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LIQUID CRYSTALS

I. SYNTHESIS AND APPLICATION AS STATIONARY PHASES IN GAS–LIQUID CHROMATOGRAPHY*

K. P. NAIKWADI, D. G. PANSE, B. V. BAPAT and B. B. GHATGE*
National Chemical Laboratory, Poona-8 (India)
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SUMMARY

2-R_1-4'-R-4-(4-*n*-alkoxybenzoyloxy)azobenzenes, where R = *n*-butyl, methyl and methoxy, R_1 = H and methyl and *n*-alkoxy = methoxy, ethoxy and *n*-butoxy were synthesized. They have long liquid crystalline "nematic" ranges and were used as stationary phases for the separation of positional isomers of di- and trisubstituted benzene. It was observed that lateral substitution (R_1) on the middle ring has a profound influence on the relative retentions of these compounds. The separation of mixtures of free phenolic isomers such as *m*- and *p*-cresols was difficult, whereas the separation of α- and β-naphthols could be easily achieved. Similarly, the separation of mixtures of free bases such as toluidines or picolines was difficult, but napthylamines were separated with great ease. Also, the complete separation of all positional isomers of monochlorobiphenyl was achieved by using these liquid crystalline substrates.

INTRODUCTION

The first application of liquid crystals as stationary phases in gas–liquid chromatography (GLC) was described in 1963[1], and subsequent papers have been reviewed by Kelker and Von Schivizhoffen[2] and Schroeder[3]. Recently several reports on the separation of the alkylnaphthalenes[4], polycyclic aromatic hydrocarbons and their derivatives[5–8], phenol ethers[9], disubstituted benzenes[10,11] and high-boiling hydrocarbons[12] using liquid crystalline stationary phases have appeared. The synthesis and use as stationary phases of nematic compounds with $-C(=O)-O-$, $-CH=N-$ and $-N(\uparrow O)=N-$ linkages have been described[3]. Recently, liquid crystals with $-C(=O)-O-$ and $-N(\uparrow O)=N-$ linkages[12] have been investigated for their substrate behaviour.

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However, the use of liquid crystals with lateral substitution (R^1) as stationary phases in GLC has not previously been studied. Therefore, it was decided to explore the possibility of applying such laterally substituted liquid crystalline stationary phases in GLC. This paper dexcribes the synthesis of such laterally substituted liquid crystals and a study of the effect of lateral substitution on selectivity when they are used as stationary phases in GLC.

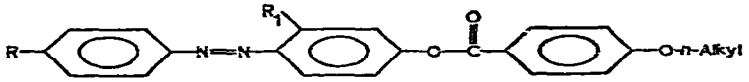
EXPERIMENTAL

Materials

Liquid crystalline compounds I–V were synthesized by known methods[13,14]. Compounds III, IV and V were synthesized by using *m*-cresol instead of phenol with *p*-substituted phenyldiazonium chloride. All of the compounds were purified to give constant transition temperatures. The structures and the transition temperatures of the compounds studied as stationary phases are given in Table I.

TABLE I

STRUCTURES AND TRANSITION TEMPERATURES OF THE COMPOUNDS STUDIED



Compound No.	*R*	R_1	*Alkyl*	*Transition temperatures (°C)**		*Nematic range (°C)*
				C–N	*N–I*	
I	OCH_3	H	*n*-C_4H_9	116	280	164
II	*n*-C_4H_9	H	*n*-C_4H_9	94	234	140
III	OCH_3	CH_3	C_2H_5	125	244	119
IV	CH_3	CH_3	C_2H_5	125	220	95
V	OCH_3	CH_3	CH_3	160	253	93

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

The solid support used was 80–120-mesh Celite. The Celite was coated with the liquid crystalline compounds by using benzene or ethanol as solvent followed by gradual elimination of the solvent by evaporation on hot water-bath. This coated Celite was dried in an oven at 80°C for 1 h and packed in aluminium column of 4.0 mm I.D. The column parameters are given in Table II.

Solutes

Individual positional isomer samples were GC pure; only metamethylanisole showed a detectable anisole impurity.

The oven temperatures and flow-rates of the carrier gas (hydrogen) are given in Table III.

Apparatus

An AIMIL dual-column chromatograph equipped with a thermal conductivity detector with hydrogen as the carrier gas was used to obtain retention

TABLE II

COLUMN PARAMETERS

Column No.	*Stationary phase*	*Length of column (m)*	*Total wt. of packing (g)*	*Amount of stationary phase used (wt.-%)*
1	I	2.00	10.220	10
2	II	2.00	9.700	10
3	III	1.74	7.900	10
4	IV	1.77	8.820	10
5	V	1.77	8.293	10
6	II	1.76	7.260	3
7	III	1.78	8.389	3

TABLE III

COLUMN TEMPERATURES AND CARRIER GAS FLOW-RATES

Parameter	*Column No.*												
	1			*2*		*3*		*4*		*5*		*6*	
Operating temperature (°C)	117	130	163	95	129	130	142	126	138	161	178	96	166
Flow-rate of hydrogen (ml/min)	30	29.7	23.1	37.5	30.7	27.2	26.6	42.8	36.3	32.8	25.5	40.0	37.0

times. The chromatograms shown in Figs. 1 and 2 were obtained on a Hewlett-Packard 700 chromatograph.

Procedure

Individual samples were injected with a 10-μl syringe using the smallest detectable sample volume. All columns were conditioned at 200°C for 6 h. The injector and detector temperatures were 150°C and 225°C, respectively, and retention times 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

Table IV lists the measured retention times at various temperatures for a number of di- and tri-substituted benzene isomers. Table V gives relative retentions calculated from Table IV.

When the retention times at two different temperatures are observed on any column, it is found that with an increase in temperature, that is sufficiently higher than the crystal to nematic transition temperature, the selectivity of the stationary phase decreases.

Changes in the oven temperature have a profound influence on the nature of the stationary phase. These changes affect the nature of the column packing and the flow-rate of the carrier gas (see Table III).

TABLE IV

RETENTION TIMES OF SUBSTITUTED BENZENE ISOMERS IN COLUMNS WITH LIQUID CRYSTALLINE STATIONARY PHASES

Compound	*Column Nos. and operating temperatures (°C)*										
	1		*2*		*3*		*4*		*5*		*6*
	117	*130*	*95*	*129*	*130*	*142*	*126*	*138*	*161*	*178*	*96*
m-$CH_3C_6H_4CH_3$	1.48	1.12	2.34	1.37	0.73	—	0.97	—	—	—	0.78
p-$CH_3C_6H_4CH_3$	1.68	1.25	2.61	1.50	0.85	—	1.10	—	—	—	0.87
m-$ClC_6H_4CH_3$	3.25	2.38	5.01	2.83	1.67	1.36	2.12	1.70	0.75	—	1.82
p-$ClC_6H_4CH_3$	3.95	2.86	6.07	3.34	2.05	1.63	2.56	2.06	0.90	—	2.09
m-ClC_6H_4Cl	5.25	3.61	8.02	4.37	2.60	2.11	3.30	2.63	1.15	0.97	2.72
p-ClC_6H_4Cl	6.47	4.47	10.47	5.25	3.35	2.65	4.32	3.45	1.40	1.15	3.57
m-$BrC_6H_4CH_3$	6.20	4.41	10.50	5.28	3.02	2.39	3.88	3.08	1.31	1.12	3.42
p-$BrC_6H_4CH_3$	7.71	5.31	12.93	6.18	3.82	2.95	4.83	3.78	1.56	1.30	4.18
m-$CH_3C_6H_4OCH_3$	—	—	—	—	2.73	—	3.35	2.62	1.15	—	3.07
p-$CH_3C_6H_4OCH_3$	—	—	—	—	3.40	—	4.17	3.13	1.35	—	3.62
1,2,3-$Cl_3C_6H_3$	—	—	—	—	—	—	—	—	3.25	2.62	1.50**
1,2,4-$Cl_3C_6H_3$	—	—	—	—	—	—	—	—	4.20	3.31	1.83**
m-$ClC_6H_4NH_2$	7.20*	—	—	—	—	—	—	—	7.97	6.00	—
p-$ClC_6H_4NH_2$	8.37*	—	—	—	—	—	—	—	9.20	6.88	—

* Operating temperature 163°C.

** Operating temperature 166°C.

TABLE V

RELATIVE RETENTIONS (α) OF *p*-DISUBSTITUTED BENZENES (*m*-ISOMER = 1.000)

Compound	*Column Nos. and column temperatures (°C)*											*Maximum α-value in literature*
	1		*2*		*3*		*4*		*5*		*6*	
	117	*130*	*95*	*129*	*130*	*142*	*126*	*138*	*161*	*178*	*96*	
p-$CH_3C_6H_4CH_3$	1.135	1.116	1.115	1.09	1.169	—	1.128	—	—	—	1.115	1.16 (ref. 3)
p-$ClC_6H_4CH_3$	1.215	1.20	1.21	1.18	1.227	1.199	1.208	1.206	1.20	—	1.148	—
p-ClC_6H_4Cl	1.232	1.238	1.30	1.20	1.288	1.256	1.309	1.311	1.21	1.186	1.312	1.26 (ref. 3)
p-$BrC_6H_4CH_3$	1.244	1.204	1.21	1.17	1.265	1.234	1.245	1.227	1.200	1.161	1.223	—
p-$CH_3C_6H_4OCH_3$	—	—	—	—	1.246	—	1.245	1.195	1.174	—	1.180	—
1,2,4-$Cl_3C_6H_3$	—	—	—	—	—	—	—	—	1.292	1.263	1.22	—
p-$ClC_6H_4NH_2$	1.162	—	—	—	—	—	—	—	1.154	1.147	—	—

When the relative retention (α) for any sample on column 1 is compared with that on column 2, it is found that column 1 is more selective than column 2. This is in accordance with previous results[2,3] that compounds with a longer nematic range have a higher selectivity. The same trend of selectivity based on the nematic range is observed for most of the samples on columns 3–5.

Compounds III and IV have lateral substitution (R_1), whereas compounds I and II have not, which affects the relative retentions. Compounds I, II, III and IV have nematic ranges of 164°C, 140°C, 119°C and 95°C, respectively. Now, based on previous results, compound I and II are supposed to show a higher selectivity. However, compounds III and IV, with narrow nematic ranges, show a higher selectivity than compounds I and II for most of the samples (Table V). This observation leads us to conclude that a certain lateral substitution in a typical liquid crystalline compound may decrease the nematic range but may give a higher selectivity. These results encouraged us to synthesize liquid crystalline compounds with other lateral substitutions, the results of which will be published elsewhere.

The relative retentions (α) observed on our columns and those observed on other liquid crystals that were assumed to be more selective are given in last row of Table V. The compounds we have studied show higher α-values. Of the five stationary phases studied, column 3 (stationary phase III) gave the most promising results.

Changes in the percentage of stationary phase seem to have a negligible effect on relative retention; this can be seen for columns 2 and 6.

In order to avoid long retention times and broadening of the peaks, higher boiling compounds were separated on columns 6 and 7 with a low percentage of stationary phases. Retention times and relative retentions observed on column 6 are given in Table VI.

TABLE VI

RESULTS FOR HIGHER BOILING SAMPLES ON 3 WT-% STATIONARY PHASE II (COLUMN 6)

Compound	*Retention time at 166°C (min)*	*Relative retention (α)**	*Literature value of α*
2-Chlorobiphenyl	6.55		
3-Chlorobiphenyl	10.92		
4-Chlorobiphenyl	15.33	1.404	1.27 (ref. 15)
α-Naphthylamine	16.47		
β-Naphthylamine	21.02	1.277	
α-Naphthol	16.42		
β-Naphthol	21.50	1.309	1.30 (ref. 16)

* Relative to 3- or α-isomer = 1.00.

Separation of monochlorobiphenyls

The separation of chlorinated biphenyls is important owing to their toxicological properties. A good separation of monochlorobiphenyl isomers is achieved on the liquid crystalline stationary phases (Fig. 1). Stationary phase II (column 6) gives higher relative retentions (α) for monochlorobiphenyl isomers than those in the literature[15,17,18].

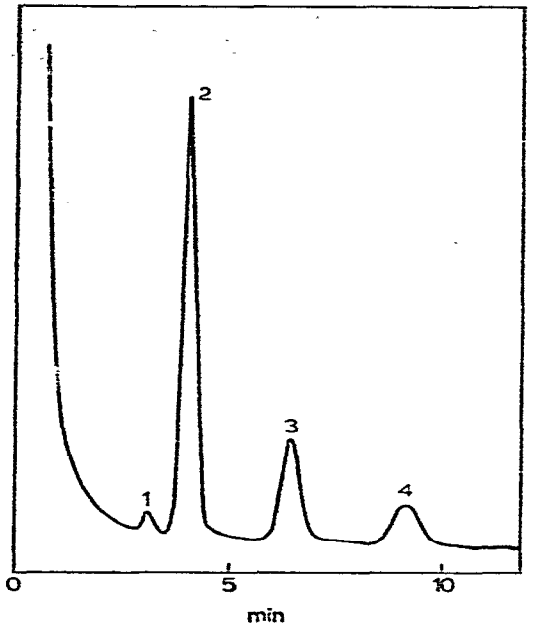


Fig. 1. Gas chromatogram of a mixture of monochlorobiphenyls on column 7. Oven temperature, 190°C; injector temperature, 240°C; detector temperature, 290°C; flame-ionization detector; nitrogen flow-rate, 40 ml/min. Peaks: 1 = biphenyl; 2 = 2-chlorobiphenyl; 3 = 3-chlorobiphenyl; 4 = 4-chlorobiphenyl.

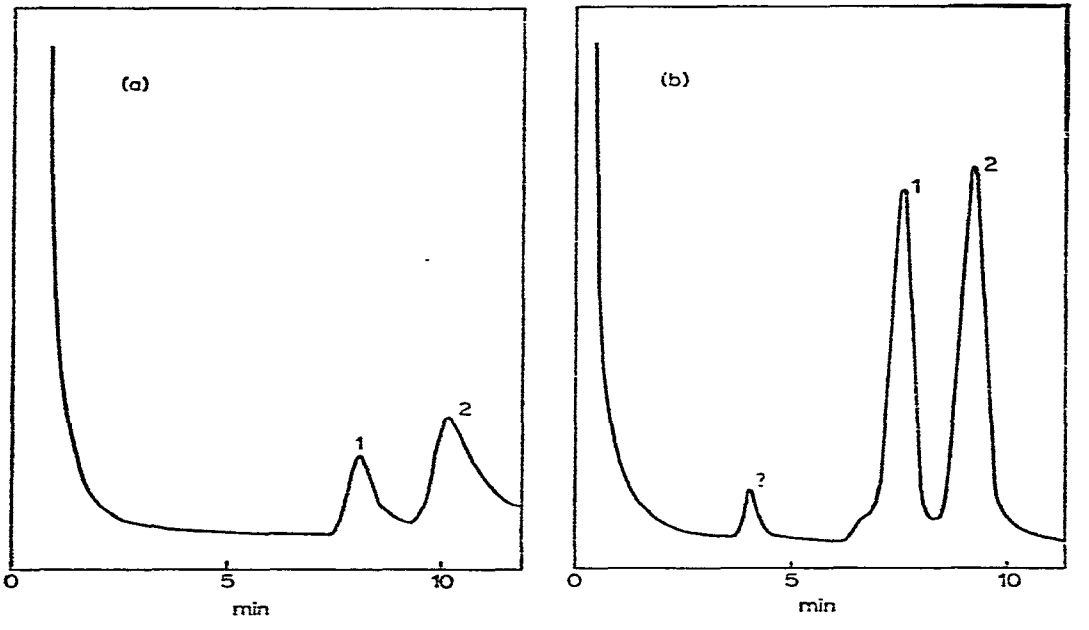


Fig. 2. (a) Gas chromatogram of naphthols on column 7. Oven temperature, 195°C; other conditions as in Fig. 1. Peaks: 1 = α-naphthol; 2 = β-naphthol. (b) Gas chromatogram of naphthylamines on column 7. Conditions as in Fig. 2a. Peaks: 1 = α-naphthylamine; 2 = β-naphthylamine.

Complete separations of α-naphthol from β-naphthol and of α-naphthylamine from β-naphthylamine were achieved (Fig. 2a and b). The relative retentions (α) are comparable to previous results[12,16].

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