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SHAPE SELECTIVITY OF STATIONARY PHASES FOR THE SEPARATION OF ISOMERIC HYDROCARBONS BY CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

The selectivity coefficients and retention ranges of isomeric hydrocarbons on various stationary phases were compared. The advantage of liquid crystals, used as shape-selective stationary phases in capillary gas chromatography for the separation of structural and geometric isomers and diastereoisomers of hydrocarbons, is demonstrated.

INTRODUCTION

The increasing need for the analysis of isomeric compounds necessitates the study of the separation of new systems. The separation problems are connected with the high number of theoretically possible isomers and their similar physicochemical characteristics. With the linearly increasing number of carbon atoms in the molecule the number of theoretically possible isomers increases geometrically. The physicochemical characteristics of structural isomers are, as a rule, closer when the functional group is shifted from the end to the middle of the carbon chain.

The use of classical interaction forces offers only limited possibilities for the separation of isomeric hydrocarbons with similar characteristics. For example, the separation of the neighbouring C_{15}–C_{18} *n*-alkene positional isomers with the double bond in the middle of the carbon chain on polar and non-polar stationary phases requires an efficiency of $n_{req} = 10^6$–10^7 plates[1]. This efficiency is more than one order higher than that which present separation systems are capable of.

Separation systems that combine the high efficiency of capillary columns with the shape selectivity of liquid crystals may be suitable for the separation of complex isomeric mixtures[2]. This work evaluates the possibilities of liquid crystals as shape-selective stationary phases for the separation of structural, geometric and diastereomeric hydrocarbon isomers in capillary gas chromatography, on the basis of their separation characteristics in comparison to other mesogenic and non-mesogenic stationary phases.

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EXPERIMENTAL

The separations were performed on glass capillary columns, coated with squalane, Carbowax 20M, various silicones, crown ethers and liquid crystals as the stationary phases. The preparation of the capillary columns was as described previously[1,2]. A Perkin-Elmer F-11 gas chromatograph, equipped with a flame ionization detector, was used to measure the retention characteristics of various isomeric hydrocarbons. The model mixtures comprised positional isomers of *n*-alkenes, *n*-alkynes and alkylbenzenes, geometric isomers of *n*-alkenes and *n*-alkadienes and diastereoisomeric branched alkanes.

RESULTS AND DISCUSSION

Selectivity coefficients and retention ranges of isomers on various stationary phases

The selecitivity coefficients of the isomeric pair *p*-/*m*-xylene, $\alpha = t'_{R,p\text{-}x}/t'_{R,m\text{-}x}$ on various types of stationary phases are presented in Table I. The lowest α value, 0.88, is shown by Bentone-34, which indicates selectivity for *m*-xylene[3]. The most selective stationary phase for *p*-xylene is α-cyclodextrin (α = 3.80)[5], but it was not possible to prepare high-efficiency capillary columns, which are necessary for the separation of complex isomeric mixtures. The α value for *p*-/*m*-xylene on the liquid crystal 4-methoxy-4′-ethoxyazoxybenzene (MEAB) is lower than that on α-cyclodextrin, but it is significantly higher in comparison to those on other non-mesogenic and mesogenic stationary phases. High-efficiency capillary columns can be prepared with MEAB[2].

The retention range, defined as the difference between the highest and the lowest retention index from measured groups of isomers, δI, characterizes the possibilities of separation of an isomeric mixture. The retention ranges for isomeric *n*-decenes on various stationary phases are compared in Table II.

In complexation gas chromatography involving π-coordination on the column with silver nitrate in water[9] or 1-triethoxysilyl-2-(*p*,*m*-diphenylphosphinomethylphenyl)ethane bonded to silica and then allowed to react with copper(II) chloride or bromide[10] the retention range of *n*-decenes is wider (76 i.u.)[9]. It is mainly determined by the higher group retention of *cis*- (and 1-isomers) in comparison to *trans*-isomers.

TABLE I

SELECTIVITY COEFFICIENTS (α) FOR *p*-/*m*-XYLENE ON DIFFERENT STATIONARY PHASES

Stationary phase	*Temperature (°C)*	$\alpha_{p\text{-}/m\text{-}xylene}$
Bentone-34 + silicone oil[3]	70	0.88
18-Crown-6	80	0.96
Carbowax 20M	80	0.96
Squalane	80	0.98
Silicones OV-22–OV-101	80	0.99–1.01
Di-*n*-propyl tetrachlorophthalate[4]	90	1.05
Graphitized thermal carbon black[15]	250	1.14
4-Methoxy-4′-ethoxyazoxybenzene	80	1.14 (1.25 at 40°C)
α-Cyclodextrin[5]	100	3.80

TABLE II

RANGES OF RETENTION INDICES OF *n*-DECENES ON DIFFERENT STATIONARY PHASES AT 50°C

Stationary phase	*Retention interval, I*	*δI*
Squalane	979.2–999.2	20.0
Apiezon L[6]	983.0–1005.7	22.7
7,8-Benzoquinoline[7]	998.0–1028.0	30.0
Di-*n*-butyl tetrachlorophthalate[8]	998.0–1029.8	31.8
Polyethylene glycol 4000[6]	1035.7–1068.9	33.2
4-Methoxy-4′-ethoxyazoxybenzene at 70°C	973.3–1030.0	56.7

The retention range of *n*-decenes on different stationary phases, presented in Table II, is identical with the retention range of *cis*-isomers. Therefore, the conditions for the separation of mixtures of structural isomers are more suitable on liquid crystals than in complexation gas chromatography.

As Table II shows, the retention range of isomeric *n*-decenes is increased in the same direction as the stationary phase polarity, but the most impressive increase in δ*I* values is shown by the influence of the liquid crystal shape-selectivity effect. For *n*-decenes on MEAB the retention range is on average about 100% larger than on the other stationary phases. The importance of such an extension of the retention range for isomer separations is documented in Fig. 1. This illustrates the chromatograms of isomeric C_{10}–C_{13} *n*-alkenes obtained on capillary columns with similar efficiency, but each of containing a different stationary phase, one coated with silicone oil DC-550 and the other one with the liquid crystal MEAB. The alkene mixture contains all theoretically possible structural (including geometric) isomers of C_{10}–C_{13} *n*-alkenes and, because the number of peaks obtained on the liquid crystal shows

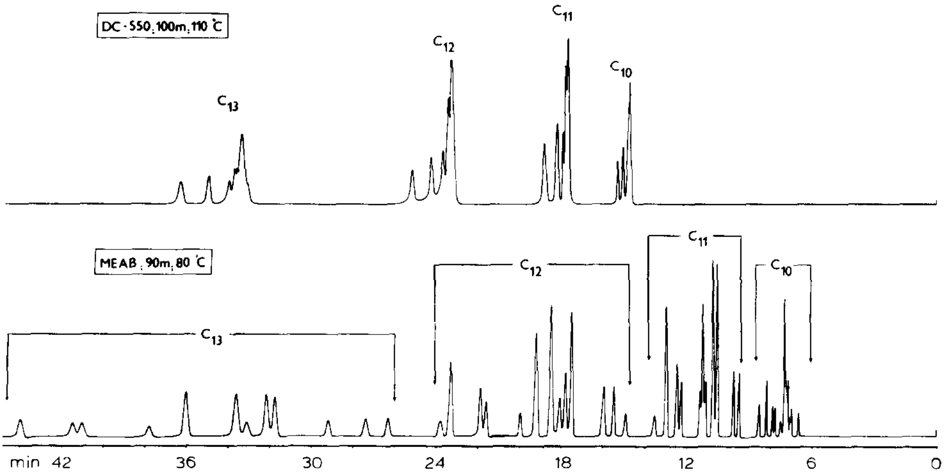

Fig. 1. Separation of isomeric C_{10}–C_{13} *n*-alkenes obtained on a column coated with silicone oil DC-550 (100 m × 0.25 mm) at 110°C and on a column coated with MEAB (90 m × 0.25 mm) at 80°C.

nearly complete separation of the isomeric present in the sample, it also documents the effect of liquid crystal shape selectivity on the separation of structural and geometric isomers.

Retention of isomers on the liquid crystal stationary phases

Positional isomers. The retention of positional isomers is, as a rule, decreased when the functional group is shifted from the end to the middle of the carbon chain. The separation of neighbouring positional isomers on a non-polar stationary phase is made more difficult by shifting the double bond to the centre of the molecule. By increasing the stationary phase polarity, the differences among the retention of neighbouring *cis-n*-alkene isomers increases because the applied dipole–dipole interactions are increased in the direction of the double bond shift to the end of the molecule. Thus, they are increased in the same direction as the retention of the positional isomers is increased. This effect is compensated by the interfacial adsorption effect of isomers on the polar stationary phase–gas interface. This adsorption effect is inversely proportional to the polarity of the individual isomers. (It increases with the shift of the double bond to the centre of the carbon chain.) With increasing number of carbon atoms, the adsorption effect is also increased. Thus the stationary phase polarity effect, which is favourable for the separation of structural isomers, could be eliminated[1]. On liquid crystals the mesophase shape selectivity is also important. It is proportional to the length of the isomeric molecules and increases with the shift of the double bond from the end to the middle of the carbon chain. Because the retention of the positional isomers changes in the same direction, they are separated more completely and more rapidly on liquid crystals than on non-mesogenic stationary phases. Fig. 2 illustrates the separation of isomeric *n*-pentadecenes on capillary columns with non-polar (Apolan 87), polar (Carbowax 20M) and liquid crystal (MEAB) stationary phases. The separation on the liquid crystal is 20 times more rapid for the resolution of closely similar isomers.

The chromatograms in Figs. 1 and 2 illustrate the good separation of isomers with the double bond in the middle of the carbon chain, which are the most difficult to separate on a non-mesogenic stationary phase. This result is based on the alternation effect, which occurs in the retention of positional isomers on liquid crystals[2]. The influence of this effect on the separation of the pairs *trans*-5-/*trans*-6- and *cis*-5-/*cis*-6-dodecane is illustrated in Fig. 3. The systematic increase in isomer retention with the shift of the double bond to the end of molecule on the mesogenic stationary phase MEAB (broken lines) is influenced by an increased retention of *trans*-isomers with an even position of the double bond and *cis*-isomers with an odd position of the double bond (solid line). A shift of the double bond changes the orientation, causing a lengthening of the carbon zigzag chain in the direction of the molecular axis and increases the linearity of the alkene molecule and thereby also its retention on the liquid crystal. In the case of the pair *cis*-5-/*cis*-6-dodecene, *cis*-5-dodecene (on a non-mesogenic stationary phase squalane it is eluted second) exhibits an increased retention and the retention difference between the two isomers is higher. In the pair *trans*-5-/*trans*-6-dodecene, *trans*-6-dodecene (on a non-mesogenic phase it is eluted first) exhibits an increased retention. This leads to an opposite retention order for these isomers, *i.e.*, *trans*-6- is eluted after *trans*-5-dodecene on MEAB in comparison with squalane. The contribution of the alternation effect to the retention of positional

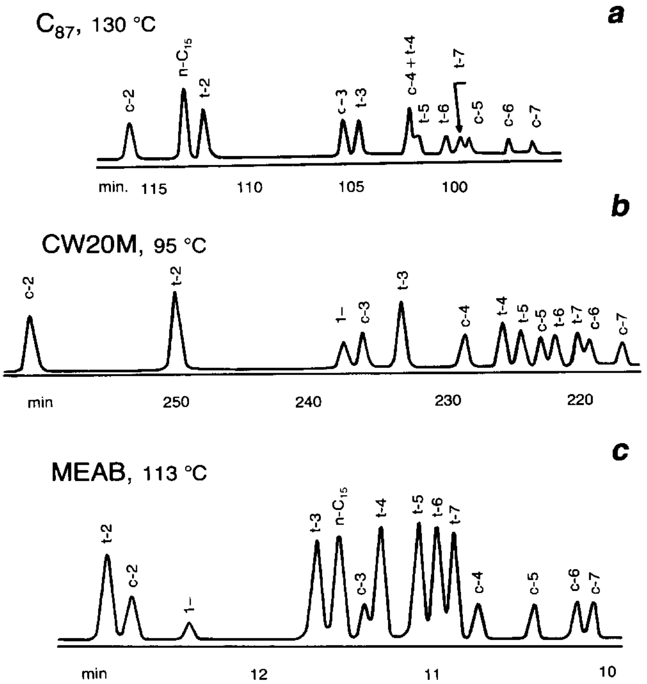

Fig. 2. Chromatograms of the separation of *n*-pentadecene isomers on columns coated with: (a) Apolan-87 (200 m × 0.25 mm, N = 670 000 plates), (b) Carbowax 20M (300 m × 0.25 mm, N = 400 000 plates) and (c) MEAB (90 m × 0.25 mm, N = 200 000 plates). c- = *cis*-, t- = *trans*-isomer, *n*-C_{15} = *n*-pentadecane.

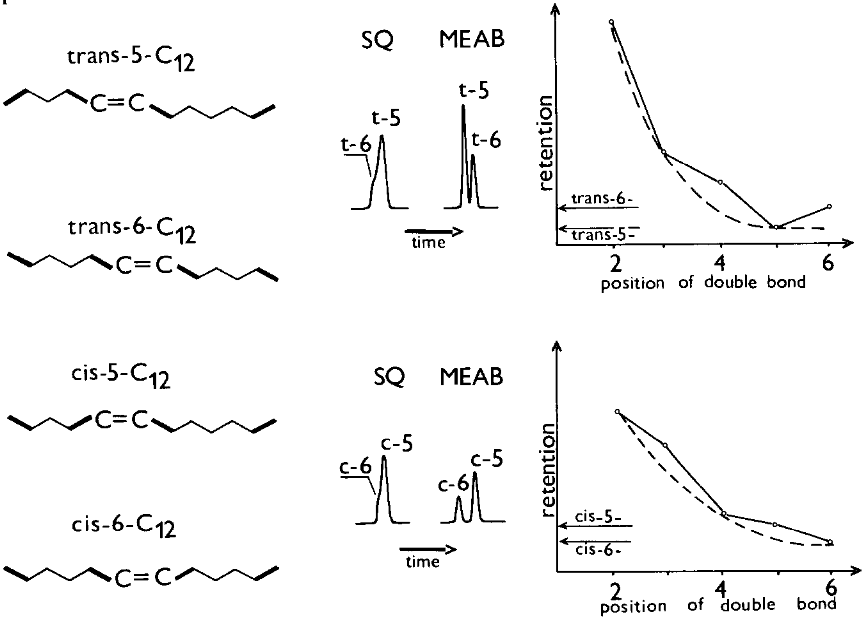

Fig. 3. Changes in retention of isomeric *trans*- and *cis*-dodecenes with change of the position of double bond on a liquid crystal column. c- = *cis*-, t- = *trans*-isomer, SQ = squalane.

TABLE III

DIFFERENCES IN RETENTION INDICES, δI, OF NEIGHBOURING POSITIONAL ISOMERS OF *n*-DODECENES ON MEAB AND SQUALANE AT 87°C

Positional isomers	δI		Δ (δI)
	MEAB	*Squalane*	
trans-2-/*trans*-3-	31.3	11.9	19.4
trans-3-/*trans*-4-	6.5	4.9	1.6
trans-4-/*trans*-5-	8.3	0.3	8.0
trans-5-/*trans*-6-	−2.6	1.1	3.7
cis-2-/*cis*-3-	31.7	17.0	14.7
cis-3-/*cis*-4-	19.8	5.4	14.4
cis-4-/*cis*-5-	5.1	4.1	1.0
cis-5-/*cis*-6-	6.6	0.8	5.8

isomers is relatively small, but in combination with the high efficiency of capillary columns should be utilized for their separation. The differences in retention indices between the neighbouring positional *cis*- and *trans*-isomeric *n*-dodecenes on squalane and MEAB are presented in Table III.

The number of carbon atoms of positional isomers with the double bond in the middle position can influence their separation as follows. Thus, in the pair *trans*-6-/*trans*-7-tetradecene, the *trans*-6-isomer, which is eluted second from a non-mesogenic stationary phase, exhibits an increased retention on liquid crystals, as a consequence of the alternation effect, and the difference in retention between the two isomers is increased. In the pair *cis*-6-/*cis*-7-tetradecene the *cis*-7-isomer, which is eluted first from a non-mesogenic phase, exhibits an increased retention. This leads to the opposite retention order of these two isomers on liquid crystals, *i.e.*, the effect is similar to that in the *trans*-5-/*trans*-6-dodecenes. This retention behaviour is characteristic for isomers with the double bond in the middle position and with an even number of carbon atoms in the molecule. A similar situation is observed after each change in the carbon atom number in the chain by 4.

In *n*-alkenes with an odd number of carbon atoms the *trans*-isomers with an odd position of the double bond and the *cis*-isomers with an even position of the double bond exhibit an increased retention, as the consequence of the retention alternation. With a shift of the double bond to the middle of the carbon chain the effect of retention alternation dwindles. Thus, the selectivity coefficient for *trans*-5/*trans*-6-tridecene on liquid crystals is lower than on squalane. This is connected with the change in the orientation of the ends of the carbon chain for both isomers when the double bond is shifted in the carbon chain.

The alternation effect was found on liquid crystals for all types of hydrocarbons studied. It applies to *n*-alkanes with an even and 1-alkenes with an odd number of carbon atoms[2]. In *n*-alkynes, 1-alkynes with an odd number of carbon atoms, 2-alkynes with an even number of carbon atoms, 3-alkynes with an odd number of carbon atoms, etc., exhibit an increased retention[11]. In alkylbenzenes the *n*-alkylbenzenes with an odd number of carbon atoms in the molecule and those dialkylbenzenes which have in the main (longer) chain an odd number of carbon atoms exhibit an increased retention[5].

TABLE IV

DIFFERENCES IN RETENTION INDICES, δI, OF GEOMETRIC ISOMERS OF *n*-DODECENES ON MEAB AND SQUALANE AT 87°C

Geometric isomers	*δI*		*Δ (δI)*
	MEAB	*Squalane*	
trans-2-/*cis*-2-	8.5	−4.2	12.7
trans-3-/*cis*-3-	8.9	0.9	8.0
trans-4-/*cis*-4-	22.2	1.4	20.8
trans-5-/*cis*-5-	19.0	5.2	13.8
trans-6-/*cis*-6-	28.2	4.9	23.3

Geometrical isomers. The selectivity of liquid crystals is higher for *trans*-*n*-alkene isomers than for corresponding *cis*-isomers[2]. Because the retention order of the geometric isomers on non-mesogenic stationary phases is different, their mutual separation on mesogenic stationary phases could be better or worse than on the non-mesogenic phases. On the highly selective MEAB, all *trans*-*n*-alkenes have higher retention than the corresponding *cis*-alkenes[2]. The δI values of geometric isomers of *n*-dodecenes on MEAB and squalane are compared in Table IV.

For the optimization of the separation of geometric isomers on liquid crystals the characteristic temperature dependence of the retention could be used. The temperature coefficients for *cis*-isomers are higher than for the corresponding *trans*-isomers. On MEAB, $\mathrm{d}I/\mathrm{d}T$ (*cis*- − *trans*-isomer) $\approx$ 0.2 i.u./°C. With a change from 80 to 105°C, the opposite order of retention for *cis*-3- and *trans*-4-pentadecenes occurs (column efficiency 100 000 plates).

Diastereoisomers. The influence of the mesogenic structure enables the separation of diastereoisomers[12]. Better separation of diastereoisomers on a mesogenic stationary phase could be attained if the isomer with the more elongated molecular structure has nearly the same retention as the other on a non-mesogenic stationary phase. In Table V are presented the δI values for the diastereoisomers of alkanes up to C_{10} most difficult to separate (excluding 3,4-dimethylhexane), which are 3,5-dimethylheptane and 3,6-dimethyloctane, on non-mesogenic phases and the liquid crystal 4-*n*-pentylacetophenone (O-4-pentyloxybenzoyloxime) (PBO). In these cases and in the separation of norpristane, pristane and phytane diastereoisomers, the racemic form has an higher retention on liquid crystals than the *meso*-form[12].

TABLE V

DIFFERENCES IN RETENTION INDICES, δI, OF DIASTEREOMERIC ALKANES ON DIFFERENT STATIONARY PHASES AT 40°C

Alkane	*Squalane*[13]	*Ucon*[13]	*SE*[14]	*PBO*
3,5-Dimethylheptane	0.0	0.0	1.1	1.5
3,6-Dimethyloctane	0.0	0.0	0.8	1.1

CONCLUSIONS

Separation systems combining the high efficiency of capillary columns with the shape selectivity of liquid crystals enable more rapid and better separation of isomeric hydrocarbons. This is connected with the fact that the retention of the structural isomers and the shape selectivity of the liquid crystals are increased in the same direction, mostly with the shift of the functional group from the middle to the end of the carbon chain.

The higher temperature dependence of isomer retention on liquid crystals enables easier temperature optimization of isomeric separations, especially the resolution of geometric isomers.

The possibility of using the alternation of the retention effect for the separation of structural isomers with a functional group in the middle of the carbon chain, which are the most difficult to separate on non-mesogenic stationary phases, is the most specific separation characteristic of liquid crystals.

REFERENCES

1 L. Soják, J. Krupčík and J. Janák, *J. Chromatogr.*, 195 (1980) 43.
2 L. Soják, G. Kraus, P. Farkaš and I. Ostrovský, *J. Chromatogr.*, 249 (1982) 29.
3 J. V. Mortimer and P. L. Gent, *Nature (London)*, 197 (1963) 789.
4 S. H. Langer, C. Zahn and G. Pantazoplos, *J. Chromatogr.*, 3 (1960) 154.
5 E. Smolková-Keulemansová and L. Soják, *ACS Symp. Ser.*, 342 (1987) 247.
6 O. Eisen, A. Orav and S. Rang, *Chromatographia*, 5 (1972) 229.
7 W. Meltzow and B. Fell, *Erdoel, Kohle, Erdgas, Petrochem.*, 25 (1972) 311.
8 M. Ryba, *Chromatographia*, 5 (1972) 23.
9 E. N. Viktorova, V. G. Berezkin and V. S. Gavrichev, *J. Chromatogr.*, 398 (1987) 317.
10 W. Wasiak, *Int. Lab.*, Sept. (1986) 96.
11 L. Soják, P. Farkaš, J. Janák, S. Rang and O. Eisen, *J. Chromatogr.*, 287 (1984) 271.
12 L. Soják, I. Ostrovský, G. Kraus and T. G. Andronikashvili, *J. Chromatogr.*, 436 (1987) 47.
13 A. Matukuma, in C. L. A. Harbourn (Editor), *Gas Chromatography 1968*, Institute of Petroleum, London, 1969, p. 55.
14 A. J. Lubeck and D. L. Sutton, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 328.
15 W. Engewald, L. Wennrich and J. Pörschmann, *Chromatographia*, 11 (1978) 435.