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Short Communication

Application of substituted liquid crystals as stationary phases in gas–liquid chromatography for the separation of mono- and dimethyl naphthalenes

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ABSTRACT

Thirteen mono- and dilaterally substituted liquid crystalline compounds were investigated for their gas chromatographic behaviour as stationary phases for the separation of mono- and dimethylnaphthalenes. A normal packed column system was used. These compounds offered a good separation for some pairs of methylnaphthalenes.

INTRODUCTION

Liquid crystalline stationary phases are being increasingly used for the separation of close boiling positional isomers by gas–liquid chromatography (GLC) [1–14]. In general, liquid crystalline compounds with longer nematic ranges give the best separation of close boiling positional isomers [11]. However, investigations using laterally substituted liquid crystalline compounds as substrates have shown that higher relative retention values (α) are obtained for positional isomers of disubstituted benzenes than when laterally unsubstituted liquid crystalline compounds with longer nematic ranges are used as stationary phases [10].

In continuation of the work carried out in this laboratory [14] on the screening of laterally substituted liquid crystalline compounds for the separation of close boiling positional isomers and the effect of lateral substitution on selectivity, thirteen methyl-, chloro- and nitro-substituted aromatic liquid crystalline stationary phases have been studied. These compounds were synthesized in this laboratory some time ago [15]. A normal packed column system was used for this purpose. The analysis of

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methylnaphthalenes is very important as a result of their solubility in water and their toxicity towards aquatic life. Their analysis has always been difficult because of their close boiling points and other similar properties. Liquid crystalline stationary phases in GLC are known to separate such pairs on the basis of the shape of the solute molecules [1,12,13,16–34].

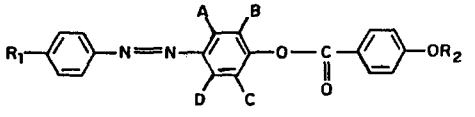
EXPERIMENTAL

The synthesis of these liquid crystals has been described elsewhere [15]. All the liquid crystalline compounds were purified by crystallization from a light petroleum (b.p. 60–80°C)–benzene mixture to give constant transition temperatures, which were determined by the open capillary melting point method. All the melting points are uncorrected. The substituents and transition temperatures are presented in Table I. The solid support used was 80–120 mesh Celite (BDH, Poole, UK). The Celite was coated with the liquid crystalline compound (5%, w/w, coating) using chloroform as the solvent. The chloroform was gradually evaporated on a water-bath. The coated Celite was dried and packed in aluminium columns (6 ft. × $\frac{1}{4}$ in. I.D.). An AIMIL gas–liquid chromatography with thermal conductivity detection and hydrogen as the carrier gas at a flow-rate of 30 ml/min was used to record the retention times.

All the columns were conditioned for 5 h at 10°C below the nematic to isotropic transition temperature of the liquid crystalline compound used as the stationary phase.

TABLE I

STRUCTURE, SUBSTITUENTS AND TRANSITION TEMPERATURES OF THE LIQUID CRYSTALLINE COMPOUNDS USED FOR THE COLUMNS STUDIED HERE



Column No.	R1	R2	A	B	C	D	Transition temperature[a] (°C)	
							C–N	N–I
1	CH_3	CH_3	CH_3	H	H	CH_3	125	170
2	CH_3	C_2H_5	CH_3	H	H	CH_3	123	180
3	OC_2H_5	CH_3	CH_3	H	H	CH_3	140	210
4	OC_2H_5	CH_3	H	CH_3	CH_3	H	182	205
5	OC_2H_5	CH_3	CH_3	CH_3	H	H	198	275
6	OCH_3	CH_3	CH_3	CH_3	H	H	200	270
7	CH_3	n-C_6H_{13}	CH_3	CH_3	H	H	120	200
8	CH_3	CH_3	CH_3	CH_3	H	H	168	236
9	OC_2H_5	n-C_4H_9	CH_3	CH_3	H	H	140	240
10	CH_3	CH_3	CH_3	H	H	H	140	207
11	CH_3	CH_3	Cl	H	H	H	180	230
12	CH_3	C_2H_5	Cl	H	H	H	128	185
13	CH_3	CH_3	H	NO_2	H	H	121	190

[a] C–N = Nematic; N–I = isotropic.

TABLE II

RELATIVE RETENTION TIMES OF MONO- (MN) AND DIMETHYL (DMN) NAPHTHALENES WITH RESPECT TO NAPHTHALENE

Compound	Boiling point at 760 mmHg (°C)	Conditions: (column No.) temperature (°C)												
		(1) 162	(2) 162	(3) 176	(4) 182	(5) 199	(6) 200	(7) 169	(8) 166	(9) 171	(10) 172	(11) 180	(12) 170	(13) 170
		Relative retention time												
Naphthalene	217.7	2.15	1.73	0.93	1.83	0.92	0.97	1.47	0.73	1.20	1.50	1.00	1.88	1.37
1-MN	240.4	2.02	1.94	1.53	1.85	1.66	1.57	1.87	1.92	2.23	2.35	1.88	1.79	1.79
2-MN	241.42	1.78	1.73	1.37	1.70	1.58	1.47	1.71	1.67	2.17	2.22	1.63	1.63	1.62
1,2-DMN	266	4.15	4.00	2.94	3.59	3.10	3.01	3.91	3.49	4.61	4.91	4.00	2.78	3.94
1,3-DMN	263	3.40	3.24	2.44	2.95	2.63	2.34	3.20	3.04	3.46	4.09	3.00	2.19	3.29
1,4-DMN	268	3.80	3.71	2.66	3.45	2.83	2.73	3.48	3.05	3.75	4.45	3.46	2.33	3.3
1,5-DMN	265	3.67	3.60	2.77	3.37	2.85	2.75	3.50	3.40	4.00	4.25	3.35	2.42	3.52
1,6-DMN	264	3.38	3.31	2.42	3.16	2.66	2.53	3.24	3.29	3.82	4.33	3.40	2.32	3.22
2,3-DMN	269	3.94	3.73	2.88	3.49	3.02	2.78	3.59	3.26	4.23	4.19	3.39	2.43	3.52
2,6-DMN	262	3.02	2.89	2.23	2.74	2.48	2.44	3.15	2.88	3.73	3.67	2.66	2.13	2.73

The injector temperature was maintained at 190°C and detector temperature at 240°C. The transition temperatures observed by GLC were 2–5°C lower than the actual transition temperatures, which might be due to the uneven heating of the columns at the injector and detector ends. The retention times were measured from the air peak maxima to the sample peak maxima. The flow-rate of the carrier gas was measured using a soap film flow meter.

RESULTS AND DISCUSSION

Most of these stationary phases gave good separations for a number of combinations of pairs. A literature survey [1,12,13,16–34] shows that the separation mechanism for mono- and dimethylnaphthalene isomers is complex.

The retention time data determined here (Table II) show that the elution order of all the methylnaphthalene isomers is more or less the same on all the liquid crystalline stationary phases under investigation. The separation mechanism for the liquid crystalline phases depends on the interaction of the solute and solvent molecules according to the shape parameter. For isomeric methylnaphthalenes the main factor determining their retention behaviour is the symmetry of substitution [22] (the mutual arrangement of the methyl groups relative to each other and to the aromatic skeleton).

In these observations, when the retention pattern of monomethyl naphthalenes is considered, it is seen that the lower boiling 1-methylnaphthalene is retained on the column and the higher boiling 2-methylnaphthalene isomer elutes first, thus following the shape parameter.

The elution order of dimethylnaphthalene (DMN) shows the predominance of

TABLE III

SEPARATION FACTORS (α) FOR MONO- AND DIMETHYL NAPHTHALENES

Name of pair[a]	Column number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1-MN/2-MN	1.14	1.16	1.12	1.08	1.05	1.06	1.09	1.14	1.03	1.06	1.15	1.1	1.1
1,2-DMN/2,3-DMN	1.05	1.07	1.07	1.03	1.06	1.08	1.09	1.07	1.08	1.17	1.22	1.05	1.11
1,2-DMN/2,6-DMN	1.37	1.38	1.31	1.3	1.29	1.23	1.24	1.21	1.24	1.34	1.5	1.3	1.45
1,2-DMN/1,3-DMN	1.22	1.24	1.2	1.22	1.29	1.22	1.22	1.15	1.33	1.2	1.33	1.27	1.19
1,2-DMN/1,4-DMN	1.09	1.08	1.11	1.04	1.13	1.1	1.12	1.14	1.23	1.1	1.16	1.19	1.19
1,2-DMN/1,5-DMN	1.13	1.11	1.06	1.06	1.13	1.09	1.12	1.03	1.15	1.16	1.19	1.15	1.12
1,2-DMN/1,6-DMN	1.23	1.21	1.21	1.14	1.12	1.2	1.21	1.06	1.21	1.13	1.18	1.19	1.22
2,3-DMN/2,6-DMN	1.30	1.29	1.29	1.22	1.22	1.14	1.14	1.13	1.14	1.14	1.23	1.24	1.3
2,3-DMN/1,4-DMN	1.04	1.01	1.08	1.01	1.06	1.01	1.03	1.07	1.13	1.06	1.05	1.13	1.06
1,3-DMN/2,6-DMN	1.13	1.12	1.1	1.07	1.06	1.04	1.01	1.06	1.07	1.06	1.13	1.03	1.21
1,4-DMN/2,6-DMN	1.26	1.28	1.19	1.26	1.14	1.12	1.11	1.06	1.01	1.21	1.30	1.1	1.21
1,5-DMN/2,6-DMN	1.22	1.25	1.25	1.23	1.15	1.13	1.11	1.18	1.07	1.16	1.26	1.14	1.3
1,6-DMN/2,6-DMN	1.12	1.15	1.09	1.15	1.07	1.03	1.03	1.14	1.02	1.18	1.28	1.09	1.19
1,6-DMN/1,3-DMN	1.01	1.02	1.00	1.07	1.01	1.07	1.01	1.08	1.1	1.06	1.13	1.06	1.02
1,5-DMN/1,6-DMN	1.09	1.08	1.15	1.06	1.07	1.08	1.08	1.03	1.05	1.01	1.01	1.04	1.09
1,4-DMN/1,5-DMN	1.03	1.03	1.04	1.02	1.00	1.09	1.0	1.1	1.06	1.04	1.03	1.04	1.06

[a] MN = Methylnaphthalene; DMN = dimethylnaphthalene.

the "*ortho* effect" present in 2,3- and 1,2-DMN, which are retained for longer times on all columns.

The change of position of the dimethyl substituents on the substrate does not have any distinct effect on the separation capacity (Table III, columns 3–5). In similar manner the change from methoxy to ethoxy at position R1, R2 has a negligible effect on (columns 5 and 6, 1 and 2).

An increase in the alkoxy chain length has very little effect on the selectivity, as seen when the results on columns 7 and 8 are compared.

All the columns under investigations have very good pair separations for (1,2- and 2,6-) and (2,3- and 2,6-)DMN. A comparison of the results obtained on columns 10 and 11 shows that the substitution of a chloro group in place of the methyl group on the liquid crystalline moiety influences the selectivity towards the resolution of DMN isomers (Table III, column 13). The behaviour of this column shows that the introduction of the nitro group onto the substrate molecule gives a longer nematic range and a good separation of these positional isomers.

Different pair combinations may be separated on a variety of columns. The choice of column depends on the pair of interest. Pairs which are usually difficult to separate, such as (1,2- and 2,6-), (2,6- and 2,3-)DMN and 1-methyl- and 2-methyl-naphthalenes are well resolved on all the columns. Column 1, 2, 10, 12, 13 can separate ten out of the sixteen pair combinations under investigation.

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