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## Evaluation of shape selectivity of liquid crystals in capillary gas chromatography

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### Abstract

The shape selectivity of 4-octoxyphenyl 4-pentoxybenzoate as a liquid crystal stationary phase was monitored in the separations of *o*-, *m*- and *p*-xylene and *cis*- and *trans*-1,2-dimethylcyclohexane and -decalin in the temperature range 54–83°C with both increasing and decreasing column temperatures in 5°C steps. Retention indices were used to study the dependence of retention on temperature. The influence of temperature on the shape selectivity of the liquid crystal stationary phase was measured as the dependence of  $\log \alpha$  on  $1/T$ . The use of saturated cyclic compounds for measuring the shape-selective properties of a liquid crystal stationary phase is superior to the use of xylenes as they are less polar than xylenes and their selectivity factors are more sensitive to selectivity changes.

### 1. Introduction

The exceptional separating properties of liquid crystals as stationary phases in gas chromatography (GC) were first described in the 1960s [1,2], and the GC separation of various samples on liquid crystal stationary phases has been reviewed [3,4]. The use of liquid crystals as stationary phases in capillary GC is extremely advantageous because in this technique the "shape selectivity" of the stationary phase is combined with the high efficiency of the capillary column [3,4]. The shape selectivity of these stationary phases is usually determined with respect to samples whose molecules differ in shape whereas the other factors that determine the retention of sample molecules are very similar; *m*- and *p*-xylene are usually used to test the liquid crystal shape selectivity [3,4]. How-

ever, the polarities of *m*- and *p*-xylene differ, which can substantially influence their retention on polar liquid crystal stationary phases. It is clear that for the determination of shape selectivity non-polar solutes differing in shape should be used.

The aim of this work was to evaluate the shape selectivity of a glass capillary column coated with a 4-octoxyphenyl 4-pentoxybenzoate liquid crystal stationary phase for separating *o*-, *m*- and *p*-xylene and stereoisomers of 1,2-dimethylcyclohexane and decalin.

### 2. Experimental

GC was performed with a Fractovap 2350 gas chromatograph (Carlo Erba, Milan, Italy) equipped with an all-glass inlet split injection port and using flame ionization detection (FID). Hydrogen was used as the carrier gas at a flow-

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rate of 40 cm/min. Signals were registered with an HP 9366 integrator and via Peak 96 were sent to an IBM-compatible PC where they were evaluated with HP CHEM software (all products were purchased from Hewlett-Packard, Waldbronn, Germany). For computer reconstruction of chromatograms unpublished software was used [5].

A capillary column was prepared from soft glass using a published procedure [6]. The column was 30 m  $\times$  0.30 mm I.D., with a 0.12- $\mu$ m stationary phase film thickness. 4-Octoxyphenyl 4-pentoxibenzoate was used as a liquid crystal stationary phase, exhibiting transition temperatures of Cr-53-N-85-Is (crystalline nematic isotropic).

The shape selectivity of the prepared capillary column was measured for the separation of mixtures of  $C_7$ – $C_{12}$  *n*-alkanes, *o*-, *m*- and *p*-xylene and *cis*- and *trans*-1,2-dimethylcyclohexane and -decalin. The shapes of these molecules

are shown in Fig. 1. The gas hold-up time was measured using methane.

### 3. Results and discussion

The shape selectivity of 4-octoxyphenyl 4-pentoxibenzoate was measured from the data obtained by separating a test sample isothermally at the temperatures of its transition state with both increasing (54  $\rightarrow$  83°C) and decreasing (83  $\rightarrow$  54°C) temperatures in 5°C increments. In Fig. 2, the chromatogram obtained in the separation of a test sample at 83°C is shown. The shape selectivity of the liquid crystal is very high, as *m*- and *p*-xylene are separated very well. However, some problems occurred with the separation of *p*- and *o*-xylene. *Cis*- and *trans*-1,2-dimethylcyclohexane and -decalin were separated without any overlapping problems.

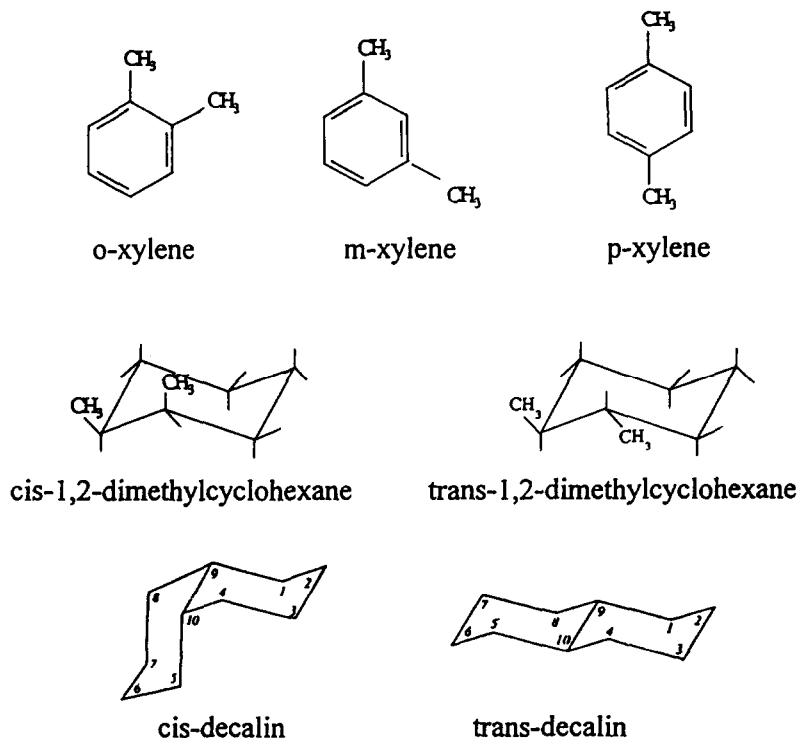


Fig. 1. Molecular shapes of the isomers tested.

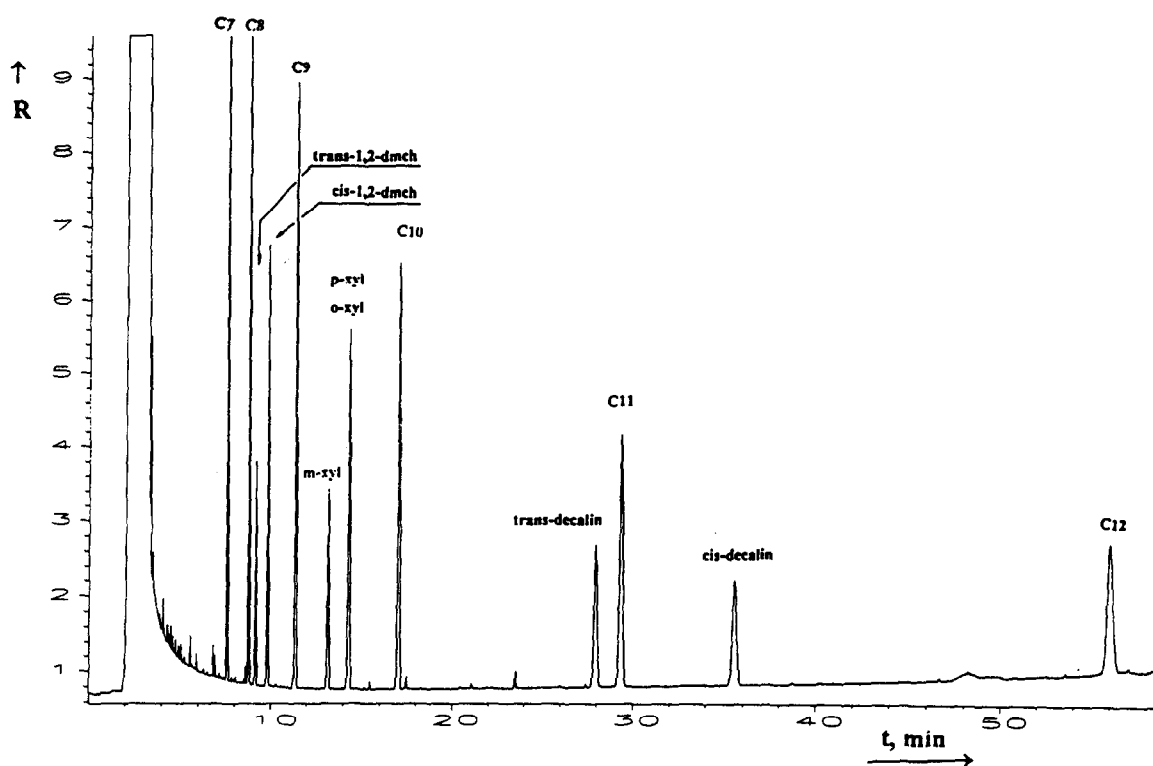


Fig. 2. Separation of a test sample at 83°C. C<sub>8</sub>–C<sub>12</sub> = *n*-alkanes; 1,2-dmch = 1,2-dimethylcyclohexane; xyl = xylene.

Retention indices ( $I$ ) were used to monitor the dependence of retention on temperature (Figs. 3 and 4). Retention indices were measured with a repeatability of  $\pm 1$  index units. Their reproducibility was not measured as this depends on, *inter alia*, the film thickness of the stationary phase. Regression analysis of the dependences shown in Figs. 3 and 4 showed that the retention at any chosen temperature in the interval 54–83°C varies substantially depending on the temperature change mode. The most pronounced difference was found for *cis*- and *trans*-decalin, as follows also from comparison of the slopes of lines for these compounds in Figs. 3 and 4. The dependence of the polarity of the liquid crystal stationary phase on temperature in the range considered is less pronounced than the temperature dependence of the shape selectivity as the

difference in the slopes of the corresponding lines for the xylenes is smaller than that for the decalins in Figs. 3 and 4.

The temperature dependence of the shape selectivity of the liquid crystal stationary phase was further monitored by determining the selectivity factor ( $\alpha$ ) using the dependence of  $\log \alpha$  on  $1/T$ , as shown in Fig. 5. The semi-logarithmic dependence of the shape selectivity factor ( $\log \alpha$ ) on  $1/T$  was derived from the equation used for the calculation of partial molar free energies of solution [7]:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

and the equation used for the calculation of the difference in the partial molar free energies for solutes  $i$  and  $j$  from chromatographic data [8]:

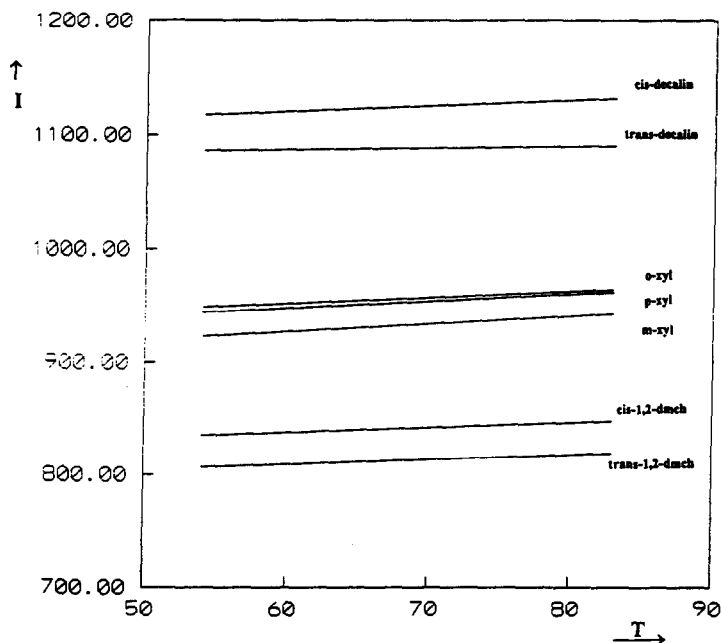


Fig. 3. Dependence of retention indices ( $I$ ) on temperature ( $T$ ) in the temperature-increasing mode (54 → 83°C). Abbreviations as in Fig. 2.

$$\Delta(\Delta G_{j,i}) = -RT \ln \alpha \quad (2)$$

After rearrangement of these equations we obtain

$$\ln \alpha = -\frac{\Delta(\Delta H_{j,i})}{RT} + \frac{\Delta(\Delta S_{j,i})}{R} \quad (3)$$

where  $R$  is the gas constant and  $\Delta(\Delta H_{j,i})$  and  $\Delta(\Delta S_{j,i})$  are the enthalpy and entropy differences of solutes  $i$  and  $j$  differing in shape, respectively.

An increase in the temperature of the liquid crystal stationary phase diminishes its shape selectivity as a result of the decrease in the degree of molecular ordering of liquid crystals with temperature.

From Eq. 3 and Fig. 5, it follows that the dependence of the shape selectivity of the stationary phase on temperature can easily be studied using the enthalpic  $\Delta(\Delta H_{j,i}/R)$  term. For example, for the lines shown in Fig. 5, the following slopes  $[\Delta(\Delta H_{j,i}/R)]$  were found by regression analysis:  $-2.93$  for *cis*- and *trans*-1,2-

dimethylcyclohexane;  $-2.73$  for *p*- and *m*-xylene;  $-2.11$  for *o*- and *p*-xylene; and  $-3.34$  for *cis*- and *trans*-decalin. From these data, it follows that *cis*- and *trans*-1,2-dimethylcyclohexane and -decalin are better solutes for measuring the stationary phase shape selectivity than xylenes, as their slopes  $\Delta(\Delta H_{j,i})/R$  are substantially higher.

#### 4. Conclusions

The shape selectivity of a liquid crystal stationary phase can be successfully monitored using either *o*-, *m*- and *p*-xylene or *cis*- and *trans*-1,2-dimethylcyclohexane and -decalin. The use of cyclic compounds for measuring the shape-selective properties of a liquid crystal stationary phase is superior to the use of xylenes as saturated cyclic compounds are less polar than xylenes and their shape selectivity factors are more sensitive to stationary phase shape-selectivity changes.

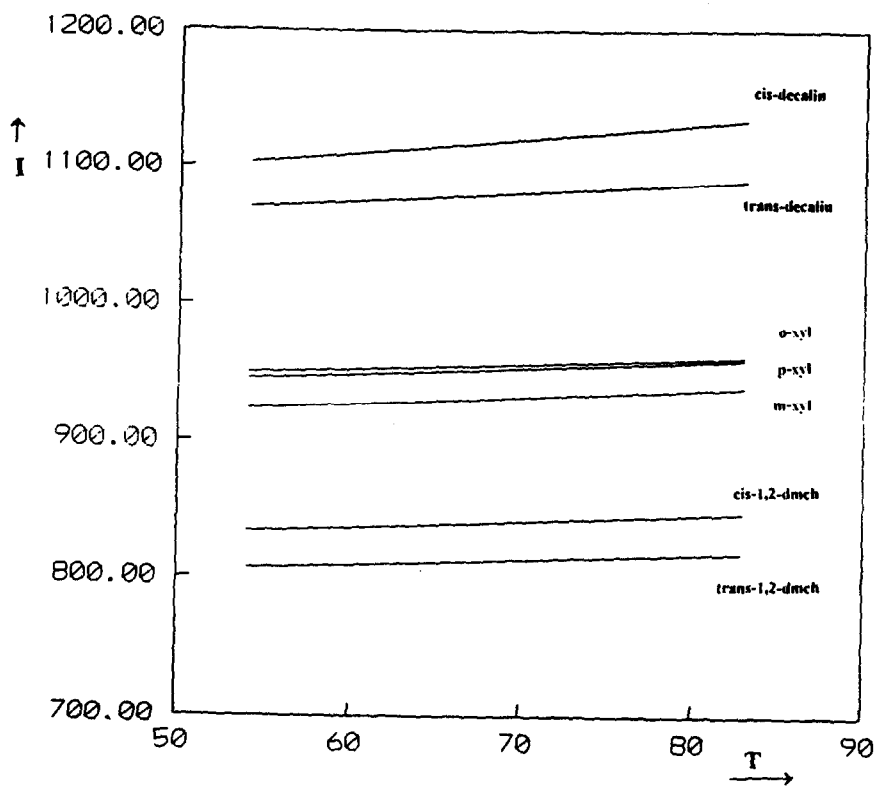


Fig. 4. Dependence of retention indices ( $I$ ) on temperature ( $T$ ) in the temperature-decreasing mode (83→54°C). Abbreviations as in Fig. 2.

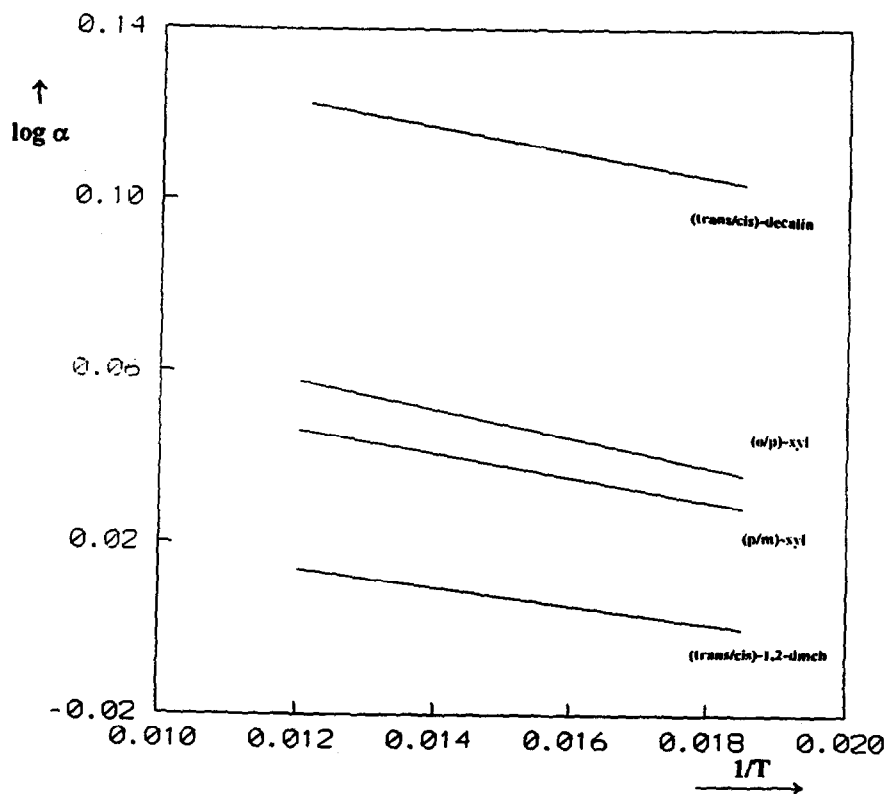


Fig. 5. Dependence of  $\log \alpha$  on  $1/T$  in the temperature-increasing mode (54→83°C). Abbreviations as in Fig. 2.

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