Journal of Chromatography, 609 (1992) 277–281
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 306

Investigation of a scyllitol-derived (saturated) disc-shaped liquid crystal stationary phase in capillary gas chromatography[☆]

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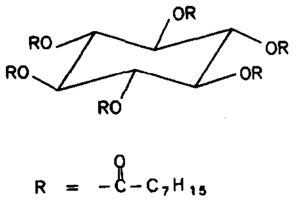
(First received July 10th, 1991; revised manuscript received April 23rd, 1992)

ABSTRACT

Hexa-O-octanoyl-*scyllo*-inositol, a scyllitol-derived disc-shaped liquid crystal, was tested as a stationary phase in gas chromatography. The retention indices of series of isomers selected as test substances differing in chemical structure, molecular geometry and physico-chemical properties were measured, and conclusions about the mechanism of interaction between the stationary phase and the test molecules are discussed. The polarity of the phase was measured according to Rohrschneider. The determination of the phase transition temperatures using the capacity factor in the heating and cooling cycles showed that the liquid crystal can be supercooled.

INTRODUCTION

Rod-shaped and polymeric liquid crystals of various structures are being widely investigated and used as stationary phases in gas chromatography (GC). Little information is available on the properties and separation mechanisms of discotic liquid crystalline stationary phases. In 1984 Witkiewicz *et al.* [1] investigated discotic nematic triphenylene derivatives and in 1988 Zhang and Wang [2] used rufigallol hexaalkanoates.



Hexa-O-octanoyl-*scyllo*-inositol (1).

We became interested in filling this gap by studying the discogen **1**, a hexaester [3–5] of the naturally occurring *scyllo*-inositol (scyllitol)[☆☆] with an extremely wide discotic mesophase ($\Delta T \approx 120$ K), as a stationary phase in capillary GC to broaden our knowledge about the mechanisms of interaction between such a phase and various test molecules and about structure selectivities [7,8]. **1** has the following melting and clearing temperatures

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[☆] Part 66 on liquid-crystalline compounds of the Berlin research group; Part 65: K. Praefcke, B. Kohne, S. Diele, G. Pelzl and A. Kjaer, *Liq. Cryst.*, 11 (1992) 1–8.

[☆☆] *scyllo*-Inositol is one of the possible eight stereoisomers of inositol [6] having all hydroxyl groups in equatorial positions with the result of a totally flat structure.

0021-9673/92/$05.00

K → D_{ho} 79.6°C
D_{ho}→Is 119.3°C

where K indicates crystalline, D_{ho} indicates discotic hexagonal orthorhombic, and Is indicates isotropic state. Between these temperatures the compound is a discotic hexagonal orthorombic liquid crystal. Between these temperatures the compound is a discotic hexagonal orthorombic liquid crystal.

EXPERIMENTAL

The measurements were carried out using a modified gas chromatograph, GCHF 18.3 (ZWG/Chromatron), equipped with a flame ionization detector and split injector. Nitrogen was used as the carrier gas. The glass capillary column was made of soft glass (25 m × 0.25 mm I.D.). After etching with gaseous HCl and deactivating with Carbowax 20M, the capillary was coated dynamically with a solution of 10% of the liquid crystal I in dichloromethane. The efficiency of the column was 66 500 theoretical plates for *o*-methylanisole with capacity factor $k' = 2.89$.

RESULTS AND DISCUSSION

Transition temperatures

The GC determination of the transition temperatures using the k' values of methylanisoles in the heating and cooling cycles shows that the phase can be supercooled to 61.5°C (Fig. 1) and that a change of phase in the wide discotic range of temperature can be excluded, as no jumps can be observed. Comparing the transition temperatures determined by GC with the values obtained with a polarization microscope we conclude that there are higher deviations for disc- than for rod-shaped liquid crystals [7,8].

The ratio of the capacity factors at the melting point ($\Delta k'$ high) and at the clearing temperature ($\Delta k'$ relatively small) correlates with the ratio of the transition enthalpies of the phase at these temperatures, as determined by differential scanning calorimetry [5]:

K → D_{ho} $\Delta H = 43.30$ kJ/mol
D_{ho} → Is $\Delta H = 9.47$ kJ/mol

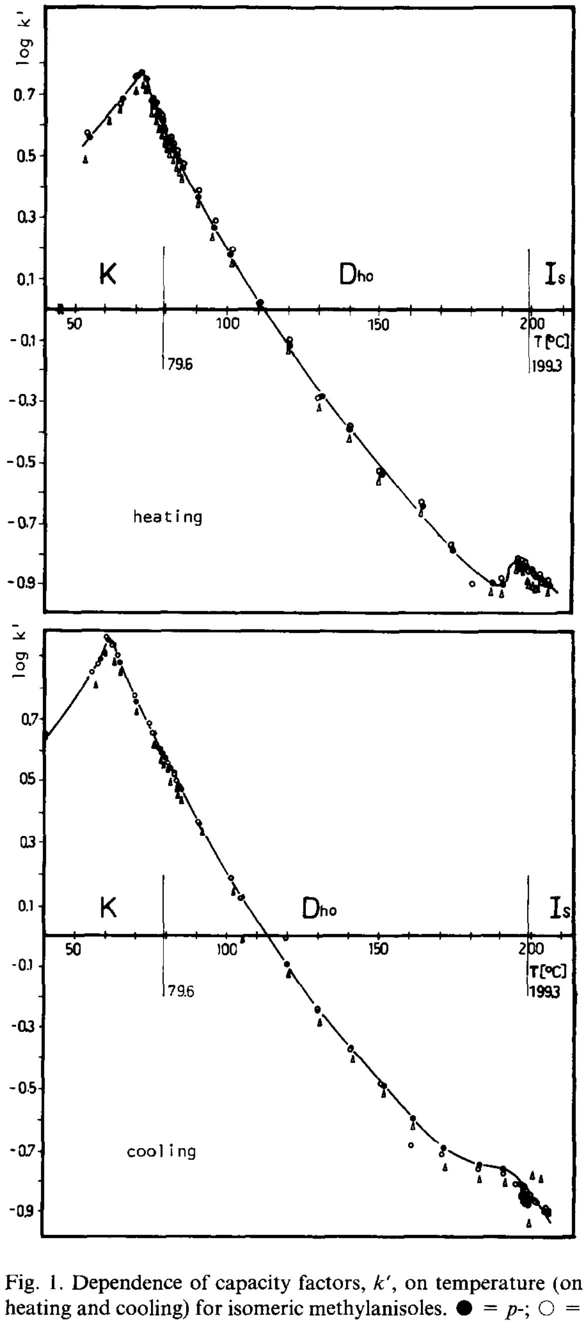

Fig. 1. Dependence of capacity factors, k', on temperature (on heating and cooling) for isomeric methylanisoles. ● = *p*-; ○ = *m*-; △ = *o*-methylanisole.

Structure selectivity and retention behaviour

Generally, stationary phases consisting of rod-shaped liquid crystals are (more or less) suitable for

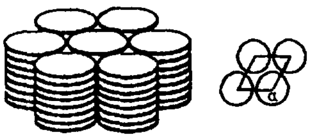

Fig. 2. Structure of a discotic columnar D_{ho} phase.

separating close-boiling geometrical isomers according to their length-to-breadth ratio, taking advantage of the ordered structure in the liquid crystalline state [7,8]. This so-called structure selectivity (α) leads to, for instance, $\alpha_{p/m} > 1$ for disubstituted benzenes.

To elucidate possible separation effects caused by the liquid crystal structure of the used discotic phase (Fig. 2), several types of substances with different molecular structures and space requirements were used. Taking into account the rule "like dissolves like", we assumed, for example, stronger interactions of the cyclohexane structures with the stationary phase than of the other substances used.

The Kováts retention indices, determined in the mesophase range, in the isotropic liquid phase and in the supercooled state, show that the elution order mainly follows the order of the boiling temperatures of the test substances (Figs. 3–8). As expected, no structure selectivity concerning the length-to-breadth ratio is observed for the isomeric disubstituted benzenes ($\alpha_{p/m} < 1$) and *cis*- and *trans*-decalines (Figs. 3 and 4). Deviations from the elution or-

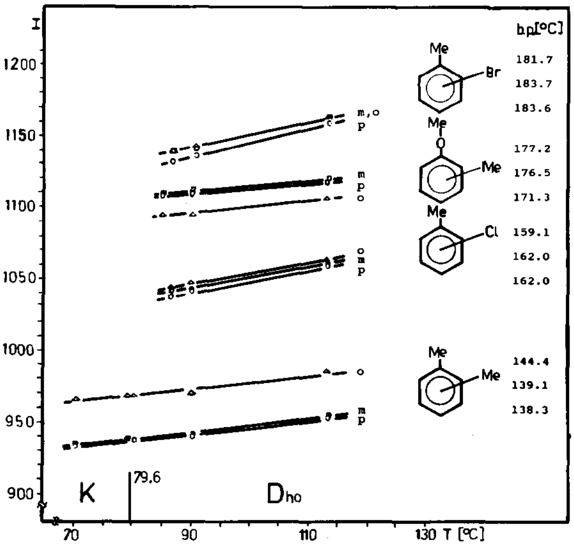

Fig. 3. Dependence of retention indices (*I*) of isomeric benzene derivatives on temperature. Me = Methyl.

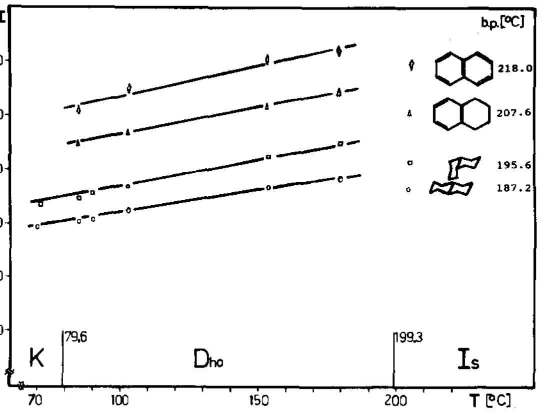

Fig. 4. Dependence of retention indices of naphthalene, tetralin and decalines on temperature.

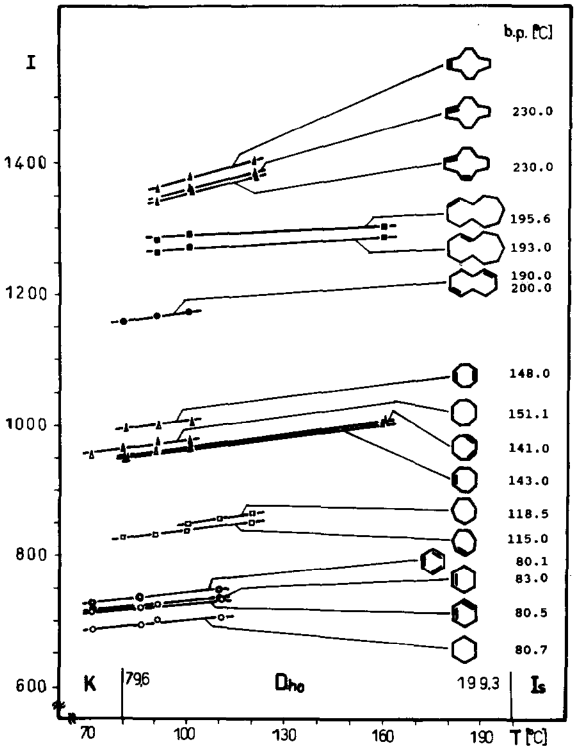

Fig. 5. Dependence of retention indices of cyclic hydrocarbons on temperature.

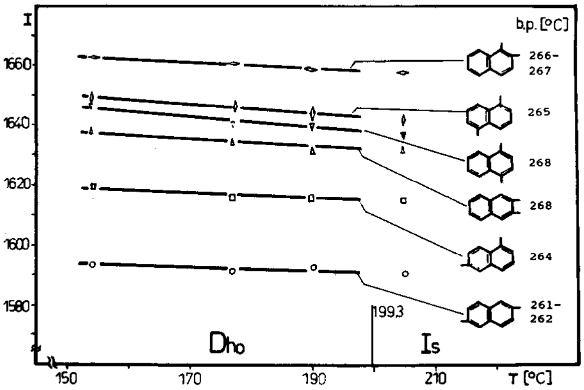

Fig. 6. Dependence of retention indices of isomeric dimethylnaphthalenes on temperature.

der according to boiling points can be observed for the elution of cyclohexane, -hexene and -hexadiene and benzene and for the pair cyclooctane (b.p. 151.1°C)/and *cis,cis*-cycloocta-1,5-diene (b.p. 148°C) (Fig. 5).

In addition to the supporting effect of the polarity of the stationary phase, the probable reason seems to be that interactions of the substrate molecules take place only within the gaps (*e.g.*, the empty spaces between the columns) of the hexagonal columnar discotic phase (Fig. 2) with parts of the radical–symmetrical arranged lateral functions of the disc, but not with or between the centres of the discotic molecules of columnar structure. Therefore, the results confirm the structural attributes of this discotic phase, discussed by Kohne and Praefcke [4,5]. These are perfect space filling (minimum dead space in the centre of the discotic molecule) and an optimum coverage of the area in the periphery of the "core", which can become slightly puckered by the radical–symmetrical arranged lateral functions.

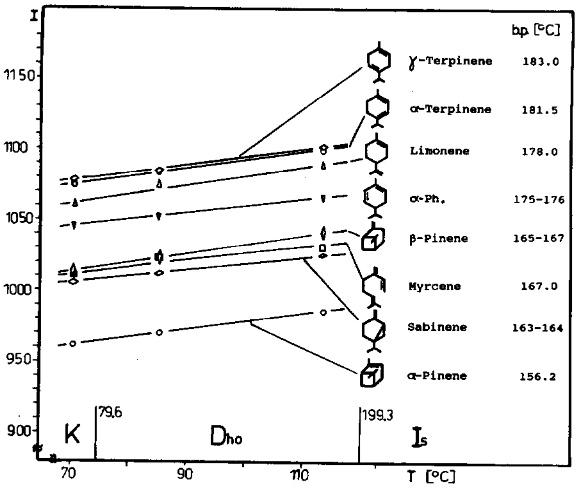

Fig. 7. Dependence of retention indices of terpenes on temperature. α-Ph = α-phellandrene.

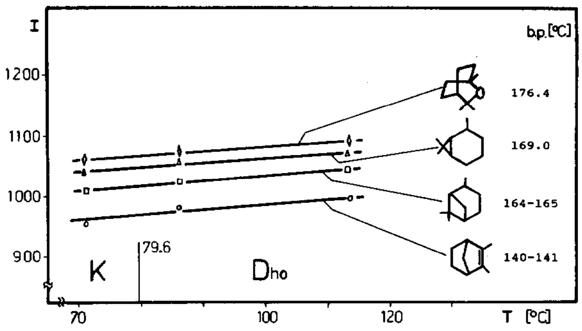

Fig. 8. Dependence of retention indices of 1,8-cineole, carane, pinane and santene on temperature.

This interaction characteristic would explain the retention of the six-membered hydrocarbons, where the flatter cyclohexadiene (b.p. 80.5°C) is eluted after cyclohexane (b.p. 80.7°C) and nearly co-eluted with the higher boiling cyclohexene (b.p. 83.0°C). The lowest boiling benzene with the flattest structure is eluted last. This can also explain the lack of selectivity of the discotic phase concerning the length-to-breath ratio (*e.g.*, xylenes). The dimethylnaphthalenes (Fig. 6) are eluted as on normal low-polarity stationary phases [9,10].

Unexpectedly, the *o*-halotoluenes with the lowest boiling temperatures are eluted after or together with the corresponding *meta* isomers (Fig. 3). Comparing our results with the measurements of Witkiewicz *et al.* [1], we find a corresponding elution order of the test substances used in both instances. The elution of *n*-nonane before cyclooctane, considered by Witkiewicz *et al.* to characterize their discotic phases and for comparison also tested in our measurements, seems to be normal. It follows the boiling points and the rules of GC polarity established by Schomburg [11].

In general, the explanation of the retention mechanism given by Witkiewicz *et al.* does not contradict our suggestions, because the structures of the investigated discotic stationary phase differ considerably.

Polarity

The polarity values of **I** were determined according to Rohrschneider: benzene, x = 0.85; ethanol, y = 1.53; 2-butanone, z = 1.23; nitromethane, u = 1.64; pyridine, s = 1.30. In the discotic hexagonal columnar state, the phase is of low polarity like a methylsilicone substituted by a small proportion of phenyl groups.

CONCLUSIONS

Taking into consideration the structure of the investigated *scyllo*-inositol derivative [4,5], which shows perfect space filling in the centre of the molecule and an optimum coverage of the area in the periphery of the "core" which can become slightly puckered by radical–symmetrical arranged lateral functions (yielding a "flexible super disc"), we can conclude that the interactions of the test compounds take place favourably within the empty spaces between the columns of the columnar structure with random parts of the lateral substituents but not between the centres of the discotic molecules.

REFERENCES

1 Z. Witkiewicz, J. Szulz and R. Dabrowski, *J. Chromatogr.*, 315 (1984) 145.
2 P. Zhang and L. Wang, *Kexue Tongbao (Foreign Lang. Ed.)*, 33 (1988) 1171; *Chem. Abstr.*, 110 (1989) 105610s.
3 B. Kohne, K. Praefcke, W. Stephan and P. Nürnberg, *Z. Naturforsch.*, B: Chem. Sci., 40 (1985) 981.
4 B. Kohne and K. Praefcke, *Chem. Ztg.*, 109 (1985) 121.
5 B. Kohne and K. Praefcke, *Angew. Chem.*, 96 (1984) 70; *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 82.
6 Th. Pasternak, *Les Cyclitols*, Hermann, Paris, 1962.
7 Z. Witkiewicz, *J. Chromatogr.*, 251 (1982) 311.
8 G. Kraus, *Habilitation*, Martin-Luther-Universität Halle, Halle, 1983.
9 W. Engewald, *Habilitation*, Universität Leipzig, Leipzig, 1978.
10 F. Hahne, *Dissertation*, Martin-Luther-Universität Halle, Halle, 1990.
11 G. Schomburg, *J. Chromatogr.*, 23 (1966) 18.