 9, higher α values were obtained for *para*-isomers with the stationary phase in the nematic state (Table III). The stationary phase used in this column has a longer nematic range (115°C) than the other stationary phases studied (Table I). This indicates that laterally substituted liquid crystalline stationary phases having longer nematic ranges give higher α values and hence better separations.

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