

High-resolution gas chromatography with liquid crystal glass capillaries

XI^a. Separation of isomeric C₈ and C₉ hydrocarbons

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ABSTRACT

Pyrimidine mesogenic stationary phases were investigated for the separation of geometric and positional isomers and diastereomers of hydrocarbons. Owing to the high selectivity of the stationary phase, combined with a suitable mesogenic temperature range and the efficiency of capillary columns, enhanced separations of C₈ and C₉ isomeric alkanes, alkenes and alkadienes could be achieved.

INTRODUCTION

The separation of lower boiling isomeric hydrocarbons using liquid crystals as stationary phases in capillary gas chromatography demands special requirements. Previously investigated selective liquid crystalline phases had too high temperatures of the mesogenic range, and some phases with a low mesogenic temperature range had too low selectivities for the separation of isomeric hydrocarbons. The highest selectivity of the liquid crystal was found on 4-methoxy-4'-ethoxyazoxybenzene (MEAB)^{1,2}, but its mesophase range is too high for the efficient separation of lower boiling hydrocarbons. Another liquid crystal, 4-*n*-pentylacetophenone-(O-4-*n*-pentyl)oxybenzoyl oxime (PBO)³, has a low mesogenic temperature range, but its selectivity with respect to the present separation problem is low.

The aim of this work was to test new pyrimidine mesophases combining high selectivity, mesogenic range at low temperatures and a high efficiency of the capillary column for the separation of isomeric C₈ and C₉ hydrocarbons.

^a For Part X, see ref. 10.

EXPERIMENTAL

The separations were carried out on 4-*n*-pentylbenzoic acid 4',5-*n*-hexylpyrimidine-2-ylphenyl ester (PBHP) having a mesophase range of 37–159°C and possible supercooling to about 25°C^{4,5}, and on 4-*n*-propylbenzoic acid 4',5-*n*-hexylpyrimidine-2-ylphenyl ester (PrBHP) having a mesophase range of 65–170°C and possible supercooling to about 28°C. After etching with gaseous hydrogen chloride, the glass capillaries were coated dynamically with a 5% (w/w) solution of liquid crystal in chloroform. The first capillary with PBHP (82 m × 0.25 mm I.D.) had an efficiency of 210 000 theoretical and 103 000 effective plates at $k = 3.1$ for *trans*-3-nonene at 33°C. The second capillary with PrBHP as the stationary phase (112 m × 0.11 mm I.D.) had an efficiency of 306 000 theoretical and 130 000 effective plates at $k = 1.83$ for 3,5-dimethylheptane at 40°C.

The phase behaviour and selectivity of the mesophase were measured using a glass column (3 m × 3 mm I.D.) packed with 10% (w/w) of stationary phase on Chromosorb W HP.

All possible isomeric *n*-nonenes and *n*-nonane, the isomeric *n*-octadienes with conjugated double bonds (isomerization product of the α,ω -octadiene) and the diastereomeric 3,4-dimethylhexanes and 3,5-dimethylheptanes served as model mixtures.

RESULTS AND DISCUSSION

Systems for the separation of lower boiling hydrocarbons should have good sorption qualities, high efficiencies and high selectivity combined with a suitable temperature of the mesogenic range. The mesogenic pyrimidine compounds mentioned above fulfilled all these requirements.

Fig. 1 shows the dependence of the specific retention volume, V_g^0 , of *n*-octane on the reciprocal temperature measured on a packed column⁶, and demonstrates that the nematic mesophase range can be extended to about 25°C by supercooling.

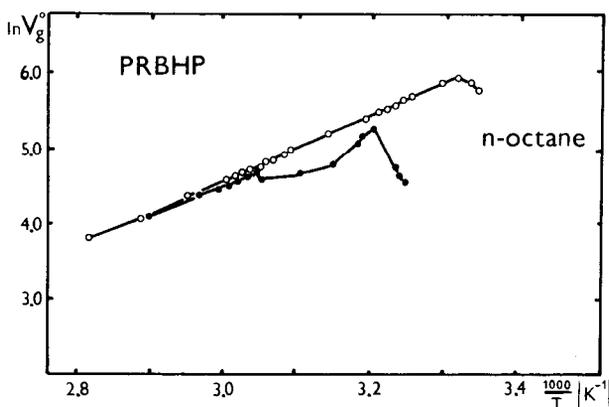


Fig. 1. Dependence of the specific retention volume of *n*-octane on the reciprocal temperature on PBHP. ● = Heating; ○ = cooling.

TABLE I
SELECTIVITY FACTORS, α , AND MESOPHASE RANGES OF DIFFERENT LIQUID CRYSTALS

Liquid crystal	$\alpha_{p-m-x}^{50^\circ}$	Mesophase range ($^\circ\text{C}$)
MEAB	1.20 ^a	70–150
PrBHP	1.16	28–170
PBHP	1.15	25–155
PBO	1.07	35–95

^a In the capillary column with a thick film of stationary phase, supercooling to 42°C was achieved².

Table I gives the selectivity factors, α , for *p*- and *m*-xylene at 50°C and mesogenic ranges for MEAB, PrBHP, PBHP and PBO liquid crystal. Just above the melting point, the selectivity factor for PBHP is 1.13, reaching a value of 1.20 on supercooling to 25°C . In comparison, MEAB can usually be supercooled only to 70°C with a corresponding α -value of 1.16²; this demonstrates that PBHP, with a favourable temperature of the mesophase range and with a selectivity comparable to that of MEAB, is more suitable for the separation of lower boiling hydrocarbons which require a lower temperature of the separation column.

The contribution of mesophase selectivity to the separation of lower boiling hydrocarbons with similar physico-chemical properties is relative small and requires its combination with the high efficiency of capillary columns for optimum separations. The pyrimidine phases permit a good coating in glass capillaries, as shown by an efficiency of more than 100 000 effective plates for C_8 and C_9 hydrocarbons.

The performance of these systems for the separation of positional, geometric and diastereomeric C_8 and C_9 hydrocarbons with similar physico-chemical properties is illustrated by the following examples.

Separation of isomeric *n*-nonenes

Fig. 2 shows the separation of all isomeric *n*-nonenes and *n*-nonane. With the

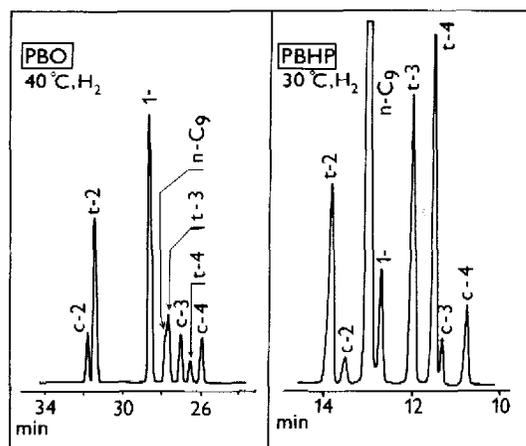


Fig. 2. Separation of isomeric *n*-nonenes and *n*-nonane on PBO and PBHP. t = *trans*; c = *cis*.

TABLE II

RELATIVE RETENTIONS OF POSITIONAL AND GEOMETRIC ISOMERIC *n*-NONENES ON PBO AND PBHP AT 40°C

Pair of <i>n</i> -nonenes	Relative retention	
	PBO	PBHP
<i>trans</i> -2— <i>trans</i> -3-	1.174	1.206
<i>trans</i> -3— <i>trans</i> -4-	1.057	1.051
<i>cis</i> -2— <i>cis</i> -3-	1.229	1.257
<i>cis</i> -3— <i>cis</i> -4-	1.055	1.078
<i>trans</i> -2— <i>cis</i> -2-	0.985	1.020
<i>trans</i> -3— <i>cis</i> -3-	1.031	1.063
<i>trans</i> -4— <i>cis</i> -4-	1.029	1.091

non-mesogenic stationary phases, incomplete separations with long separation times were obtained, in spite of the high efficiency, which could be improved by using the mesogenic stationary phase PBO⁷. The complete separation of all *n*-nonene isomers and *n*-nonane succeeded with PBHP despite the lower separation efficiency in comparison with the PBO column. Whereas on the mesogenic system with PBO, having a separation efficiency of 280 000 effective plates, the separation of these isomers is possible in 34 min, the separation system using more selective mesophase PBHP achieved an enhanced separation in about 14 min. This 2.5-fold faster separation is attributed to the higher mesophase selectivity for positional and geometric isomeric alkenes and the related more effective temperature optimization of the separation.

The higher isomeric selectivity of PBHP in comparison with PBO is obvious considering the change in the retention sequence of the pairs of *cis*-3—*trans*-4- and *cis*-2—*trans*-2-nonene isomers as the *trans* isomers have higher retention values (Table II). It also finds expression in the greater retention of *n*-nonane than 1-nonene, although the polarity of PBHP is higher than that of PBO. In both instances the measurements were carried out at the optimized temperatures and a temperature difference of 10°C gave no change in the retention sequence.

Table II also shows the lower relative retention of the *trans*-3—*trans*-4-nonene pair on PBHP in comparison with those on PBO. We observed a similar effect with the *trans*-5—*trans*-6-tridecene pair⁸. This similar situation found for *trans*-*n*-alkenes with an odd number of carbon atom and the double bond in the middle of the carbon chain is observed after a change in the carbon number in the chain by four. This is connected with the change in the orientation of the carbon chain ends for both isomers when the double bond is shifted within the carbon chain.

Separation of isomeric n-octadienes

In Fig. 3, the separation of all isomeric conjugated *n*-octadienes on the PBHP capillary is compared with the separation on a 200-m squalane capillary column (300 000 effective plates)⁹. Despite the high efficiency of the squalane column, three pairs of isomers could not be separated, whereas the use of the three times less effective PBHP capillary led to a baseline separation of all conjugated *n*-octadiene isomers, even with a shorter analysis time.

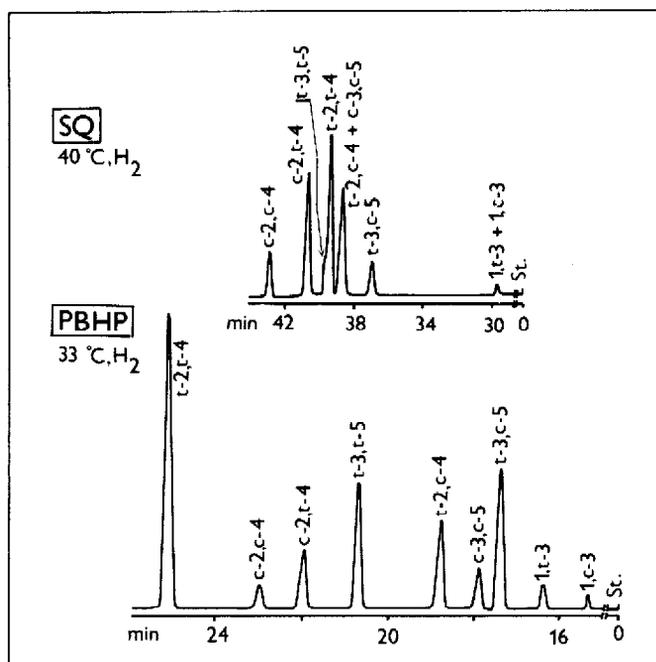


Fig. 3. Separation of isomeric conjugated *n*-octadienes on squalane and PBHP.

The retention sequence of *n*-octadiene isomers on PBHP differs from that on squalane. The peaks were identified on the basis of structure-retention correlations; for 1,*trans*-3-, *trans*-2-, *trans*-4- and *trans*-3,*trans*-5-octadienes it was confirmed by the reaction with maleic anhydride⁹. The high selectivity of PBHP is mostly obvious in the increase in the retention of *trans*-2,*trans*-4-octadiene, which is eluted as the last component of the mixture, and in the separation of 1,*trans*-3-octadiene after the 1,*cis*-3- isomer.

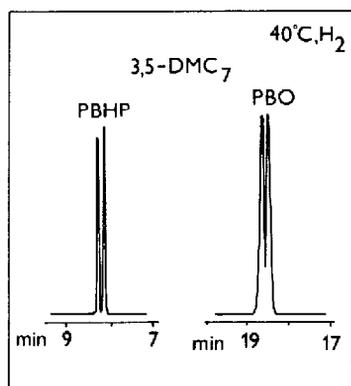


Fig. 4. Separation of diastereomeric 3,5-dimethylheptanes on PBO and PBHP.

TABLE III

RETENTION INDICES OF DIASTEREOMERIC 3,5-DIMETHYLHEPTANES ON PBO AND PBHP AT 40°C

Liquid crystal	Retention index of diastereomeric 3,5-dimethylheptanes	
PBO	811.9	813.4
PBHP	792.0	795.3

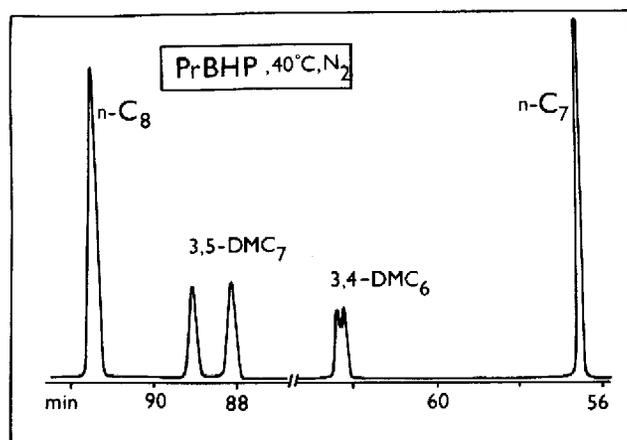


Fig. 5. Separation of diastereomeric 3,4-dimethylhexane and 3,5-dimethylheptane on PrBHP.

TABLE IV

DIFFERENCE IN RETENTION INDICES, δI , FOR DIASTEREOMERIC C₈-C₁₀ ALKANES ON THE DIFFERENT STATIONARY PHASES AT 40°C

Diastereomeric alkane	δI				
	Squalane ^b	Ucon LB ^b	SE ^{b,c}	PBO	PBHP
3,4-Dimethylhexane	0.0	0.0	0.3	0.0	0.9
3,5-Dimethylheptane	0.0	0.0	1.1	1.5	3.3
3,6-Dimethyloctane	0.0	0.0	0.8	1.1	2.4 ^a

^a Hypothetical value.^b See ref. 10.^c Silicones similar to SE-30 and SE-54.

Separation of diastereomeric C₈-C₉ alkanes

In a previous study¹⁰, the separation of diastereomeric C₈-C₁₀ alkanes on mesogenic PBO phase was investigated. Fig. 4 compares the separation of diastereomeric 3,5-dimethylheptanes on PBO and PBHP. PBO was coated on a capillary giving 280 000 effective plates, whereas the PBHP capillary had a lower efficiency of 103 000 effective plates. Fig. 4 clearly demonstrates a better and faster separation of the diastereomers on PBHP owing to its higher selectivity. At 40°C the selectivity factor α (relative retentions) of diastereomers is 1.032 on PBHP and 1.014 on PBO. The retention index difference is 3.3 i.u. on PBHP and 1.1 i.u. on PBO. A decrease in temperature to 30°C leads to $\alpha^{\text{PBHP}} = 1.049$ and $\delta I = 4.6$ i.u. The higher selectivity of PBHP is also shown in the lower retention indices of the diastereomeric 3,5-dimethylheptanes (Table III).

A higher sorption of lower boiling hydrocarbons and hence the separation of diastereomeric 3,4-dimethylhexanes was achieved on a second column with a lower phase ratio β , based on a smaller I.D. of the capillary. The separation of diastereomeric 3,5-dimethylheptanes with this separation system is longer than that on the first column (Fig. 5).

In Table IV the differences in retention indices (δI), are given for the most difficult to separate diastereomeric C₈-C₁₀ alkanes. The contribution of the liquid crystal PBHP to their separation is evident.

CONCLUSIONS

Different mesophase selectivities are shown in the different retention behaviours of positional and geometric isomers and diastereomers of hydrocarbons. With the geometric isomers of aliphatic hydrocarbons a change in their retention sequence on the different types of liquid crystals was found.

The mesogenic pyrimidine compounds PBHP and PrBHP, with high selectivity, suitable mesophase range and good efficiency of glass capillary columns, permit better and faster separations of isomeric C₈-C₉ alkenes and alkadienes and of diastereomeric alkanes compared with non-mesogenic and other mesogenic stationary phases.

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