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High-resolution gas chromatography with liquid crystal glass capillaries

XII^a. Separation of isomeric C₁₇–C₁₈ *n*-alkenes

L. SOJÁK*, I. OSTROVSKÝ and R. KUBINEC

Chemical Institute, Komenský University, Mlynská dolina, 842 15 Bratislava (Czechoslovakia)

and

G. KRAUS and A. KRAUS

Department of Chemistry, Martin-Luther University, 4020 Halle/Saale (G.D.R.)

ABSTRACT

The separation of isomeric C₁₅–C₁₈ *n*-alkenes and *n*-alkanes was studied on high-efficiency glass capillary columns coated with liquid crystalline 4-*n*-propylbenzoic acid–4',5-*n*-hexyl pyrimidin-2-yl phenyl ester. The separation was optimized with respect to the stationary phase film thickness and column temperature. The separation system permits better and faster separations of isomeric *n*-heptadecenes and *n*-octadecenes compared with previously obtained separations on non-mesogenic and mesogenic stationary phases.

INTRODUCTION

Interest in the detailed analysis of isomeric compounds, including those with very similar physicochemical properties, is directed to higher-molecular-weight compounds. The possibilities of utilizing capillary gas chromatography with non-mesogenic polar or non-polar stationary phases for the complete separation of higher-molecular-weight isomeric *n*-alkenes (up to C₁₈) are limited [1–3]. The number of theoretical plates required for the separation of the pairs of positional isomers was up to 10⁷ plates. Most difficult to separate are positional isomers with the double bond in the middle of the carbon chain, and *trans* isomers are more difficult to separate than *cis* isomers. With a shift of the position of the double bond from the middle to the end of the carbon chain the separation of pairs of neighbouring positional isomers becomes easier, but geometric isomers cause complications because they elute between them.

Separation systems combining the high efficiency of capillary columns with the isomeric selectivity of liquid crystals as stationary phases permit the separation of complex mixtures of isomers including those with very close physicochemical

^a For Part XI, see ref. 7.

properties [4,5]. In a previous study [6] the separation of isomeric C_{15} – C_{17} *n*-alkenes on liquid crystalline 4-methoxy-4'-ethoxyazoxybenzene (MEAB) as stationary phase was investigated. In glass capillary columns with an efficiency of $2 \cdot 10^5$ plates the resolution of all isomeric *n*-pentadecenes and *n*-hexadecenes at one column temperature was achieved; the resolution of isomeric *n*-heptadecenes required separation at two column temperatures.

Recently, suitable separation properties of a new liquid crystal, 4-*n*-propylbenzoic acid-4',5-*n*-hexylpyrimidin-2-yl phenyl ester (PrBHP), were found [7]. Therefore, the possibilities of using this liquid crystal as a stationary phase in capillary gas chromatography for the separation of isomeric *n*-heptadecenes and especially the *n*-octadecenes were investigated.

EXPERIMENTAL

As a model mixture, the products of the catalytic dehydrogenation of C_{15} – C_{18} *n*-alkanes, in which the *n*-alkene content was enriched by displacement liquid chromatography, were used. They contain a mixture of 60 possible isomeric C_{15} – C_{18} *n*-alkenes and the corresponding *n*-alkanes.

The gas chromatographic measurements were carried out on a Carlo Erba GI 452 gas chromatograph with a flame ionization detector. Model mixtures were separated in glass capillary columns with liquid crystalline PrBHP, having a mesophase range of 65–170°C and possible supercooling to about 28°C, as the stationary phase. The capillary columns were prepared from Unihost-glass (Kavalier, Teplice, Czechoslovakia). After etching with gaseous hydrogen chloride the glass capillaries were coated dynamically with a solution of PrBHP in dichloromethane.

For the determination of the PrBHP film thickness, statically coated columns were used, the density of stationary phase being considered to be unity. The effective efficiency of a prepared column of 90 m \times 0.25 mm I.D. for the compounds studied was about 200 000 plates (for a film thickness of 0.03 μ m, a column temperature of 117°C and an average linear velocity of hydrogen carrier gas of 30 cm s⁻¹). Retention indices of *n*-alkenes were measured with a standard deviation of 0.2 i.u.

RESULTS AND DISCUSSION

The use of liquid crystals as stationary phases expands the retention range of *n*-alkene isomers by about 100% in comparison with non-mesogenic phases [8] because their selectivity and the retention of positional isomers increase in the same direction, the corresponding possibilities of the separation thus being easier. Liquid crystals also permit the utilization of different zig-zag carbon chain-end orientations of isomers, which can be in the direction or off the direction of the molecular axis, for the separation of positional isomers with a central position of the double bonds because of the different length to breadth ratios of the molecules. The different temperature dependence of the retentions of the individual isomers on liquid crystals simplifies temperature optimization of the separation mainly for the geometric isomers. All these effects are enhanced with increasing isomer selectivity of the liquid crystal. Therefore, the separation of isomeric C_{15} – C_{18} *n*-alkenes on liquid crystalline PrBHP, which has an isomer selectivity similar to that of the most selective liquid crystal MEAB [6] but

the advantage of a larger temperature range of the mesophase, was studied. Moreover, the different chemical structure of new liquid crystal may have a different influence to MEAB on the mutual separation of geometric isomers and the separation of complex isomeric mixtures.

The isomer selectivity of liquid crystals increases with decrease in the mesophase temperature. At the same time, with a decrease in temperature the differences in the retentions of the positional isomers increase. Therefore, the use of a thin film of mesogenic stationary phases for the separation of C_{15} – C_{18} *n*-alkenes was studied. It results in a higher column efficiency and faster separations.

The dependence of the effective efficiency of the prepared glass capillary columns on the PrBHP film thickness is shown on Fig. 1, which demonstrates that the efficiency of the column increases significantly with decreasing PrBHP film thickness. For thin films in range 0.002–0.030 μm the efficiency of a 90 m \times 0.25 mm I.D. column at 117°C is about 200 000 effective plates. This value is comparable to that of the MEAB column which was used previously for the separation of isomeric C_{15} – C_{17} *n*-alkenes [6]. In the temperature range 110–130°C the efficiency of the column is almost the same; at 100°C it decreases by about 10%.

Using thin PrBHP films, the influence of the absorption–adsorption mechanism of the retention on the separation of isomeric *n*-alkenes becomes significantly higher [6]. It influences the character of the dependences of the selectivity factor α (relative retention) and the retention indices of isomers on the PrBHP film thickness and also the dependence of the retention indices of isomeric *n*-alkenes on the column temperature.

The dependence of the selectivity factors of neighbouring positional and corresponding geometric isomers of C_{15} – C_{18} *n*-alkenes on the number of carbon

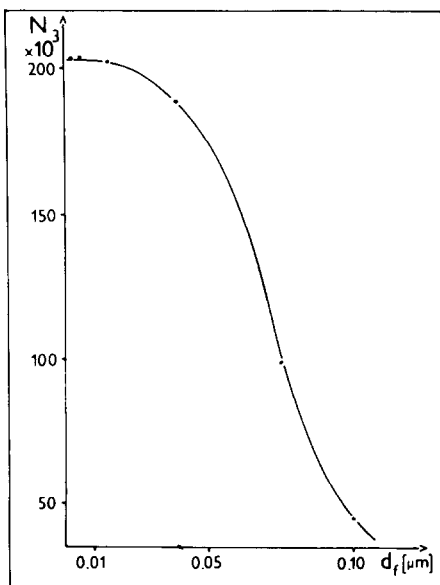


Fig. 1. Dependence of effective efficiency on the film thickness for PrBHP in a 90 m \times 0.25 mm I.D. column at 117°C and $u^s = 30 \text{ cm s}^{-1}$ (hydrogen) for *n*-alkenes with $k' \geq 2.4$.

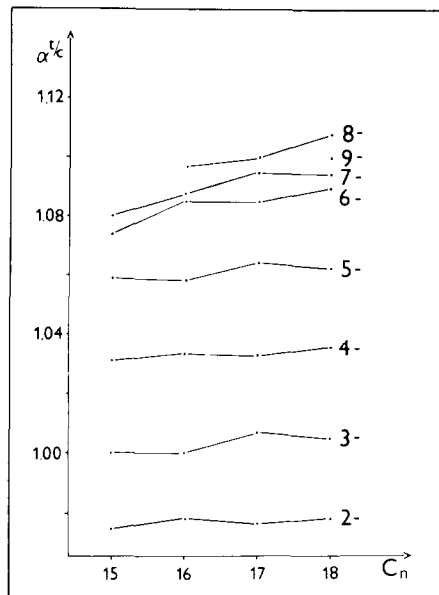
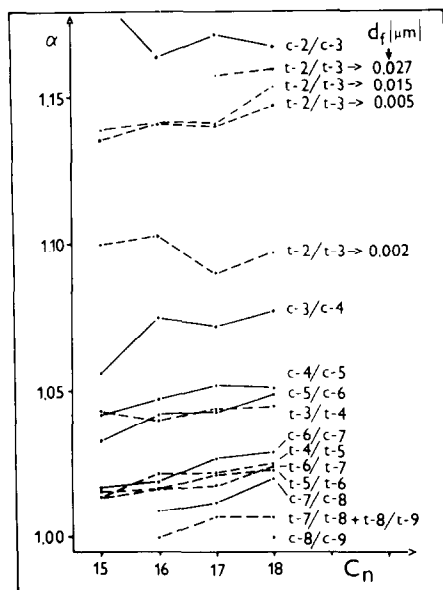


Fig. 2. Dependence of the selectivity factor α on the number of carbon atoms for positional C_{15} – C_{18} *n*-alkene isomers on PrBHP at 117°C and on film thickness.

Fig. 3. Dependence of the selectivity factor α on the number of carbon atoms for geometric C_{15} – C_{18} *n*-alkene isomers on PrBHP at 117°C.

atoms at 117°C for the PrBHP column are shown in Figs. 2 and 3. The dependences are characterized by alternation of the α -values with the number of carbon atoms and with the position of the double bond [6]. For pairs of *trans*-2- –*trans*-3-*n*-alkene the dependence of the α -values on the film thickness is also illustrated (Fig. 2). It is shown that the selectivity factors of positional isomers for a given range of thin films increase with increasing film thickness of PrBHP.

The dependence of the retention indices of the isomeric *n*-octadecenes on the PrBHP film thickness at 117°C is shown in Fig. 4. For the thinnest film ($d_f = 0.002 \mu\text{m}$) the retention range of the isomeric *n*-octadecenes is the smallest. With increase in the film thickness to $0.005 \mu\text{m}$ the retention range of the isomers increases significantly, but further increases in film thickness have little effect. The influence of film thickness on the separation of isomers is most significant for the pairs *trans*-2- –*cis*-2- and *trans*-6- –*cis*-4-octadecenes, because the first pair is not separated on the thinnest and the second on thicker films of PrBHP. This result shows that with increase in PrBHP film thickness the retention of *cis* isomers in comparison with *trans* isomers of the *n*-alkenes increases.

The dependence of the retention indices of the isomeric *n*-octadecenes on column temperature for PrBHP is shown in Fig. 5. With decreasing temperature the range of isomer retention increases, leading to changes in mutual retention mainly of the geometric isomers, which becomes most evident for the pairs *trans*-2- –*cis*-2- and *trans*-6- –*cis*-4-octadecenes, which have similar retentions. This is a similar situation to

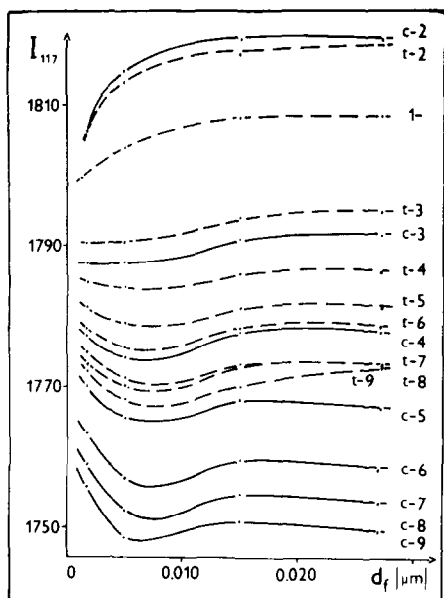


Fig. 4. Dependence of retention indices of isomeric *n*-octadecenes on the film thickness of PrBHP at 117°C.

that of the influence of increasing film thickness of PrBHP, with increasing column temperature the retention of *cis* isomes becoming relatively higher in comparison with those of *trans* isomers. The temperature coefficients of the retention indices of *n*-alkene

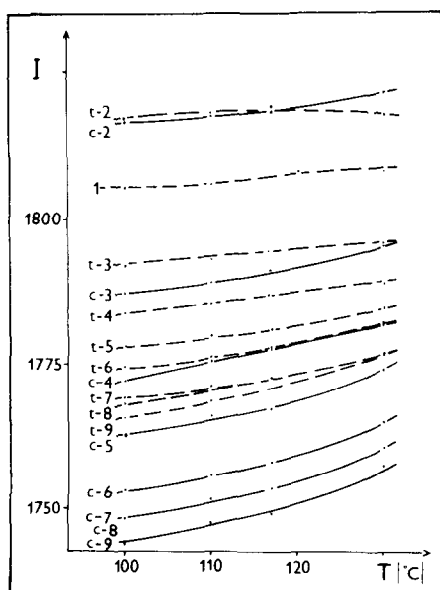


Fig. 5. Dependence of retention indices of *n*-octadecenes on column temperature for a film thickness of PrBHP of 0.015 μm .

isomers depend on the film thickness of PrBHP and on the selected temperature range of the mesophase. These values are nearly the same as those found on MEAB [6] using comparable conditions.

These dependences were utilized for the optimized separation of isomeric *n*-heptadecenes and *n*-octadecenes. A column of 90 m \times 0.25 mm I.D., a film thickness of 0.005 μm and a column temperature of 117°C were established as optimum.

Separation of isomeric *n*-heptadecenes

In previous work [6] with 80 m \times 0.25 mm I.D. capillary column coated with MEAB and having an efficiency $N = 215\,000$ plates for $k' = 5$ at 85°C, separation of the pair *cis*-3- –*trans*-4-heptadecene and that of *cis*-4- –*trans*-8-heptadecene at 105°C were not obtained. As is shown in Fig. 6, using a column with PrBHP the separation of all isomeric *n*-heptadecenes and *n*-heptadecane was achieved at one temperature and the time of separations was drastically reduced in comparison with that on an MEAB column. This result not only reflects the influence of small differences between the isomer selectivities of PrBHP and MEAB but also their different polarities. With PrBHP column a 50% thinner film and higher column temperature were used, thus resulting in not only a faster separation but also a positive shift of the retention of *cis* in comparison with *trans* isomers.

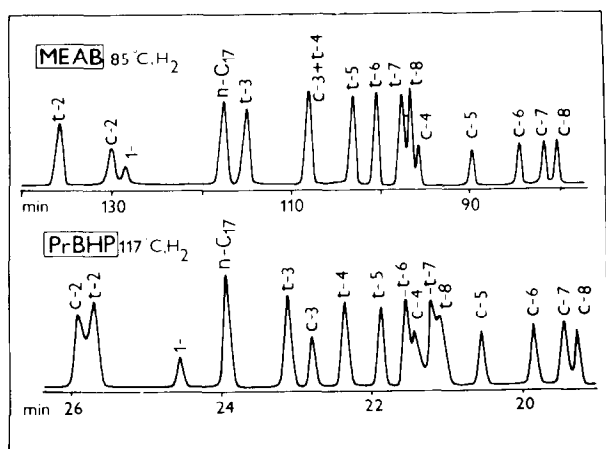


Fig. 6. Separation of isomeric *n*-heptadecenes in a 90 m \times 0.25 mm I.D. column with PrBHP (film thickness 0.005 μm) at 117°C and $u^s = 30\text{ cm s}^{-1}$ (hydrogen).

As is obvious from the dependence of the α -values on the position of the double bond for neighbouring positional heptadecene *trans* isomers (Fig. 7), the value of α for *trans*-7- –*trans*-8-heptadecene on PrBHP is nearly the same as that found on the non-mesogenic phase Apolan 87. This value, which is lower than expected, is in good agreement with the similar lower α -values for *trans*-3- –*trans*-4-nonene [7] and *trans*-5- –*trans*-6-tridecene [8] obtained on other liquid crystals. For these pairs of *trans* isomers the same situation is repeated every fourth carbon atom in the chain when the chains on each side on the double bond have the same length but their orientations are different (along or off the axis of the molecule). In these instances the previously

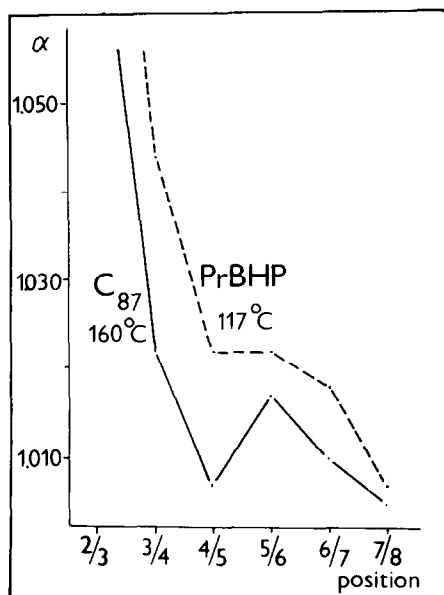


Fig. 7. Dependence of the selectivity factor α on the position of the double bond for neighbouring isomeric *trans*-heptadecenes on PrBHP at 117°C and on Apolan 87 at 160°C.

formulated rule [9] that the *trans* isomers with an even number of carbon atoms and with an even position of double bond have a higher retention, as follows from the decrease in retention with a shift of the double bond from the end to the middle of the carbon chain, is not valid. The deviation from this rule increases with decreasing length of the carbon chain of *n*-alkenes.

Separation of isomeric *n*-octadecenes

In Fig. 8 the separation of isomeric *n*-octadecenes obtained on a 200 m \times 0.25

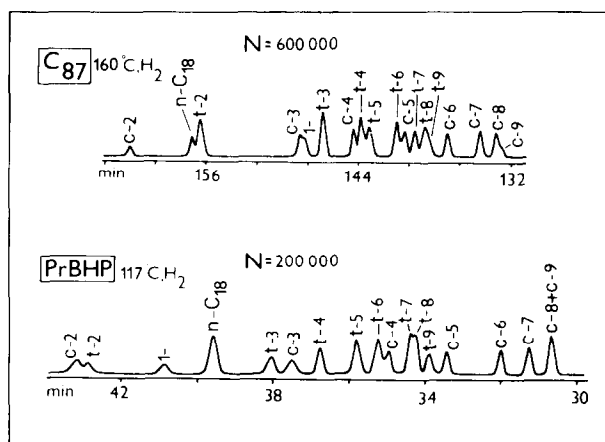


Fig. 8. Separation of isomeric *n*-octadecenes in a 90 m \times 0.25 mm I.D. column with PrBHP (film thickness 0.005 μ m) at 117°C and $u^s = 30$ cm s⁻¹ (hydrogen).

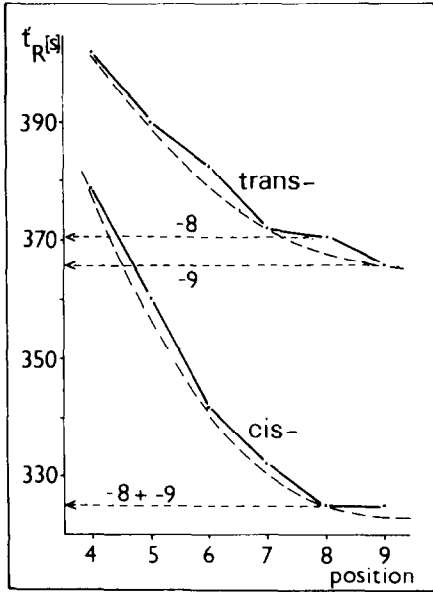


Fig. 9. Dependence of the retention of *cis*- and *trans*-positional isomers of *n*-octadecenes on the position of the double bond on PrBHP.

TABLE I

RETENTION INDICES AND THEIR TEMPERATURE COEFFICIENTS OF *n*-HEPTADECENES AND *n*-OCTADECENES ON PrBHP AT 117°C

dI/dT values were measured within the temperature range 117–130°C and the film thickness of PrBHP was 0.005 μm .

<i>n</i> -Alkene	C ₁₇		C ₁₈	
	I_{117}	dI/dT	I_{117}	dI/dT
<i>cis</i> -9-	—	—	1748.6	0.56
<i>cis</i> -8-	1653.3	0.43	1748.6	0.56
<i>cis</i> -7-	1656.0	0.39	1752.3	0.53
<i>cis</i> -6-	1660.1	0.39	1756.9	0.52
<i>cis</i> -5-	1667.2	0.39	1756.7	0.43
<i>cis</i> -4-	1675.1	0.40	1774.3	0.40
<i>cis</i> -3-	1687.8	0.31	1787.9	0.24
<i>cis</i> -2-	1713.2	0.35	1814.7	0.09
<i>trans</i> -9-	—	—	1768.4	0.37
<i>trans</i> -8-	1672.8	0.31	1770.4	0.36
<i>trans</i> -7-	1674.2	0.30	1771.1	0.31
<i>trans</i> -6-	1677.1	0.31	1775.8	0.28
<i>trans</i> -5-	1680.3	0.32	1779.1	0.26
<i>trans</i> -4-	1684.7	0.33	1784.1	0.21
<i>trans</i> -3-	1691.0	0.25	1790.7	0.14
<i>trans</i> -2-	1711.8	0.26	1813.5	0.00
1-	1703.2	0.24	1804.4	0.10

mm I.D. column Apolan 87 with an efficiency of about 600 000 effective plates [3] is compared with that achieved on the PrBHP column. With the latter column the separation of all isomers except the pair *cis*-8--*cis*-9-octadecene was achieved in a shorter time.

As is obvious from the dependence of the retention on the position of the double bond for *cis*- and *trans*-positional *n*-octadecene isomers shown in Fig. 9, *trans*-8-octadecene in connection with the alternation of retention on liquid crystal has about a 2 i.u. higher retention. This permits the quantitative separation of *trans*-9- from *trans*-8-octadecene, which is the most difficult separated pair of all isomeric pairs of *n*-alkenes up to C₁₈ (on Apolan 87, Apiezon L and Carbowax 20M, $N_{\text{req}} = 10^7$ plates). In Fig. 3 this effect is expressed by the anomalously higher α -value of 8-octadecenes in comparison with 9-octadecenes. For the pair *cis*-8--*cis*-9-octadecene the latter has an increased retention on the liquid crystal but it is not so high that the isomer is eluted after *cis*-8-octadecene as was found with *cis*-6--*cis*-7-tetradecene [9]. This effect requires a liquid crystal that is more selective than PrBHP and MEAB, which is not available at present.

Retention indices and their temperature coefficients for isomeric *n*-heptadecenes and *n*-octadecenes on PrBHP measured on-column with a film thickness of 0.005 μm in the temperature range 117–130°C are given in Table I.

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