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Note

Liquid crystals

V*. Comparative study of laterally halogen-substituted liquid crystalline stationary phases

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Liquid crystalline stationary phases in gas chromatography (GC) have acquired considerable interest and several have been reported¹⁻⁹. In our laboratory, several laterally substituted liquid crystals have been synthesized and used as liquid substrates for GC¹⁰⁻¹².

In continuation of our earlier work of chloro-substituted compounds, the behaviour of bromo- and iodo-substituted liquid crystals as stationary phases in GC was studied.

EXPERIMENTAL

All laterally substituted liquid crystals (Table I) were synthesised by the method reported earlier¹³. The method of impregnation, the solutes examined and the instrumentation were as reported previously¹².

RESULTS AND DISCUSSION

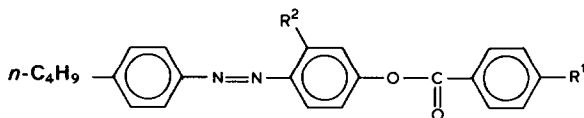
In previous work, the behaviour of laterally (methyl- and chloro-) substituted stationary phases was studied. In order to investigate the effect of laterally substituted bulky halogens, bromo- and iodo-substituted liquid crystals were synthesized (see Table I for the general structure of the liquid crystals), in which one end group (*n*-butyl) was kept unchanged to facilitate a comparative study.

Table I indicates that laterally bromo-substituted liquid crystals do not show any appreciable change in the nematic range compared with the nematic range of chloro-substituted liquid crystals of the same type. Iodo-substituted liquid crystals, however, show decrease in the nematic range.

Retention times (t'_R) are reported in Table II. The relative retention values of the liquid crystalline stationary phases were compared and it was observed that chloro-substituted show higher values than bromo- or iodo-substituted stationary phases. This can be explained on the basis of the structures of the liquid crystals used in

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TABLE I
LIQUID CRYSTALS AND THEIR TRANSITION TEMPERATURES



Column No.	R ¹	R ²	Transition temperature (°C)		Nematic range (°C)
			C-N	N-I	
1	OCH ₃	Br	89	173	84
2	OC ₂ H ₅	Br	82	165	83
3	OC ₄ H ₉	Br	78	160	82
4	OCH ₃	I	108	158	50
5	OC ₂ H ₅	I	104	166	62
6	OC ₄ H ₉	I	81	147	66
7**	OCH ₃	Cl	92.5	176	83.5
8**	OC ₂ H ₅	Cl	90	177	87
9**	OC ₄ H ₉	Cl	87	168	81

* C = crystalline, N = nematic, I = isotropic.

** For ease of reference, all the data for chloro-substituted phases were taken from a previous paper¹¹.

columns. In chloro-substituted phases the size of the gaps between adjacent molecules might be optimal for holding a *p*-disubstituted sample molecule more tightly than the *m*-isomer. As chlorine is replaced by more bulkier groups (bromine or iodine), this gap might be widened, thus decreasing the retention time for *p*-isomer.

The above result indicates that the nature (size) of a lateral substituent is more important than nematic range for the selectivity of liquid crystalline stationary phases towards the separation of disubstituted aromatic hydrocarbon isomers.

The retention times of a model compound (*m*-xylene) on these stationary phases were measured at different temperatures in order to investigate phase transitions by GC, by plotting the logarithm of the retention volumes of sample solutes against reciprocal temperature (Fig. 1).

The retention time decreased linearly on increasing oven temperature for laterally bromo-substituted stationary phases. The retention time did not change at the crystal to nematic transition temperature (Fig. 1a). This behaviour is similar to that of the chloro- (or methyl-)substituted stationary phases studied earlier. With iodo-substituted stationary phases, however, the retention time was higher at lower oven temperatures and decreased up to the crystal to nematic transition temperature. At a temperature 2–3°C higher than the transition temperature, a sudden increase in the retention time was observed and thereafter it decreased with increase in oven temperature (Fig. 1b).

The behaviour of iodo-substituted phases differed from that of the other laterally monosubstituted stationary phases. This may be due to the bromo- (or chloro- or methyl-)substituted phases having a long supercooling effect. Indeed, chloro-substituted stationary phases remain in the supercooled state even below room temperature when they have been heated above the crystal to nematic transition temperature¹⁴.

TABLE II
RETENTION TIMES (min) OF DISUBSTITUTED AROMATIC HYDROCARBONS AT DIFFERENT OVEN TEMPERATURES

I	Column No.													
	2	3	4	5	6	7*	8*	9*						
	100°C	110°C	110°C	109°C	104°C	115°C	81°C	101°C	90°C	110°C	89°C	120°C	85°C	110°C
<i>o</i> -Xylene	—	—	—	0.96	1.813	—	3.516	—	—	—	4.02	—	—	—
<i>m</i> -Xylene	1.683	3.55	4.35	0.75	1.43	—	2.763	—	2.845	—	3.15	—	—	2.193
<i>p</i> -Xylene	1.815	3.95	4.637	0.805	1.523	—	2.93	—	3.233	—	3.603	—	—	2.456
<i>o</i> -Dichlorobenzene	—	6.508	6.616	3.783	4.7	—	—	5.1	—	8.9	—	6.021	—	4.45
<i>m</i> -Dichlorobenzene	—	5.025	5.00	3.88	2.85	—	3.88	3.88	8.083	6.893	6.4	4.58	—	3.42
<i>p</i> -Dichlorobenzene	—	5.675	5.688	4.38	3.166	—	3.983	4.3	9.583	8.03	8.403	5.49	—	3.91
<i>o</i> -Bromotoluene	—	5.716	5.89	4.53	3.473	—	4.34	4.658	—	—	—	5.45	—	4.016
<i>m</i> -Bromotoluene	—	6.208	6.208	4.73	3.673	—	4.683	5.016	8.82	8.346	7.7	5.725	—	4.25
<i>p</i> -Bromotoluene	—	7.16	6.95	5.39	3.99	—	5.216	5.42	11.2	10.14	9.73	6.65	—	4.792
<i>o</i> -Methylanisole	—	4.216	4.266	3.73	2.47	—	3.175	3.308	—	5.83	—	4.05	—	2.966
<i>m</i> -Methylanisole	—	5.6	5.05	3.98	2.978	—	3.803	4.00	—	7.39	6.87	4.87	—	3.6
<i>p</i> -Methylanisole	—	6.29	5.733	4.54	3.388	—	4.3	4.453	—	8.36	8.21	5.62	—	3.91

* For ease of reference, the data for chloro-substituted phases were taken from a previous paper¹.

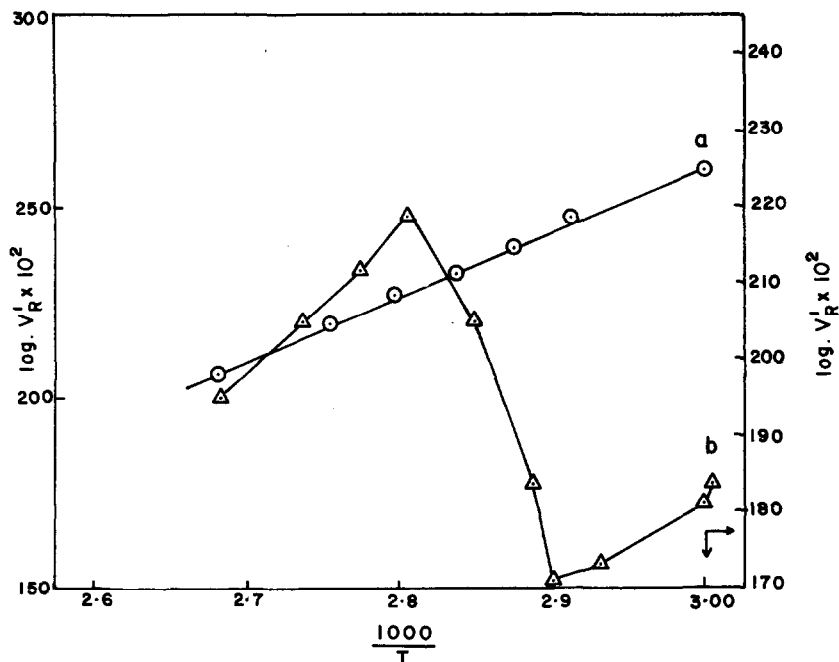


Fig. 1. Graph of reciprocal temperature vs. $\log V_R' \times 10^2$: (a) column 3; (b) column 6. Right-hand scale is for b; left-hand scale is for a.

Liquid crystal phase transition were also monitored by differential scanning calorimetric (DSC) thermograms, which could be recorded with heating and cooling programmes.

The DSC thermograms were plotted on a Perkin-Elmer DSC-2 instrument, which was calibrated using indium (m.p. 156.6°C) as a reference. Fig. 2 shows the thermogram of a support-coated laterally chloro-substituted liquid crystal (compound 7). The liquid crystal was coated over Celite, employing the low-boiling solvent diethyl ether so that heating to remove excess of solvent is avoided. The loading of the liquid crystal was 8% (w/w). From the thermogram it is clear that on heating the coated phase, the crystal to nematic transition resembles the transition monitored by

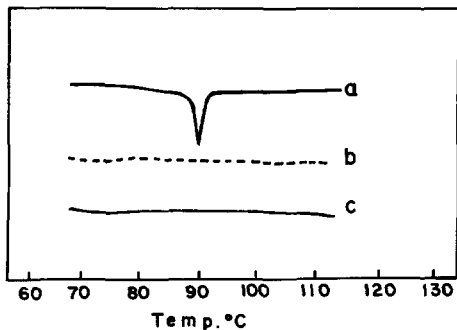


Fig. 2. DSC scans of compound 7 coated on Celite. Scan rate, 5°C/min. Loading, 8% (w/w). Solid lines, heating; broken line, cooling.

the melting point method with a neat liquid crystal (Fig. 2a). However, on cooling the nematic melt, phase transition was not observed (Fig. 2b). Phase transition also could not be obtained by DSC when the same sample was re-run after 24 h (Fig. 2c).

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