

Note

Liquid crystals

IV*. Study of the supercooling effect on laterally substituted liquid crystalline compounds**

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In earlier papers^{1,2} we stated that for some laterally monosubstituted stationary phases, the retention time for any solute molecule decreases with increase in oven temperature. Near the crystal to nematic transition temperature retention times were found not to increase, which is the normal property of any liquid crystalline stationary phase. These phases have shown higher relative retention values for disubstituted aromatic hydrocarbons below the crystal to nematic transition temperature, *i.e.* in the solid state.

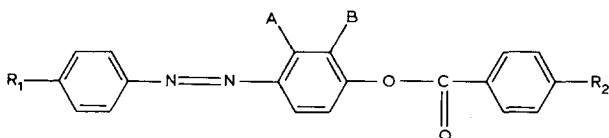
Studies of liquid crystalline stationary phases below their crystal to nematic transition temperatures have been carried out by several workers. Wasik and Chesler³ reported the use of nematic liquid crystalline stationary phases 65°C below the crystal to nematic transition temperature of 181°C. Holzek and Gutwillinger⁴ demonstrated the use of liquid crystals as stationary phase up to 65°C, which is 100°C below the crystal to nematic transition temperature. Liquid crystals as stationary phases in gas-liquid chromatography (GLC) have been studied below the crystal to nematic transition temperatures⁵⁻⁷.

Janini and Ubeid⁸ and others^{9,10} have studied the effect of the solid support on the chromatographic properties of liquid crystalline stationary phases.

In this work, the objective was to investigate the extent of the supercooling property of laterally mono- and disubstituted liquid crystalline phases, liquid crystals having an azo group linkage in two aromatic rings being employed.

EXPERIMENTAL

The liquid crystals synthesized and used as stationary phases in column packing were of the formula



* For Part III, see ref. 12.

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TABLE I
LIQUID CRYSTALLINE COMPOUNDS AND THEIR NEMATIC RANGES

See formula in text.

Compound No.	R_1	R_2	A	B	Transition temperature ($^{\circ}\text{C}$)	Nematic range ($^{\circ}\text{C}$)
1	$n\text{-C}_4\text{H}_9$	CH_3	Cl	H	88-176	88
2	$n\text{-C}_4\text{H}_9$	C_2H_5	Cl	H	90-177	87
3	$n\text{-C}_4\text{H}_9$	$n\text{-C}_4\text{H}_9$	Cl	H	87-175	88
4	$n\text{-C}_4\text{H}_9$	CH_3	CH_3	CH_3	114-215	101
5	$n\text{-C}_4\text{H}_9$	$n\text{-C}_4\text{H}_9$	CH_3	CH_3	112-216	104
6	C_2H_5	$n\text{-C}_4\text{H}_9$	Cl	H	117-172	55

where $A = \text{Cl}$ or CH_3 , $B = \text{CH}_3$ or H , $R_1 = \text{ethyl}$ or $n\text{-butyl}$ and $R_2 = \text{methyl}$, ethyl or $n\text{-butyl}$. They were synthesized by the method reported previously¹¹. Liquid crystals used to prepare stationary phases were thoroughly purified by repeated crystallization to give constant transition temperatures. Structures and transition temperatures are given in Table I.

The solid supports used were Celite (60-80 mesh), Chromosorb W AW, Chromosorb 750 and Anakrom ABS (60-80 mesh).

The usual method of impregnation is to transfer a solution of a weighed amount of liquid crystal in an appropriate solvent to a weighed solid support. Excess of solvent is removed gently on a water-bath below 60°C and the semi-dried, coated support is dried in an oven at $60\text{-}70^{\circ}\text{C}$.

To study the supercooling effect of liquid crystals, modified methods of impregnation were employed: (1) physical mixing and (2) impregnation by using a very low-boiling solvent such as diethyl ether.

Method 1

A weighed amount of support was placed in a stoppered bottle and a suitable amount of finely powdered liquid crystal of particle size 300-400 mesh was accurately weighed and added to the support material. The mixture was mixed in a roller mill for 48 h and then packed in a stainless-steel column of $180\text{ cm} \times 2\text{ mm}$ I.D.

Method 2

The liquid crystalline compound was weighed accurately and dissolved in 25 ml of dry diethyl ether and the solution was poured onto the previously weighed solid support in an evaporating dish. The ether was removed at room temperature and the impregnated material, after having removed almost all of the ether, was kept in a desiccator for 24 h to remove any moisture. The support impregnated with liquid crystalline material was packed in a stainless-steel tube of $180\text{ cm} \times 2\text{ mm}$ I.D.

The concentrations of all the stationary phases were 5% (w/w). The solutes were m - and p -xylene and m - and p -bromotoluene.

Apparatus

Retention times were obtained using a Hewlett-Packard 5730A gas chroma-

TABLE II

RETENTION TIMES OF LIQUID CRYSTALLINE STATIONARY PHASES PREPARED BY PHYSICAL MIXING METHOD

Support: Celite (60-80 mesh).

Compound No.*	Temperature (°C)	m-Xylene		m-Bromotoluene	
		t_{R1} (min)	t_{R2} (min)	t_{R1} (min)	t_{R2} (min)
1	40	1.71	8.01	5.12	—
	50	1.27	5.12	3.31	—
	60	1.00	3.65	2.26	18.51
	70	0.81	2.77	1.64	—
	80	0.72	2.29	1.25	8.82
	90	1.68	1.78	6.29	6.41
	100	1.48	1.32	5.68	4.72
2	110	1.30	0.95	—	—
	40	1.05	—	6.51	—
	50	0.89	—	5.63	—
	60	0.78	—	4.83	—
	70	—	3.93	4.71	18.80
	80	0.67	2.32	—	14.32
	90	1.73	1.61	6.82	10.13
6	100	1.32	1.04	—	—
	50	—	—	1.73	6.2
	80	—	—	0.73	5.32
	100	—	—	0.65	4.21
	122	—	—	1.27	3.52
	130	—	—	1.06	3.12

* Crystal to nematic and nematic to isotropic transition temperatures: compound No. 1, 88 and 176°C; compound No. 2, 90 and 177°C; and compound No. 6, 117 and 177°C, respectively.

TABLE III

RETENTION TIMES ON A LATERALLY DISUBSTITUTED LIQUID CRYSTALLINE STATIONARY PHASE

Compound No. 5: nematic range = 104°C.

Oven temperature (°C)	m-Xylene	
	t_{R1} (min)	t_{R2} (min)
60	1.326	1.319
70	1.23	1.216
80	1.79	1.76
90	0.65	0.6
100	0.52	0.5
115	1.54	1.523
120	1.4	1.37
125	1.25	1.23
130	1.16	1.14

TABLE IV
RETENTION TIMES OF COMPOUND NO.1 ON DIFFERENT SOLID SUPPORTS

Support	Temperature (°C)	<i>m</i> -Xylene		<i>m</i> -Bromotoluene	
		t_{R1} (min)	t_{R2} (min)	t_{R1} (min)	t_{R2} (min)
Chromosorb G AW DMCS	25	2.95	—	14.92	—
	50	1.12	5.08	4.19	—
	60	0.86	—	2.74	—
	70	0.69	2.55	1.93	—
	80	0.58	1.89	1.50	8.84
	93	1.39	1.37	5.64	5.62
	105	1.07	1.05	3.9	3.86
	125	0.75	0.80	2.82	2.76
Chromosorb 750	25	—	—	—	—
	50	—	4.26	—	—
	60	—	—	—	—
	70	—	2.17	—	—
	80	—	1.65	—	—
	93	1.54	1.25	—	—
	125	1.12	0.67	—	—
	Chromosorb W AW	25	—	—	—
50	—	6.24	—	—	
60	—	—	—	—	
70	—	3.07	—	—	
80	—	2.3	—	10.49	
93	—	1.73	—	6.97	
105	1.38	1.33	5.04	4.77	
125	0.95	1.01	2.81	4.13	

tograph equipped with a flame-ionization detector connected to a 3380A reporting integrator. The columns were not pre-heated. The oven, detector and injector temperatures were either each 100°C, or 100, 250 and 150°C, respectively. The carrier gas (nitrogen) flow-rate was 30 ml/min.

Retention times t_{R1} were measured before the stationary phases had reached their crystal to nematic transition temperatures and t_{R2} were measured after the phases had been heated above these temperatures.

Retention times recorded below and above the crystal to nematic transition temperature are reported in Tables II-IV.

RESULTS AND DISCUSSION

When retention times are recorded before the column is heated above the crystal to nematic transition temperature, the retention time (t_{R1}) decreased as the oven temperature was increased up to the crystal to nematic transition temperature. At the crystal to nematic transition temperature an abrupt increase in retention time was observed, followed by a linear decrease in retention time with further increase in oven temperature (Fig. 1a).

Retention times (t_{R2}) were again observed after keeping the column at room temperature for 24 h and maintaining all the parameters the same as before. It was

TABLE V
RETENTION TIMES AND RELATIVE RETENTION VALUES OF COMPOUND NO. 1 ON SUPPORTS IN THE SOLID STATE AND NEMATIC STATE

Support	State	Oven temperature (°C)	Retention time (min)		Relative retention	Retention time (min)		Relative retention
			<i>m</i> -Xylene	<i>p</i> -Xylene		<i>m</i> -Bromotoluene	<i>p</i> -Bromotoluene	
Cromosorb G AW DMCS	Before conditioning the column	50	1.12	1.14	1.0178	4.19	4.51	1.076
	80	0.76	0.75	1.00	1.5	1.6	1.066	
	50	5.08	5.76	1.1338	—	—	—	
Anakrom ABS	After heating the column above crystal to nematic transition temperature	80	0.58	0.59	1.10	8.84	10.43	1.179
	Before conditioning the column	50	1.34	1.44	1.074	5.81	6.8	1.17
	80	0.72	0.75	1.0416	2.16	2.32	1.074	
	50	8.74	10.25	1.172	—	—	—	
	80	3.27	3.67	1.122	—	—	—	
	After conditioning the column	80	—	—	—	—	—	—

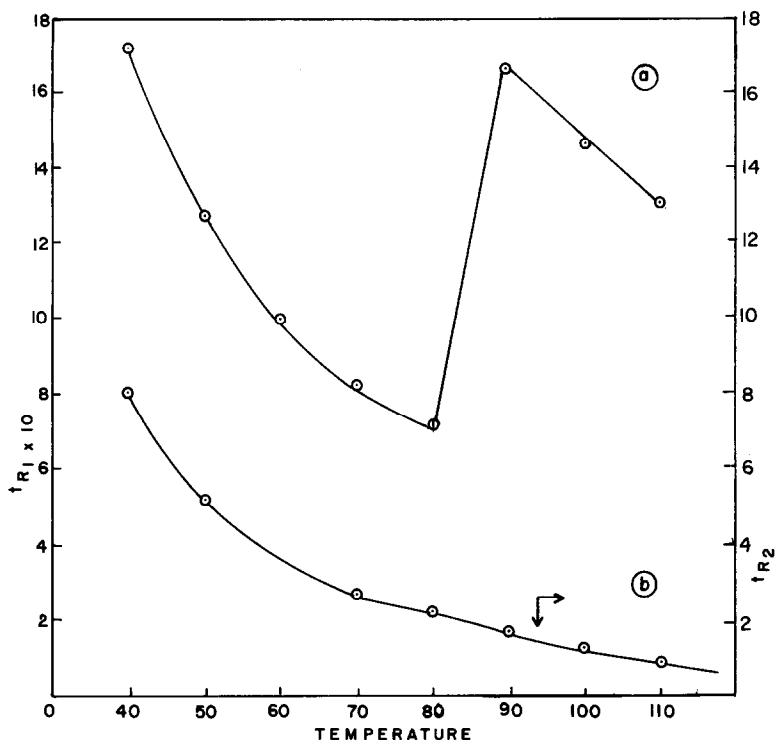


Fig. 1 Oven temperature ($^{\circ}\text{C}$) versus retention time (min) for compound No. 1. For a and b, see text.

observed that the retention time decreased with increase in oven temperature and did not show any increase even at the crystal to nematic transition temperature (Fig. 1b).

A mixture of *m*- and *p*-xylene and *m*- and *p*-bromotoluene was analysed after keeping the columns for 3 months at room temperature (Table V); the gas chromatogram is shown in Fig. 2. No change in the pattern of retention time was observed (even after about 12 months); it was found to decrease linearly with increase in oven temperature and no increase in retention time was observed at the crystal to nematic transition temperature.

These liquid crystalline stationary phases were cooled at 0°C for 24 h in order to establish whether they are transformed into the crystalline state below room temperature. It was observed from the retention time data that they retain their supercooling nature even after cooling below room temperature and the retention time did not show sudden change at the crystal to nematic transition temperature.

The same patterns of retention time were observed when impregnation was effected using a low-boiling solvent (diethyl ether).

Study of different solid supports

In order to study the effect of the solid support, different packing materials [Chromosorb G AW DMCS (80–100 mesh), Chromosorb W AW (60–80 mesh), Chromosorb 750 (60–80 mesh) and Celite (80–120 mesh)] were employed for coating the liquid crystals.

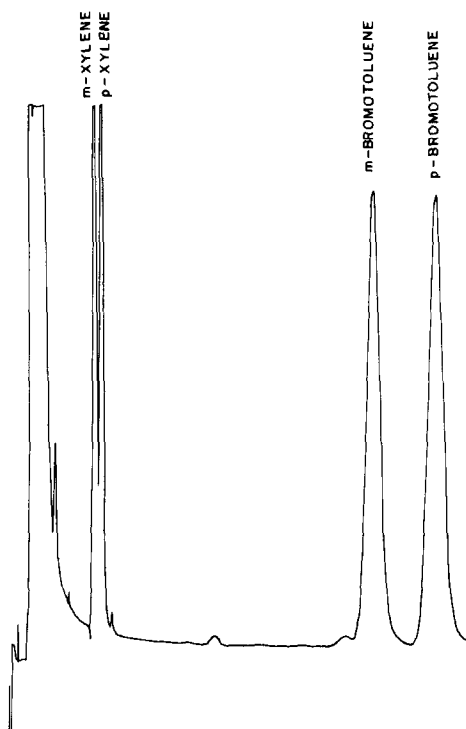


Fig. 2. Gas chromatogram of *m*- and *p*-xylene and *m*- and *p*-bromotoluene on column No. 1. Oven temperature, 70°C (20°C below the transition temperature); detector, 140°C.

Retention times were recorded below and above the crystal to nematic transition temperatures. Celite and Chromosorb W AW DMCS show absorption of solutes even before conditioning the columns, and retention times could be recorded both before and after conditioning of the columns above the crystal to nematic transition temperature.

However, Chromosorb 750 and Chromosorb W AW showed absorption of solutes only after conditioning the columns at 20°C above the crystal to nematic transition temperature and therefore retention times could be recorded only after conditioning the columns (Table IV).

Comparison of solubilities on mono- and disubstituted liquid crystalline phases

When solubility was measured for any sample molecule using a laterally monosubstituted liquid crystalline stationary phase, the retention time decreased linearly with increase in oven temperature. On the other hand, using a disubstituted liquid crystalline stationary phase the solubility of a sample molecule below the crystal to nematic transition temperature was poor and near this temperature it increased considerably and subsequently decreased with increase in temperature (Tables II and III).

It can therefore be inferred from the results that the laterally monosubstituted crystals exhibit supercooling properties even below room temperature for an indefinite period when they are coated on a solid support and do not attain their original

crystalline state. Moreover, they showed the same efficiency for isomer separation throughout the period.

This pattern has not been observed with laterally disubstituted liquid crystalline stationary phases having the same end groups. They are converted to the crystalline state as soon as they are cooled below their crystal to nematic transition temperature.

Applicability

As a result of their supercooling properties from ambient temperature, stationary phases of laterally monosubstituted liquid crystalline compounds are suitable for use in the analysis of low-boiling isomers such as xylenes to high-boiling isomers such as naphthalene and anthracene.

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